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EDITORIAL

In coming years massive expansion of schooling and growing youth aspirations will create huge demand for higher education in India. Higher education is also essential to build a work force capable of underpinning a modern competitive economy. Consequent to this during the 12th plan period, enrollment in higher education would have to be significantly increased in a demand driven manner.

Along with quantitative expansion, improvement in quality should also be our focus . During the 12th plan period, an additional enrollment of 10 million is targeted in higher education. This would significantly increase the GER bringing it broadly in line with the Global average.

The 12th plan also envisages the need to create an ecosystem that encourages research and innovation in a self sustaining manner. We must bring back the 'lost' research culture of Indian universities so as to create new knowledge and improve teaching standards. Collaborative research, setting up industry incubation parks in universities and institutions, providing more research fellowships, promoting innovation through inter disciplinary research in new and emerging fields, strengthening inter- university centers etc are emphasized in the 12th plan .This would require more funding for university based research and funding policies that create right incentives for quality research and promote collaboration among institutions.

It is thus with great pleasure and gratitude, S.N.M. College Maliankara is presenting the 2nd issue of our Inter disciplinary / multi disciplinary research journal entitled " Journal of current studies". The objective of the journal is to provide a venue for academic research scholars, post graduate students in universities / colleges and other centres of research to publish current and significant research as well as other publication activities . Research papers, short communications, review articles, books reviews and professional news items will be published.

From this issue onwards the journal insist strict peer review of each paper submitted for publication. Therefore, it is highly necessary that in future, research papers are to be submitted sufficiently earlier for the timely publication of the journal. From the next issue onwards, manuscripts submitted strictly in accordance with the style prescribed shall only be accepted for publication.

On this happy occasion I wish to express my sincere appreciation to research & Journal committee for their enthusiastic support and co-operation to this academic venture. I also extend sincere appreciation of the college management and the principal, to the valued readers and authors for their continued interest in JCS, and to every member of the editorial board to this scientific endeavour . We further gratefully acknowledge the magnanimity , benevolence , enthusiasm, support of the college manager, principal who provided the full financial support to this endeavour from the college development fund.

I also welcome valuable suggestions and criticisms of the readers for improvement and augmentation in this regard.

With warm regards

Dr. M.G. Ramesh Babu

Chief Editor

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INCREASED SENSITIVITY FOR PETROLEUM GAS DUE TO ADDITIONS OF LANTHANUM ON SnO_2 THIN FILMS

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Abstract

Detection of low concentrations of the target gas was achieved using transparent conducting SnO_2 thin films doped with 0-4 wt.% Lanthanum (La), deposited by the spray pyrolysis technique. To explain the sensing scheme, the gas detection properties of the films in 1000ppm of LPG has been performed at different conditions in a controlled atmosphere The catalytic activity coupled with the semiconductor properties of the materials provides the gas sensing activity for the detection of the inflammable gas. It was observed that tin oxide thin films doped with 1 wt.% La with a mean grain size of 30 nm at a deposition temperature of 360˚C exhibited the maximum sensitivity (86%) to LPG. The sensitivity towards gas detection exhibited by the thin films is strongly dependent on microstructure and orientation. The grain size, texture coefficients, standard deviation and lattice parameters of the films were calculated with a view to correlate the structure with the carrier transport on gas exposure. The electrical properties of doped-SnO_2 films are correlated with reference to the defect-structure induced in the oxide lattice by the foreign atoms. The La doped films were investigated for the structural, compositional and optical properties using X-ray diffraction (XRD), scanning electron microscopy (SEM), EDAX analysis and FTIR spectroscopy.

Keywords: Sensors, SnO_2, La, LPG

1. Introduction

Liquid Petroleum gas sensors with low cost and high reliability are in great demand in industrial as well as domestic appliances. These sensors work on the principle of change in electrical conductance on exposure to the detecting gas. Desirable characteristics of a gas sensor are high sensitivity, fast response, fast recovery time, selectivity and long term stability [1]. Metal oxide semiconductor gas sensors based on electrical conductivity have been extensively used for domestic gas leak detectors in house to produce alarm at a given concentration. The metal oxide films prepared for gas sensors have a polycrystalline structure and their electrical conductivity and gas sensitivity are governed by the characteristics of the intergrain barriers [2]. Among the semiconducting metal oxides used for gas sensors, tin oxide is the most widely used material with respect to practical applications due to its low cost, long life and that it requires very simple

electronics, so that little maintenance is involved [3,4]. Tin oxide films posses interesting structural and electronic properties that suggest a number of novel and useful applications for electronic gas sensors [5]. Tin oxide is an insulator in its bulk form, whereas it becomes semiconductor when it is deposited in the form of thin films. This transition of insulator to semiconductor occurs as the result of deviation of stoichiometry when it is prepared in thin film form. An interesting point is that the possibility of this stoichiometry deviation is rather high when the films are prepared by spray pyrolysis than the other deposition techniques. Appropriate doping can further enhance the conductivity of these films. The reason for the enhancement in conductivity is that the suitable dopant atoms introduce more free carriers, normally electrons in the case of almost all transparent conducting oxides. And that is why, in general these oxides are n-type conducting [6]. Several techniques have been utilized for the fabrication of thin film gas sensors. The growth technique plays a significant role in governing the properties of these films, because the same material deposited by two different techniques usually has different physical properties. This is because of their strong dependence on the structure, morphology, and nature of the impurities present. In addition, the substrate material on to which the films deposited, found to influence the film properties. The deposition techniques that have been used to grow the transparent conducting oxide films include chemical vapor deposition [7-10], sputtering [11-14], sol–gel coating [15-17] and spray pyrolysis [18-22]. Among the different techniques, spray pyrolysis offers many advantages such as low cost of the apparatus and raw materials, flexibility for doping and easy control over deposition parameters compared to other process. As the electrical properties of thin films are highly sensitive to microstructure and orientational changes which in turn depend on the deposition conditions, it is essential to study the influence of each process parameter in order to get good control over the physical properties of the films [23]. The resistivity of un-doped SnO_2 films is dependent upon oxygen vacancies whose concentration is usually difficult to control. Therefore, the doping method is preferable in which a suitable dopant is added to SnO_2 and thereby free electrons are generated [24].The gas sensing properties of SnO_2 thin films also depend on the deposition and post deposition treatment conditions as these properties change significantly with the nature of chosen doping elements, the adsorption of oxygen that takes place during film deposition, film deposition temperature and desorption during annealing treatment.

Doping of SnO_2 thin films with Cs [18] Pd [25], Pt [26], Ru [27], and Fe [28] has been reported to improve the Petroleum gas sensing properties. The effect of different concentrations of La_2O_3 in SnO_2 and the effect of calcination temperature on the sensitivity to reducing gases like LPG, H_2 and CH_4 has been studied. It has been found that increasing the doping level above 2 wt.% has no added advantage in improving the gas sensitivity and in stabilizing the SnO_2 surface [29].

In the present study, we have grown conducting Lanthanum doped SnO_2 (SnO_2:La) films using different concentrations of $LaCl_3.7H_2O$ under various spraying conditions by spray pyrolysis. The structural and electrical properties of these films were investigated and correlated their changes with the spraying process to produce better crystallinity and transparent films for gas sensing applications.

2. Experimental

2.1. Material deposition

Spray pyrolysis is one of the relatively simple and cheap methods, which can easily be adopted for mass production of large-area coatings for industrial applications. This method has been widely used for preparation of transparent conducting oxide films.

In our investigations, undoped and lanthanum doped tin oxide (SnO_2) thin films were prepared by the homemade spray pyrolysis experimental setup. The schematic diagram of the experimental set up used for the deposition is published in our earlier paper [18]. ExcelaR AR grade $SnCl_2.2H_2O$ powder (99% purity) (Qualigens) was used as the precursor of tin. The tin precursor dissolved in Analytical grade HCl (99.9996 % purity) (Merck) diluted with Isopropyl alcohol (2-Propanol-$CH_3CHOHCH_3$) (99.9% purity) (Merck) was used to prepare the basic spray solution. Distilled deionized water is used for all the preparations. The optimal deposition parameters of the as-deposited Lanthanum doped tin oxide thin films are given in table 1.

Table 1. Deposition conditions

Stannous chloride	10 gm
Isopropyl alcohol	90 ml
Lanthanum chloride	0 – 4 wt.%
Hydrochloric acid	4 ml
Substrate temperature	280°C - 360°C
Carrier gas	Compressed air at 30 kg/cm^2
Spray nozzle to distance the substrate	50 cm
Spray nozzle diameter	0.25 mm
Solution flow rate	10 ml / min.
Cooling rate	10°C / min.

The substrate temperature was maintained at predetermined temperature using a PID controller with an accuracy of ±4°C and measured using a chromel-alumel thermocouple placed in contact with it. The hazardous fumes evolving at the time of deposition were expelled out from the deposition chamber using an exhaust system connected to the spray pyrolysis unit. After

completion of the deposition process, the films were allowed to cool slowly to room temperature before being taken out from the spray chamber. All the above mentioned parameters were kept constant except the concentration of $LaCl_3$ and substrate temperature.

2.2. Film characterization

Conductivity measurements and gas sensitivity response of the samples are carried out by using an apparatus consisting of a thick walled cylindrical glass chamber provided with two side tubes. One of the side tubes is connected to a control T-valve from which connections can be given to rotary vacuum pump / portable gas cylinder. The chamber can be evacuated to a low pressure of about 10^{-3} Torr. The other side tube is connected to a Mc Leod gauge to measure the pressure inside the chamber. Resistance measurements were carried out using the van der Pauw four probe techniques. A chromel-alumel thermocouple in contact with the sample shows the milli-voltage corresponding to the working temperature of the sample. A DC power supply is used to energize the heater coil. Temperature of the sample in the chamber can be increased upto 475°C. The electrical resistance variation of the samples in the presence of LPG can be analyzed by performing the measurements in gas atmosphere.

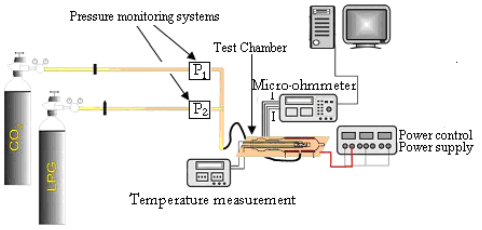

Figure 1. Sensitivity measurement setup

The La doped SnO_2 sample in which the resistance change under gas presence to be measured is placed inside the sensing chamber and electrically connected using pressure contacts. Ohmic contact has been made by using silver paste. Initially the chamber is evacuated to a base pressure of 10^{-1} Torr using a rotary vacuum pump to eliminate the humidity effect on the films. For attaining the working temperature, the chamber can be heated radially. The initial resistance of the sample R_a is noted. When the sample attains the desired operating temperature under 10^{-1} Torr pressure, LPG from the portable cylinder is admitted into the sensing chamber. The concentration is adjusted to obtain 1000 ppm inside the chamber. The resistance of the gas sensor R_g is continuously recorded starting from the gas injection moment at regular intervals of 30 seconds in an exposure time of 10 minutes. LPG is then turned off and the sample is left in air to recover. During recovering time, the resistance returns to more than 90% of its initial value proving the reversibility of the process. The samples are exposed to the gas atmosphere several times prior to the measurements. An abrupt

fall in the electrical resistance of the material is observed by the interaction of the LPG gas with the surface of SnO_2 films prepared by spray pyrolysis. The resistance of the gas sensor is compared with the initial resistance and the sensitivity (at a particular gas concentration),

$$S\ (\%) = [(R_a-R_g)/R_a]\times 100 = [\Delta R/R_a]\times 100$$

is calculated. Since tin oxide behaves as an n-type semiconductor and LPG is a reducing species, R_g is lower than R_a. Therefore, sensitivity is always positive. The sensitivity of the samples is measured at fixed concentration of LPG by varying the operating temperature. It is found that the sensor attains the peak sensitivity at an operating temperature of 350°C. The experiment is repeated for samples deposited at different deposition temperatures and the sensitivity of all the samples towards the gas is calculated. Good reproducibility of the results is verified through repetition of the measurements. On the prepared La doped SnO_2 films, the gas sensing effect is studied in relation to the crystallite size and orientation. Gas response measurements are again carried out at various operating temperatures from 280 to 400 ◦C. The measurements on sensor samples kept in our laboratory for a period of 1 year do not show much variation in resistance. Gas sensitivity measurements also do not show much aging effect.

The thickness of the films was maintained constant throughout the experiment and was measured by means of the interference method developed by Tolansky and verified using a Sloan Dektak 6M profilometer. The structural properties of the as-grown films were studied using computer controlled X-ray diffractometer (Bruker AXS D-8 Advance) using CuKα (1.5418Å) radiation. Elemental composition was confirmed using OXFORD INCA ENERGY EDAX. The surface structure and the morphology of the samples for the present investigations are characterized by Hitachi, S-2400 model scanning electron microscope. The structural analysis of the thin films and elemental identification via characteristic frequencies is carried out by recording the Fourier Transform Infra- Red spectra using Thermo Avatar, 370 FTIR Spectrophotometer from 500 cm^{-1} to 4000 cm^{-1}.

3. Results and Discussion

3.1. La-doped SnO_2 film formation

To establish the composition of the films, EDAX microanalysis is carried out in samples prepared at different deposition temperatures. The ratio of La:SnO_2 in the films calculated from the EDAX quantitative analysis data is close to that of the starting solution. Results reveal the presence of La in samples and typical spectra is shown in Figure 2. Based on this analysis, the product is confirmed as La: SnO_2. Nevertheless, the samples with lower dopant concentrations, typically less than 0.5 wt% La concentrations, show only the presence of

Sn and O, signifying the detection limit of EDAX analysis [30].

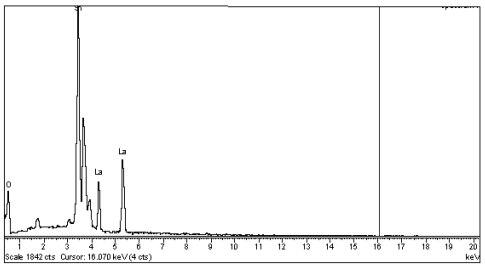

Figure 2. EDAX spectra of 1% La-SnO_2 at 360°C indicating the presence of Sn, O and La.

The constituent species in La-doped SnO_2 was explored by transmission FTIR spectroscopy using fresh samples and is depicted in figure 3. Since La being an ionic modifier, the predominant mechanism in the interaction between La ions and the SnO_2 lattice is the modification of the interface between grains. In particular, La dispersed on the grain surface can prevent the formation of Sn–O–Sn bonds between adjacent grains. The bands between 500 and 800 cm^{-1} are usually attributed to the framework vibrations of tin oxide [31].

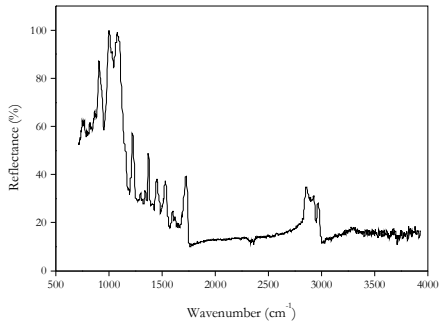

Figure 3. FTIR spectrum of La doped SnO_2 films

The band centered at 1622 cm^{-1} found on all samples is assigned to O–H stretching and deformation vibrations of weak-bound water. This may be due to the readsorption of water may have taken place from the ambient atmosphere to exhibit the bands.

3.2. Micro structural properties

Figure 4 shows the X-ray diffraction profiles of La doped SnO_2 films formed at different substrate temperatures in the scan range of 2θ between 10˚-70˚ with a step width of 0.01˚C and a step time of 0.2 seconds. The structural properties of La-doped tin oxide films have a significant effect on the electrical and gas-sensing properties. Hence structural and the grain size measurements of the samples are carried out. It is well known that the deposition temperature plays an important role in the stoichiometry and structural properties of the films [32]. So for each doping level of La (0 to 4 wt.%) in SnO_2, the substrate temperature is varied to obtain a most favorable substrate temperature for gas detection.

The XRD pattern presents reflections from the characteristic tetragonal crystallographic phase of tin oxide. The diffraction pattern of undoped SnO_2 films deposited at 360◦C (figure 4.a) presents three distinct peaks corresponding to the principal peaks of cassiterite SnO_2 at different angles of 34.152˚ (101), 51.961˚

(211) and 65.995° (301). For undoped samples, the peaks corresponding to the planes (110) and (200) are below detection and the crystallites formed along a (301) preferred direction are normal to the glass substrates.

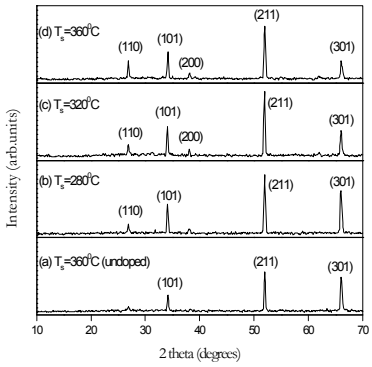

Figure 4. X-ray diffraction spectra of 1 wt. % La doped SnO_2 films at different substrate temperatures

Fig.4.b-d show the XRD patterns of 1 wt.% lanthanum-doped SnO_2 films deposited at temperatures between 280 and 360◦C. The diffraction peaks for the films deposited at different temperatures are intense and sharp thereby confirm its higher degree of crystallinity which presents the highest sensitivity to LPG. A variation in intensity of the XRD peaks is observed for the samples prepared at different substrate temperatures. The XRD patterns are indexed based on a tetragonal structure with the lattice parameters a = 4.715 Å and c = 3.174Å (calculated values) which correspond to that of bulk tin oxide in tetragonal structure [33]. The calculated d values are found to be close to those of the ASTM data reported for SnO_2 powder sample.

The structural parameters such as crystallite size, texture coefficient, standard deviation and lateral strain were calculated from the XRD data and their variation as a function of substrate temperature was studied.

The texture coefficient of the samples (TC) gives a measure of the preferred orientation compared to a randomly oriented sample and represents the texture of the particular plane, deviation of which from unity implies the preferred growth [34].

Figure 5 depicts the variation of the texture coefficient for 1 wt.% La : SnO_2 at the temperature range 280 to 360°C. The preferential (301) orientation steadily decreases, while all others, (110), (101) (200), (211), increases marginally as the deposition temperature increases. From the figure, it can be seen that the texture coefficient for (211) increases up to 320°C and beyond that remains more or less constant but TC (301) decreases steadily in the entire range of deposition temperatures.

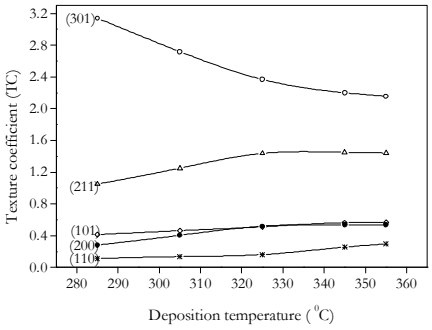

Figure 5. Texture coefficient vs. Deposition temperature for 1 wt.% La: SnO_2 films

In order to describe the difference in growth from standard data, the standard deviation 'σ ' can be calculated using the expression [32], [35].

$$\sigma = \sqrt{\frac{\sum I_{hkl}^2 - (\sum I_{hkl})^2 / N}{N}}$$

where I_{hkl} stands for the relative intensity of a (hkl) plane. The calculation of standard deviation gives an additional explanation for the growth mechanism.

Figure 6 shows the variation of standard deviation (σ) with deposition temperature for 1 wt.% La- doped SnO_2 films. From the figure it is well understood that a substrate temperature ≈320°C is high enough to saturate the σ values. That is, a saturation of σ values can be seen beyond a deposition temperature 320°C. A higher substrate temperature (>320°C) stabilizes the crystallite growth in SnO_2 even in presence of La. The highest TC and σ values for (301) plane implies that the crystallites are highly textured along the (301) orientation in the films deposited at higher temperatures. This may be due to a reduction in the lattice strain and an improvement in the grain size with substrate temperature.

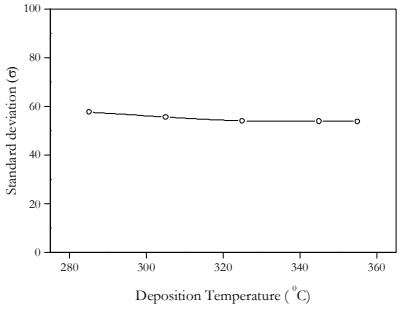

Figure 6. Standard deviation vs. deposition temperature for 1wt.% La doped SnO_2

The lanthanum doped tin oxide films are stable and robust. The average crystallite size in a direction perpendicular to the surface of the specimen is determined from the measured width of their diffraction curves by using Debye Scherrer's formula.

$$D = \frac{0.94\lambda}{\beta cos\theta}$$

where λ is the wavelength of Cu Kα radiation (λ = 1.5418Å), β is the angular width which is equal to the full width at half maximum [36]. For a particular doping level, the crystallite size of the films increases as the deposition temperature increases and the resistance decreases. This may be partially due to the incorporation of additional defects in the films. The effect of deposition temperature on the grain size is depicted in figure 7.

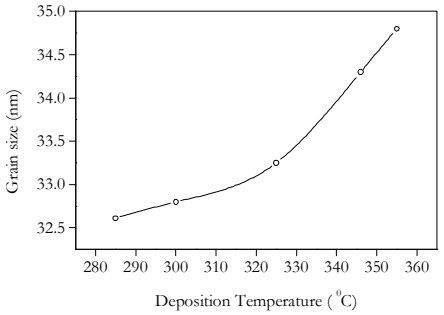

Figure 7. Grain size vs. deposition temperature for 1wt.% La-SnO_2

From the XRD results, it has been found that the size of the crystallites of SnO_2 decreases with increase in La concentration for a deposition 280ºC and observed an increase in sensitivity for 2wt.% La doping.

This may be due to the increase in surface area resulting from the decrease of grain size or due to the change in gas adsorption properties from orientational changes. For polycrystalline thin films, the structural parameters influencing gas sensitivity can be both size and orientation of crystallites [37]. The gas sensitivity is relative to grain size, surface state, oxygen adsorption and lattice defects.

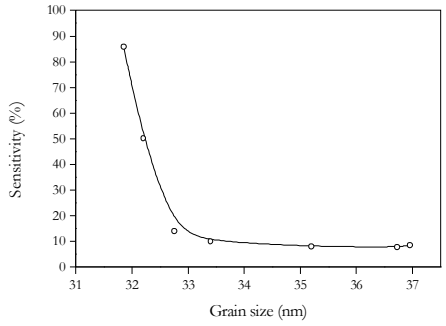

Figure 8. Sensitivity vs. grain size for 1wt.% La-SnO_2 at different deposition temperatures: sensing temperature 350°C

Figure 8 shows the variation of LPG sensitivity with grain size. The sensitivity is found to decrease when the crystallite size increases. Nevertheless, at higher deposition temperatures the crystallite size is found to increase even as the dopant concentration increases.

In the spray pyrolysis technique, the process parameters highly govern the film properties. The microstructure plays an important role in gas detection because it influences the interaction between the gas molecules and the oxygen adsorbed on the surface of SnO_2 grains. Hence their optimization is done in order to get La: SnO_2 films with enhanced gas sensitivity. Response and recovery times are determined in comparison with the film resistance value prior to gas admittance.

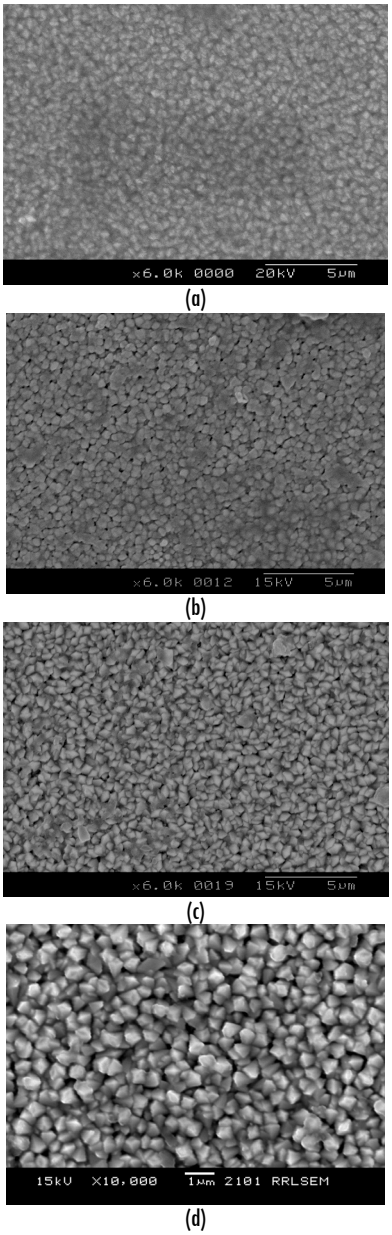

Figure 9. SEM pictures of (a) undoped at 360°C (b)1 wt.% La doped at 280°C (c) 1 wt.% La doped at 320°C (d) 1 wt.% La doped at 360°C

The micrographs recorded for the different samples show that the films are essentially homogeneous and made up of grains and voids. The studies reveal that the density of voids decreases with the increase in deposition temperature. The presence of these voids results in a decrease in mobility and thus affects the film resistance and hence conductivity

The average grain size obtained from scanning electron micrographs are found to be larger than that calculated from the XRD measurements, which may be due to the presence of twinning or agglomerations. For La doped SnO_2, when the deposition temperature is moderate, the SEM consists of mixed sized, densely packed and polygon shaped grains.

3.3.L P Gas sensitivity response

The gas sensing characteristics of La-doped SnO_2 films are studied in detail. It is found that the introduction of La leads to an increase in LPG sensitivity and the best response is observed for 1wt.% La- doped SnO_2 at the deposition temperature 360°C. The increased oxygen vacancies and defects at low dopant concentration increases conductivity in films. The maximum sensitivity of the films appears for films deposited at a higher deposition temperature. Figure 10 shows the variation in LPG gas sensitivity with response time for the La doped SnO_2 films deposited at 280°C.

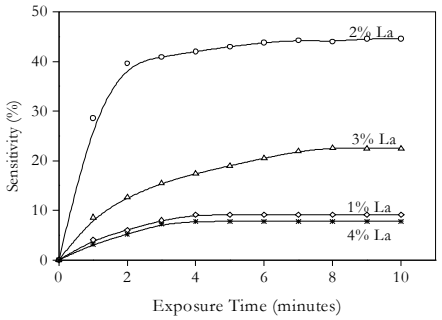

Figure 10. Sensitivity vs. response time at the deposition temperature 280°C: sensing temperature 350°C

The sensor shows the maximum sensitivity for 2wt.% La- doped SnO_2. At higher or lower concentrations, the sensitivity is close to that of undoped films. The order of sensitivity variation is not similar to that of the films deposited at higher temperatures. Figure 11 depicts the sensitivity response of La- doped SnO_2 films as a function of time for the samples deposited at 320°C. At this deposition temperature, the sensitivity response in gas is comparatively poor.

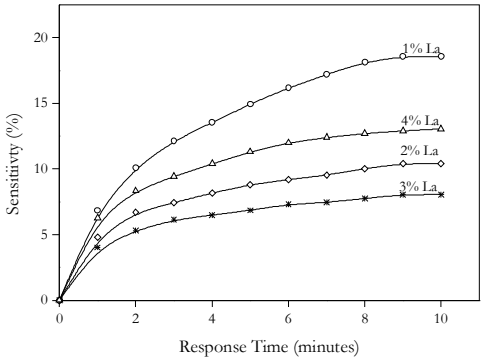

Figure 11. Sensitivity vs. response time at the deposition temperature 320°C: sensing temperature 350°C

The sensitivity variation of La- doped SnO_2 samples deposited at 360°C is shown in figure 12. When exposed to LPG, in the La- doped tin oxide films, the one having the highest gas sensitivity is with a concentration of 1wt.% La deposited at a deposition temperature of 360°C. The films are with a thickness of approximately 525 nm. The response and recovery times of doped samples are rather high. The undoped films have longer recovery times. I Stambolova *et al* [38] studied the ethanol sensitivity of La-doped SnO_2 samples. According to their studies, the grain size is decreased with La-doping which is contrary to our result.

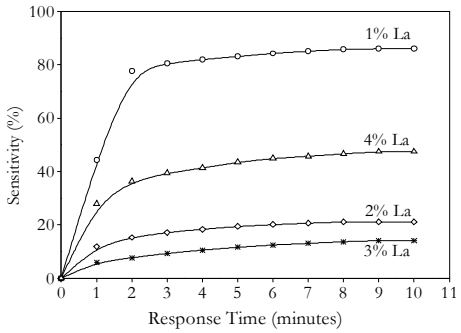

Figure 12. Sensitivity vs. response time at the deposition temperature 360°C: sensing temperature 350°C

Figure 13 shows the variation of sensitivity with initial resistance (in vacuum) at the deposition temperature 360°C. Initially the sensitivity decreases with increase of resistance. Nevertheless, for samples having higher initial resistance shows higher sensitivity to LPG.

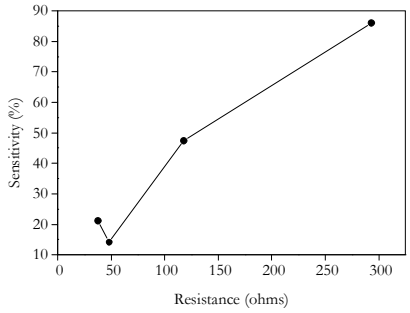

Figure 13. Sensitivity vs. initial resistance at the deposition temperature 360°C:sensing temperature 350°C

3.4. Sensor's working temperature

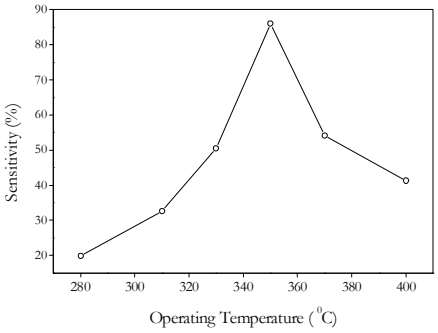

Figure 14. Variation of sensitivity with operating temperature

The sensitivity of the sensor is measured at fixed concentration of LPG by varying the operating temperature. The concentration of LPG for the measurements is 1000ppm. The sensitivity is determined at operating temperatures 280, 310, 330, 350, 370 and 400°C. The sensitivity towards LPG for 1% La-doped SnO_2, deposited at 360°C is shown as a function of operating temperature in figure14. The sensitivity increases with increase in temperature and reaches a maximum at around 350°C. P. Mitra, H.S. Maiti (2004) reported that Pd-activated ZnO

films exhibited an elevated sensitivity of 88% for 1.6 vol. % LPG in air.

The highest sensitivities to LPG are obtained at around 350°C, which can be attributed to the enhancement of reaction kinetics of oxidation of LPG with adsorbed oxygen species. Gas sensing mechanism of SnO_2-based sensors belongs to surface-controlled type or in other words the resistance change is controlled by the species and amount of chemisorbed oxygen on the surface. Therefore, it is obvious that the sensitivity is greatly dependent on the amount of chemisorbed oxygen. It is clear that the obtained highest LPG sensitivity at an operating temperature 350ºC is related to the amount of chemisorbed oxygen ions reaching maximum. In addition, maximum sensitivity is obtained for SnO_2 film doped with 1wt.% lanthanum deposited at 360°C. This implies that the amount of chemisorbed oxygen is in the order of 1wt.% La:SnO_2 deposited at 360°C >4wt% La:SnO_2 deposited at 360°C > 2wt.% La:SnO_2 deposited at 280°C >3wt.% La:SnO_2 deposited at 280°C > pure SnO_2.

3.5. Dependency on concentration of dopants

The role of different concentrations of La doping on the LPG sensitivity of SnO_2 thin films deposited at different temperatures is reported. The variations of LPG sensitivity of the La:SnO_2 as a function of concentration of La in the sprayed solution, can be seen in figure 15.

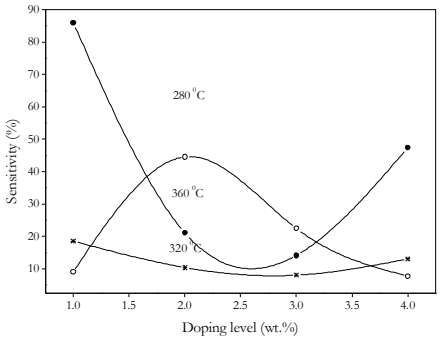

Figure 15. Variation of sensitivity with doping level of La in SnO_2 films: sensing temperature 350°C

The variation of LPG sensitivity of La-doped tin oxide films with dopant concentration at higher deposition temperatures are similar while it is entirely different for films deposited at a lower deposition temperature as seen in figure. The sensor performance of 2 wt.% La doped SnO_2 at deposition temperature 360°C is evaluated as 62.0×10^{-5} /ppm.

3.6. Dependency on deposition temperature

In order to obtain the best possible LPG-sensing characteristics, the relationships between the sensitivity and deposition temperatures of the films with different concentrations of La are studied and are plotted in figure 16.

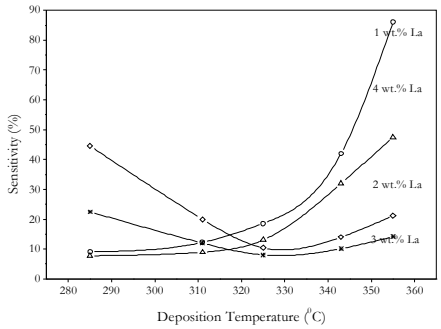

Figure 16. Sensitivity vs. deposition temperature of La-doped SnO_2 films: sensing temperature 350°C

The sensitivity for La- doped SnO_2 samples with concentrations 1wt.% and 4wt.%, is low at lower deposition temperatures but get increased when the deposition temperature increases. Nevertheless, for samples with 2wt.% and 3wt.% La, the sensitivity is high at lower deposition temperatures, reduced to minimum at 320°C and then increases when the deposition temperature increases. It can be seen that the favorable substrate temperature depends on the dopant concentration and structural property like preferred orientation, which controls the mobility of charge carriers.

3.6. Discussion

SnO_2 films have n-type conductivity and the high conductivity of these films results mainly from stoichiometric deviation. The conduction electrons in these films are supplied from donor sites associated with oxygen vacancies or excess metal ions. These donor sites can easily be created by chemical reduction (Hartnagel et al 1995). SnO_2 films have been grown by the spray pyrolysis technique doped with non-noble metals which shows variation in electrical conductivity in presence of gases. Under normal conditions the electrons in a semiconductor can establish an equilibrium state as a result of the interaction of electrons with lattice defects created by impurity atoms.

In polycrystalline thin films, the conduction mechanism is dominated by the inter-crystalline (grain boundaries) rather than intra-crystalline characteristics. These boundaries generally contain high densities of interface states, which trap free carriers from the bulk of the grain and scatter free carriers resulted from the inherent disorders and the presence of trapped charges. The interface states result in a space charge region in the grain boundaries. Due to this space charge region, band bending occurs. This result in potential barriers at grain boundaries and a modification in the charge transport.

The results obtained from the study of La doped SnO_2 thin films demonstrate the conductivity of polycrystalline deposits and the variation caused by the saturation of surface bonds in relation to the grain size and the morphology of the added catalyst. The observed increase of conductivity with increasing operating temperature might be due to a decrease in concentration of adsorbed oxygen.

For SnO_2 thin films, predominant orientation of crystallites, forming the surface of the film contacted with the surrounding atmosphere, is an important factor, influencing the gas

sensitivity characteristics. Analysis of XRD spectra indicates that the samples present a tetragonal structure. It is observed that the addition of La does not affect considerably the crystallographic orientation of the SnO_2 films. However, the samples present a small increment in the intensity of the main XRD peaks, when La concentration is increased. Since identical deposition conditions are used, it can be concluded that the addition of La leads to an increase in the preferred growth of SnO_2 films.

Every polycrystalline film has its own preferred composition of crystallographic planes participating in the reaction of gas detection. Each crystallographic plane has delicate combination of energetic parameters, describing adsorption/desorption processes on their surface.

The slow time response in the film suggests that the diffusion of charge carriers is affected by La-doping due to the variation in the force field. Then, the rate of reaching the steady state in the film is composed of not only surface phenomena adsorption and desorption but also interaction between the surface and the bulk through the charge carriers.

4. Conclusion

The resistances of the doped SnO_2 films are mainly due to grain boundary effects, since the films are polycrystalline in nature. In addition, the doping favors defects, which in turn increases the film resistance. A higher resistance of the film at higher doping concentrations could be due to the reduction in the number of charge carriers because of increased disorder or due to the reduction of their mobility. Moreover, since air is used as the carrier gas, a large number of oxygen molecules are chemisorbed in the film both at the grain boundaries and on the surface. The chemisorption of oxygen will produce potential barrier, which hinders the electrical transport causing a reduction in conductivity.

When a reducing gas such as LPG is introduced, it reacts with chemisorbed oxygen, thereby releasing an electron back to the conduction band and increasing the conductance of the semiconductor. The dopant dispersed on the surface of the grains of the sensor material activates the reducing gas and allows it to spill over on to the sensor material. Thus, the resulting variation in the conductance is enhanced and consequently the sensitivity is increased admirably than pure SnO_2. For a deposition temperature up to 320°C, the electrical properties are governed mainly by an increase of the preferred orientation, which controls the mobility of charge carriers. At deposition temperatures higher than 320°C, the preferred orientation along (110) increases which results in a change in mobility of charge carriers and gas sensitivity. This effect can be attributed to the role of the dopant in the nucleation and growth process.

Thus, the addition of La in SnO_2 has a significant impact on the electrical parameters and sensitivity to gaseous molecules. The modification in preferred crystallite orientation causes more gaseous molecules to be adsorbed into the surface. This results in a change in the electrical conductance of the sensor in gas ambient. Hence, for the present case, the highest sensitivity is obtained for 1% La- doped SnO_2 samples deposited at 360°C.

Acknowledgements

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THERMOGRAVIMETRIC ANALYSIS OF LDPE MODIFIED BY CONDUCTING NATURAL RUBBER NANOPARTICLES

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Abstract

Low-density poly ethylene with varying amount of conducting natural rubber composites are prepared by melt mixing technique. The outstanding performance of the composites confirmed using TGA analysis. It is revealed that the thermal degradation behaviour of the composite is strongly influenced by the presence of nanoparticles.

Keywords: Elastomer, LDPE, Nanocomposite

1. Introduction

Polyethylene, with one third of the world plastic production, is one of the most versatile polymers. However, its use is restricted because of several drawbacks, including lower strength poor heat resistance etc. The commercial importance of polymers has been driving intense applications in the form of composites in various fields, such as aerospace, automotive, marine, infrastructure, military etc. [1]. It reported that the thermal stability of the polymers is improved upon blending with suitable fillers. Besides the compatibility of the two polymers, the relative interactions of the constituents in the composite have an influence in the degradation properties of the same [2]. Nano composites have played a major role in material science over last decade. The application of nanometer fillers to polymer materials is a promising channel for property modification. It is reported that nano-fillers have improved polymer performance remarkably because of their high specific surface area compared to conventional fibers or particles [3]. The aim of this study is to investigate the influence of the filler particles in the thermal stability of the polymer composite.

2. Experimental

2.1. Composite and specimen preparation

The LDPE granules obtained from Reliance industries Ltd, Harzaria, Gujrat, India are made into ultrafine powder by chemical route. The filler used in this study is conducting Natural Rubber nanoparticles (CNR nanoparticles). The CNR nanoparticles are prepared by doping the natural rubber solution with antimony pentachloride, a lewis acid using reflux boiling technique. The precipitate obtained is filtered out and dried under vacuum. The LDPE-based composites

are prepared by methodical mixing of the CNR nano particles with the ultra fine LDPE powder. The samples are molded into thin films using a micro injection molding machine by melt mixing. The analysis of all characterization studies of virgin LDPE and its composites are carried out according to the ASTM standards. Five specimens are measured for each case and the average values are taken. Samples are prepared by varying the amount of CNR nanoparticles in LDPE matrix i.e. from 10 phr to 50 phr filler loading.

2.2. Thermo gravimetric analysis (TGA)

The thermal degradation of pristine LDPE and its composites with CNR nanoparticles are done using Perkin Elmer, Diamond TG/DTA in nitrogen atmosphere. Samples of around 7 mg are heated from 50°C to 700 ° C at a heating rate of 10 ° C /min. TGA is performed to determine their degradation kinetics data such as activation energy (Ea) and pre-exponential term (A), etc. The determination of detailed kinetic parameters helps to analyze their thermal degradation behavior.

3. Result and discussion

From the TGA and DTG plots ,three characteristic temperatures can be identified, they are T_i, the temperature at which decomposition initiates, T_{50}, the temperature at which the 50% of the initial weight has been lost and T_{max}, the temperature corresponding to the maximum rate of decomposition, i.e., the peak temperature in the DTG plot. The three temperatures are considered while discussing the thermal stability of the materials. Thermo analytical thermograms of virgin polymer and its composite are given in Fig.1.

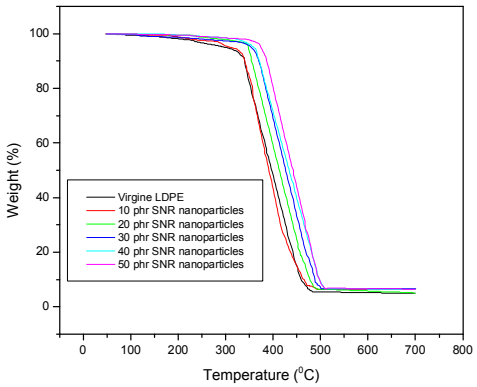

Fig.1. TGA curves of LDPE/CNR nanoparticles composite systems

The mass loss of about 5% in all the composites is between 100°C and 300°C indicates that the amount of water content in all composites is comparatively less. It is seen that the degradation of the composite materials with varying compositions starts at a higher temperature than that of pristine NR, which reveals the improved thermal stability of the composite. It has been reported that the thermal stability can be enhanced by the addition of a selected polymer [4-5]. The degradation behaviour of CNR nanoparticles/LDPE composites is strongly correlated with the morphology of the composites. In these composites the dispersed phase is CNR nanoparticles. The nano particle size of the dispersed phase

may cause an increase in the interfacial area and hence enhances the extend of interaction between the phases [6].

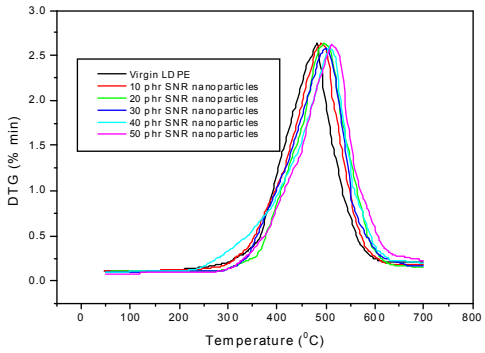

Fig.2. DTG curves of LDPE/CNR nanoparticles composite systems.

In the DTG curve the peak is observed at 482^{0}C for virgin LDPE and for the composites peak is shifted towards the higher temperature. For 50 phr composite the DTG peak is observed at 511^{0}C .The DTG peak corresponds to the complete degradation of the composite. It is seen that the degradation of the composite materials with varying compositions starts at a higher temperature than that of virgin LDPE. At the complete degradation temperature the weight loss is 97% for the virgin LDPE where as for the composite it is 93%. These two features reveal the improved thermal stability of the composite.

The degradation behavior of LDPE/CNR nano particle composites is strongly correlated with the morphology of the composites. In these composites the dispersed phase is CNR nanoparticles. The nano particle size of the dispersed phase may causes an increase in the interfacial area and hence enhances the extend of interaction between the phases. It has been reported that when composite of different polymers undergo degradation, the resulting process is affected by relative interaction of the two materials[6]. As the amount of CNR nanoparticles is increased, the DTG peak shifts to higher temperature, indicating the increased thermal stability. In general it can be say that the composite is nearly stable up to 300^{0}C, above which composite undergo thermal degradation and it will continue till the temperature range of 570^{0}C - 590^{0}C [7-8].

The degradation of LDPE (Fig.3 (a)) takes place according to a random chain scission mechanism [9-13]. Holmstrom and Sorvik reported that molecular entanglement reactions also take place simultaneously during LDPE degradation. Degradation of LDPE can be explained by the following chemical reaction. Analysis of the products (Fig.3 (b)) shown that *cis*-1, 4- polyisoprene, when pyrrolysed under an inert atmosphere, experienced a radical mechanism

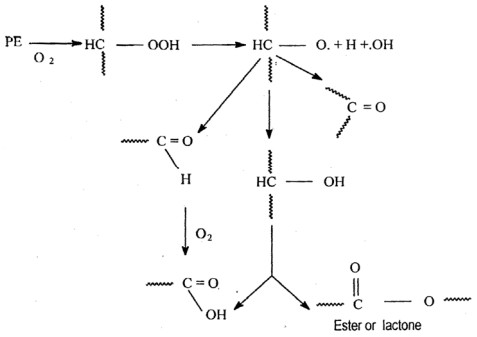

Fig.3 (a). Degradation mechanism of LDPE

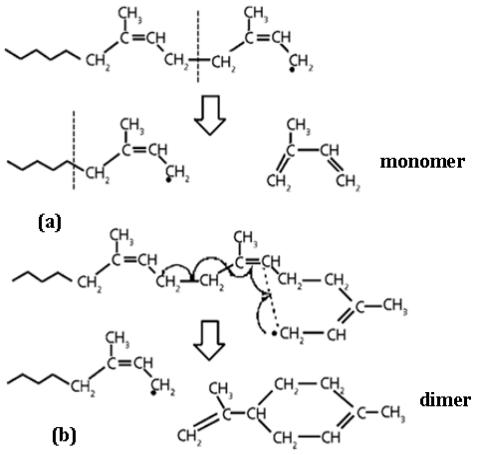

Fig.3 (b). Degradation mechanism of natural rubber

The chain scission mainly occurred at the β-position of carbon–carbon single bonds, which are adjacent to double bonds. The pyrolysis process of *cis*-1, 4-polyisoprene is accompanied by dehydrogenation and aromatization. However, dipentene is obtained as a major pyrolysis product below 430 °C and its yield decreased strongly with increasing temperature.

4. Conclusion

This work clearly shows that conducting rubber nanoparticles can be used as an efficient reinforcer in thermoplastic LDPE matrix. The excellent properties of the composites confirmed using TGA analysis shown that the reinforcer CNR nanoparticles can improve the thermal properties of the composites.

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LINEAR AND NONLINEAR OPTICAL PROPERTIES OF ZNO/POLY(STYRENE) NANOCOMPOSITE FILMS

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Abstract

Highly transparent zinc oxide (ZnO)/Polystyrene (PS) nanocomposite films are prepared using spin coating technique. Homogeneous nanocomposite films are coated on glass substrates from the ZnO incorporated polymer solution in toluene. The ZnO nanoparticles are synthesized by a chemical route at room temperature. High-resolution transmission electron microscopy (HR-TEM) images show that the ZnO nanoparticles are of size around 10 nm. The composite films are characterized by X-ray diffraction (XRD), Ultraviolet-Visible-Near Infrared (UV–Vis-NIR) spectroscopy and Z scan technique. The XRD pattern indicates the presence of polymer and ZnO nanoparticles in the nanocomposite film. The UV-Vis-NIR spectrum in the wavelength range of 200–800 nm shows that nanocomposite film with 10 wt % ZnO particles have strong absorption in the UV region. The nonlinear optical properties of the nanocomposite films are investigated using Z scan experiment. The results indicate optical limiting type nonlinearity in the films due to two photon absorption. The optical properties of the polymer are also greatly improved by the incorporation of ZnO nanoparticles.

Key words: Nanocomposite, UV shielding, Nonlinearity, Z scan technique

1. Introduction

In recent years, the design and synthesis of new polymer nanocomposites has gained increasing attention in polymer and material science. Combining the properties of two or more materials allow the preparation of high performance polymer based materials. There are several applications of polymeric nanocomposites based on their optical, electrical, mechanical and magnetic properties [1-3].

A variety of polymer/inorganic filler nanocomposites that offer attractive properties have been investigated extensively [4-6]. ZnO is an important and attractive semiconducting material. It has drawn enormous research attention due to its distinguished properties in optics, photonics and electronics [7]. Its wide band gap energy (3.3eV) at room temperature is ideal for short-wavelength optoelectronic applications. Compared with other wide band gap semiconductors, ZnO has several advantages [8]. Moreover ZnO can be

synthesized through wet chemistry, which offers a potential viable route to achieve uniform dispersion in polymer matrices through simple mixing. As the size decreases to the regime in between the bulk and isolated molecules, the semiconductor nanocrystals may have mechanical, optical, electric and thermal properties quite different from the bulk [9]. It is believed that the unique characteristics of the nanocomposites may also give rise to new opportunities for functional polymer/semiconductor nanocomposites [10].

Polystyrene (PS) is a transparent thermoplastic material which is in solid (glassy) state at room temperature. Introduction of ZnO filler into polymeric matrices can modify the optical (e.g. shielding from UV radiation), electrical and mechanical properties [11, 12]. In this work, ZnO/PS nanocomposites have been prepared by mixing ZnO powder well in polymer solution (in toluene) using ultrasonification. Highly transparent thin films of the nanocomposite are then obtained by spin-coating technique. The present work is an attempt to investigate in detail, the linear and nonlinear optical properties of the spin-coated ZnO/PS nanocomposite films.

2. Experimental

2.1 Preparation of ZnO nanoparticles

ZnO nanoparticles of the present study were synthesized using a simple chemical method at room temperature. 0.1M zinc acetate was dissolved in 100 ml methanol with magnetic stirring and then 0.2 M potassium hydroxide (KOH) was added. The mixture was stirred for ~2hours and then washed and filtered. The filtrate was dried in an oven at 50^{o} C for 5-6 hours. The white powder obtained was detected to be pure ZnO nanocrystals (average size ~10 nm) by X-ray diffraction (XRD) analysis.

2.2 Preparation of ZnO/polymer nanocomposite films

The ZnO/polymer nanocomposite solutions were prepared by adding ZnO powder (10 wt%) into polymer (PS) solution in toluene and the mixture was stirred for 2hrs and then sonicated for five minutes. This dispersion was used to prepare thin films by spin coating on glass substrates (Spin 150). Films were also prepared by casting the solution on glass substrates followed by solvent evaporation.

2.3 Characterization

The morphology and size of the synthesized ZnO nanoparticles were estimated by transmission electron microscopic (TEM) studies. The micrographs were obtained using JEOL 3010 instrument with an ultrahigh resolution pole piece. X-ray diffraction patterns of ZnO, PS and ZnO/PS, nanocomposite were obtained on a Rigaku X-ray Diffractometer with Cu - Kα (1.5418 A^{o})

radiation operating at 30 kV and 20 mA. Scanning was carried out in the 2θ range from 10– 70^o at a scan speed of 5^o per minute for the powder samples and 2^o per minute for the film samples.

UV-Visible absorption spectra of the samples were recorded on a JASCO-V 570 spectrophotometer in the wavelength range 200 to 800 nm. The nonlinear optical properties of the ZnO/PS nanocomposite films were studied using Z-scan technique. A Q-switched Nd: YAG laser with a pulse width of 7 ns at 532 nm was used in the experiment. A lens of focal length 23 cm was used to focus the laser pulses. Samples in the form of thin films were used for the experiment. The data was analyzed by using the procedure described by Sheik Bahae et al. [30] and the nonlinear coefficients were obtained by fitting the experimental Z-scan plots with the theoretical ones.

3. Results and discussion

3.1 Structural analysis

3.1.1: XRD analysis

X-ray Diffraction is perhaps the most widely used primary technique for characterizing materials. The XRD patterns of ZnO nanocrystals and composite film are shown in Fig.1. All the diffraction peaks could be indexed to match the standard diffraction pattern of wurtzite ZnO (JCPDS card no. 36-1451). The diffraction peaks corresponding to (100), (002), (101), (102), (110), (103), and (112) planes indicate the hexagonal structure of zinc oxide. The peaks get broaden and the extent of broadening is used to calculate the average size of the particles.

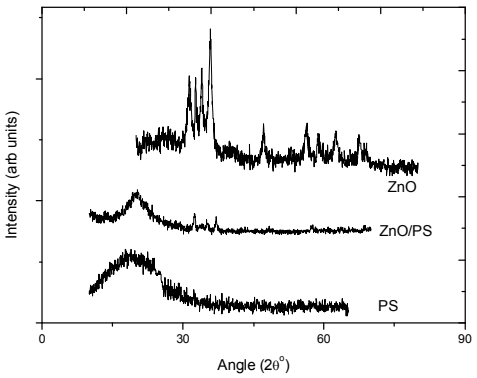

Figure 1: XRD patterns of) ZnO particles, ZnO/PS and PS films

The grain size of the particle is determined using the fwhm (β) of the maximum intensity peak (2 θ =35.8^o) and it is found to be ~10 nm. The XRD patterns of the composite films consist of a broad non-crystalline peak of polymers and sharp diffraction peaks of ZnO. The presence of ZnO produces neither new peaks nor peak shifts with respect to polymers showing that nano ZnO filled polymer composites consist of two phase structures.

3.1.2: TEM analysis

The morphology and size of the ZnO nanoparticles were estimated using transmission electron microscopy analysis. The TEM and High Resolution TEM (HRTEM) images of ZnO nanoparticles are shown in Fig.2 (a&b)). The average particle

diameters determined from the XRD peaks using the Scherrer formula are found to be close to that based on TEM analysis.

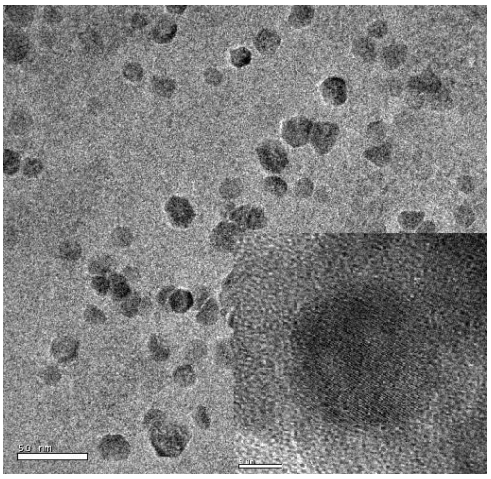

Figure 2: TEM and HRTEM (inset) images of ZnO particles of size ~ 10 nm

3.2 Optical studies

3.2.1: UV-Visible absorption spectroscopy analysis

The UV-Visible absorption spectra of the polymer and the ZnO/polymer nanocomposite films are shown in Fig.3. Pure polymer films do not show appreciable UV absorption and there is only a less intense absorption band centered around 300nm. An absorption window is found in the range 250-366 nm for the ZnO/PS nanocomposite films. Furthermore, the absorption peak wavelength of the composite film is substantially blue shifted relative to that of the bulk ZnO (~ 373nm) due to the strong confinement effect [13].

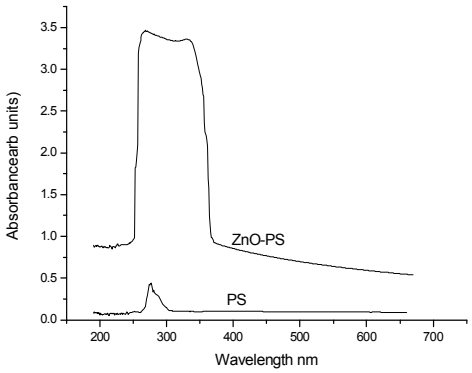

Figure 3: UV-Vis absorption spectra of ZnO/PS nanocomposite and PS films

3.2.2: Nonlinear optical studies

Nonlinear optical properties of ZnO/PS nanocomposite films were investigated by the Z-scan technique. Figure 4 shows the nonlinear absorption of ZnO/PS nanocomposite film at typical laser energy of 25 μJ for an irradiation wavelength of 532 nm. The open-aperture curve exhibits a normalized transmittance valley, indicating the presence of induced absorption. The observed nonlinearity is found to be of the third order, as it fits to a two photon absorption process (TPA). The corresponding net transmission is given by

$$T(z) = \frac{c}{q_0\sqrt{\pi}} \int_{-\infty}^{\infty} ln(1 + q_0 e^{-t^2}) dt \qquad (1)$$

where $q_0(z, r, t) = \beta I_0(t) L_{eff}$.

Here, $L_{eff} = 1 - e^{-\alpha L} / \alpha$, is the effective thickness with linear absorption coefficient α and nonlinear absorption coefficient β, L is the sample length and I_0 is the irradiance at focus [14].The solid curve in figure 4 is the theoretical fit to the experimental data.

From the open aperture Z-scan curve it is found that, the ZnO/PS nanocomposite films do exhibit large induced absorption behaviour. The observed dip in the open aperture curve shows the transmittance limiting efficiency of the nanocomposite films. In the present work, the curve of ZnO/PS films shows a better fit to the theoretical equations for TPA. The transmittance minimum is about 0.41, which highlights the better optical limiting efficiency of the the ZnO/PS films. The comparatively much lower transmittance value obtained for ZnO/PS composite films (Fig 4) shows that these films can be used as efficient optical limiters. Optical limiting (OL) devices protect light-sensitive sensors such as eye or CCD cameras, from possible damage caused by intense light exposure.

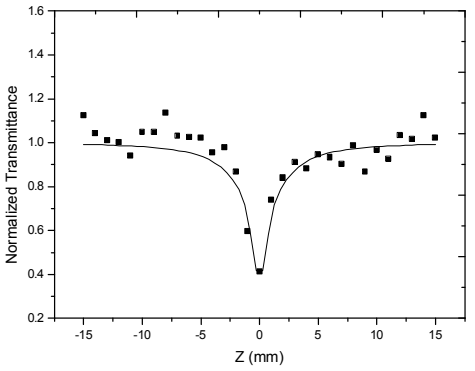

Figure 4: The open aperture Z scan curve of ZnO/PS nanocomposite film

4. Conclusion

In the present work, ZnO nanoparticles and transparent, ZnO/PS nanocomposite films have been grown using simple and reproducible methods. The ZnO/PS nanocomposite film with ZnO content of 10 wt %, exhibits strong UV absorption (around 90%), wide UV absorption window of width around 116 nm and high transmittance (around 90%) in the visible region. These nanocomposite films with strong UV absorption and high transmittance in the visible region offer prospects of applications as optical coating materials for UV protection and shielding. The technique employed in the present work for the synthesis of ZnO nanoparticles and ZnO/ PS nanocomposite films is a convenient and economical way of realizing optical nanocomposite films suitable for industrial applications.

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SYNTHESIS AND CHARACTERIZATION OF HIGHLY LUMINESCENT ZnS:Mn/PMMA NANOCOMPOSITE FILMS

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Abstract

The present work is focused on the synthesis of chitosan capped zinc sulfide nanocrystals doped with manganese (ZnS:Mn), of size about 10 nm by chemical capping co-precipitation method and the realization of highly luminescent ,transparent films of these nanocrystals embedded in the polymethyl methacrylate. ZnS nanocrystals doped with transition metal ions such as Mn^{2+} ions have been regarded as a promising new class of nanophosphors, owing to their superior luminescent properties . Capping with chitosan makes them bio-compatible and less toxic.

Thin films of the chitosan capped ZnS:Mn/ PMMA nanocomposite were deposited on glass substrates by spin - coating technique. These films were structurally characterized by XRD and FESEM spectroscopic techniques. The optical properties of these films were investigated by UV/Vis absorption and photoluminescence (PL) spectroscopic techniques. These polymer nanocomposite films are found to exhibit excellent UV shielding property in the wavelength range 200 to 300 nm. These films also show intense, orange red photoluminescence emission at 607 nm. Though, many research has already been carried out on Mn doped ZnS nanocrystals and their luminescence properties, no detailed studies exist on the development of polymer nanocomposite films of these nanocrystals. These transparent nanocomposite films of the chitosan capped ZnS:Mn /PMMA of the present studies offer prospects of applications of these films as efficient UV protection films. With high fluorescence intensity and color purity, these biocompatible, nanocomposite films can also be of application as biolabels in imaging fields.

Keywords: Chitosan; nanocomposite; bio-compatible; chemical capping; UV shielding

1. Introduction

Nanometer sized fluorescent semiconductor materials, used as bio-labels have attracted considerable attention in recent years, due to their unique physical, chemical and optical properties (Bruchez 1998, Chan and Nie 1998, Milliron et al 2003, Brus 1991, Elghanian et al 1997). Polymer based nanocomposites have attracted attention because of their ability to modify the optical, electrical, thermal, magnetic and mechanical properties of the host polymer. The properties of the polymer matrix and the inorganic filler can be combined so as to obtain desired high performance materials. Moreover, novel, functional, polymer–

inorganic nanocomposite thin films can be designed and synthesized for interesting applications in optoelectronic and bioimaging fields. ZnS is a semi-conducting luminescent material, which has a wideband gap of 3.70eV (Denzler et al 1998, Zou et al 1999). ZnS nanocrystals doped with transition metal ions such as Mn^{2+} ions have been regarded as a promising new class of nanophosphors, owing to their superior luminescent properties (Bhargava and Gallangher 1994, Igarashi et al 1995, Chen et al 2000, Xie et al 2000, Chen et al 2001, Bulanyi et al 2000, Dinsmore et al 2000). To be a suitable bio-labeling agent, the nanocrystals should have high luminescent efficiency, bio-compatibility, and proper surface groups for coupling with biomolecules. In order to achieve this, these nanocrystals are usually capped with some bio-compatible capping agents such as chitosan. The presence of reactive amine and –OH groups in chitosan makes them bio-compatible so that they can be attached to biomolecules.

Several papers showing photoluminescence properties of chitosan capped ZnS:Mn have been published earlier [Manoj Sharma et al 2010, Sonal, Mazumder et al 2010] . However, no reports have investigated the optical and photoluminescence properties of polymer composite films of these bio-compatible nanocrystals. To obtain high quality fluorescent films, it is essential to understand the effect of polymer on the photoluminescence properties of ZnS:Mn. In this paper, we report the synthesis of chitosan capped ZnS:Mn nanocrystals and the preparation of its composite films with polymer matrix polymethyl methacrylate (PMMA). The films were prepared by spin-coating method and were found to be transparent and highly luminescent. It has been observed that, PMMA encapsulated ZnS:Mn nanocrystals bring about better absorption and luminescent properties so that these films can be of applications as efficient UV protectors and bio-compatible materials in bio-imaging fields.

2. Experimental

2.1. Synthesis of chitosan capped ZnS:Mn nanoparticles

Citosan capped ZnS nanoparticles doped with manganese (Mn), were prepared by a chemical capping co-precipitation method in which zinc acetate [Zn $(CH_3COO)_2.2H_2O$], manganese acetate [$Mn(CH_3COO)_2.4H_2O$], sodium sulfide $Na_2S.9H_2O$ and chitosan were used as the reactants. Here chitosan is used as a bio-compatible surface capping agent, which prohibits the diffusion of ions from the solution and restricts the growth of ZnS:Mn nanocrystals. The experiment was carried out at room temperature in water. The synthesis procedure is similar to that described by Bhargava et al. with a suitable modification. Manganese doping was done in order to passivate ZnS and consequently high luminescence occurs at around 600 nm [12, 13]. In this experiment, 0.1 mol L^{-1} zinc

acetate and 0.01 mol L^{-1} manganese acetate were mixed in 50 ml of water along with 0.001% of chitosan to which 0.1 mol L^{-1} sodium sulfide was added dropwise to form chitosan capped ZnS:Mn nanoparticles. The mixture was kept under constant stirring for one and a half hour at room temperature. The colloidal solution thus obtained was filtered and dried in an oven at 40°C to get the nano powder which was used for structural analysis and also for preparing nanocomposite films.

2.2. Preparation of ZnS:Mn /PMMA nanocomposite film

The ZnS:Mn /PMMA nanocomposite was prepared through a simple solution mixing method by adding 1wt% of chitosan capped ZnS:Mn powder sample into PMMA solution (10%w/v) in toluene. The mixture obtained was stirred for 30 minutes and then placed in an ultrasonic bath for 8 minutes to get a homogeneous solution. This solution was used to prepare highly transparent and homogeneous thin films on ultrasonically cleaned, optically flat glass substrates using spin-coating technique (Spin 150). The thickness of the film sample was recorded using the thickness profiler (DEKTAK 6M STYLUS PROFILER) and was found to be around 1μm, which was optimized by controlling the spinning time and speed. The optical properties of the nanocomposite films prepared from chitosan capped ZnS:Mn nanocrystals embedded in polymethyl methacrylate (PMMA) was studied using UV-Visible absorption and photoluminescence (PL) spectroscopic techniques.

3. Result and Discussion

The chitosan capped ZnS:Mn powder samples and their polymer nanocomposite films were carried out using Rigaku X-ray diffractometer with CuKα radiation (1.5414 A°). Figure.1 shows the XRD pattern of the synthesized chitosan capped ZnS:Mn nanoparticles. The XRD pattern indicates the cubic crystal structure of the nanoparticles and the diffraction data is in good agreement with the JCPDS data for ZnS (JCPDS card No.050566). It is quite broad with three main peaks corresponding to the diffraction from (111), (220) and (311) planes, suggesting zinc blende crystal structure. From the diffraction peaks, the particle size is determined from the full width at half maximum (FWHM) using Debye-Scherrer formula

$$d = 0.9\lambda/\beta \cos\theta \quad (1)$$

where d, λ, β and θ are the average particle size, the wavelength of the X-rays, full width at half maximum intensity of the peaks expressed in radians and diffraction angle respectively. The size of the chitosan capped ZnS:Mn nanoparticles is found to be around 10 nm.

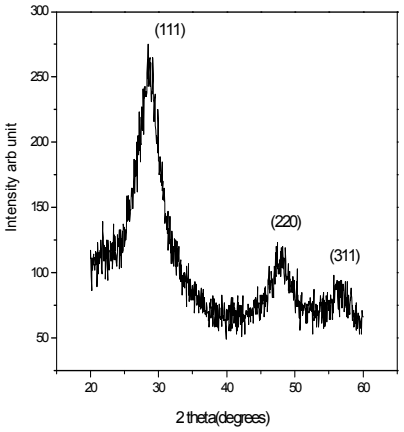

Figure.1 X-ray diffraction pattern of chitosan capped ZnS:Mn nanoparticles

The morphological analysis of chitosan capped ZnS:Mn/PMMA nanocomposite film is done by Field emission scanning electron microscopy (FESEM) using a HITACHI SU 6600 Microscope with an accelerating voltage of 20 kV. The FESEM image shown in figure.2 shows almost homogeneous dispersion of the chitosan capped ZnS:Mn nanoparticle in the polymer matrix. The efficiency of nanoparticles in improving the properties of the polymer material and vice versa is primarily determined by the degree of dispersion in the matrix.

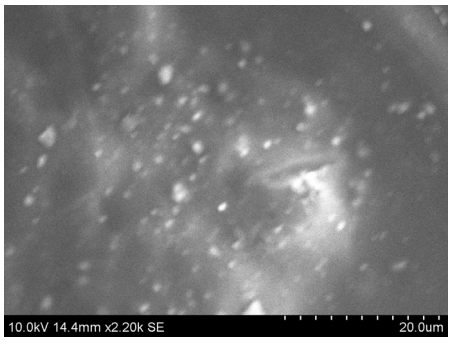

Figure.2 FESEM image of chitosan capped ZnS:Mn/PMMA nanocomposite film

The UV-Visible spectra of ZnS:Mn /PMMA nanocomposite thin film is recorded in the transmission mode using Jasco V 500 spectrophotometer in the wavelength range of 200–800 nm as shown in figure.3. For the nanocomposite films, an increase in absorption is observed at 300 nm, where the UV absorption is close to 100%. An absorption window of width around 100 nm is also observed for all the films, extending upto 200 nm. From the spectra it is clear that these films are highly transparent in the visible range and offer prospects of application as transparent UV radiation protectors in the wavelength range 300-200 nm. Moreover, this nanocomposite film can be used for the required UV shielding applications.

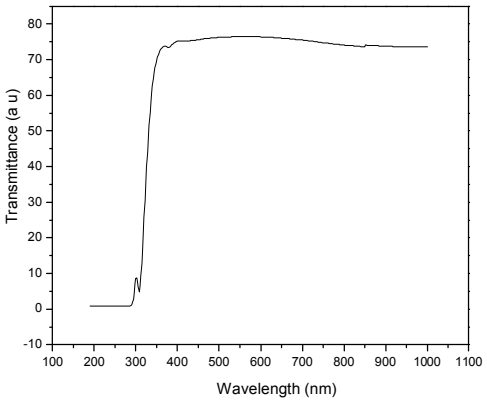

Figure. 3 UV-Visible spectrum of (ZnS:Mn /PMMA nanocomposite thin film

Photoluminescence (PL) emission spectrum of ZnS:Mn /PMMA nanocomposite thin film on glass substrate, was recorded at room temperature , using Fluoromax-3

spectrofluorimeter and the spectra are shown in figure.4. It is observed that all these nanocomposite films exhibit broad, orange emission peak at 597 nm under an excitation wavelength of 330 nm. The small broad peak observed at 420 nm can be due to defect states arising from zinc ion vacancy in the ZnS crystal lattice. These bio-ompatible, transparent and highly luminescent nanocomposite films with intense orange emission are potential candidates for bio-imaging applications.

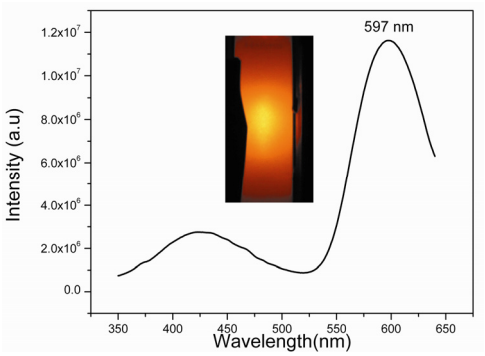

Figure.4 PL spectrum of ZnS:Mn /PMMA nanocomposite thin film

4. Conclusions

Highly luminescent and transparent ZnS:Mn /PMMA nanocomposite thin films are deposited on glass substrates using spin – coating technique . These films have been characterized for their optical properties by UV/Vis and PL spectroscopic techniques. From the UV/Vis spectra in transmission mode, it is clear that these films are highly transparent in the visible range and offer prospects of application as transparent UV radiation protectors in the wavelength range 300-200 nm. The PL spectra show broad orange emission around 597 nm. In addition, the highly luminescent ZnS:Mn / PMMA nanocomposite film are identified as possible bio-compatible materials for bio-imaging applications.

Acknowledgements:

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GROWTH AND CHARACTERISATION OF L- LYSINE DOPED POTASSIUM DIHYDROGEN PHOSPHATE SINGLE CRYSTALS FOR NONLINEAR OPTICAL APPLICATIONS

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Abstract

Nonlinear optical crystals of KDP doped with L lysine have been grown by slow evaporation technique. The crystals have been characterized by powder XRD, EDAX, UV-Vis absorption spectral analysis, SHG and open aperture z scan studies. Doping by the aminoacids have positively enhanced the optical properties especially the nonlinear optical properties. The SHG efficiency of the doped KDP crystals is found to be higher than the pristine crystal. The enhancement in the third order nonlinearity suggests the possibility of the use of the crystal as an optical limiter.
Key words: Nonlinear optical crystals, KDP, doping, SHG, Zscan.

1 Introduction

Potassium Dihydrogen Phosphate (KDP) single crystal is being considered as one of the best representative of nonlinear optical crystal and hence used as a standard to characterize other nonlinear materials. It finds wide applications in a variety of optoelectronic devices[A. K. Ghatak 1998, S. S. Jha 1995].For device application on large scale, large sized crystals are generally favoured. Hence growth of large sized KDP crystals [N. P. Zaitseva 1997] has attracted attention. The growth and quality of KDP crystals are affected by many factors such as additives, super saturation , pH value etc which influence the physical properties of the crystals like growth kinetics [L. N. Rashkovich 1991, K. Sangwal 2002] and surface morphology of crystal faces [I. Owczarek and K. Sangwal1990]. The doping of potassium dihydrogen phosphate (KDP) modifies the properties positively [G. Li, G. Suetal 2004]

Amino acids exhibit specific features of interest [J. F. Nicoud and R. J. Twieg 1987] such as (i) molecular chirality, which secures noncentro symmetric crystallographic structure, (ii) absence of strongly conjugated bonds, which leads to wide transparency ranges in the visible and UV spectral regions, and (iii) zwitter ionic nature of the molecule, which favors crystal hardness for applications in devices. Amino acids may be used as dopants in order to modify the nonlinear optical properties.

2 Crystal Growth

Potassium dihydrogen phosphate (1M) is dissolved in distilled water, to which L-lysine (.025M) is added and stirred for 2 hrs and kept for evaporation. Seed crystals were collected and grown in its supersaturated solution. Good quality crystals of L-lysine doped KDP (LKDP) crystals were harvested and collected for characterization. No fungus was seen during the growth process even after 2 months. Crystals have good chemical stability when stored at room temperature and showed no degradation.Fig:1 shows the photographs of the as grown crystals

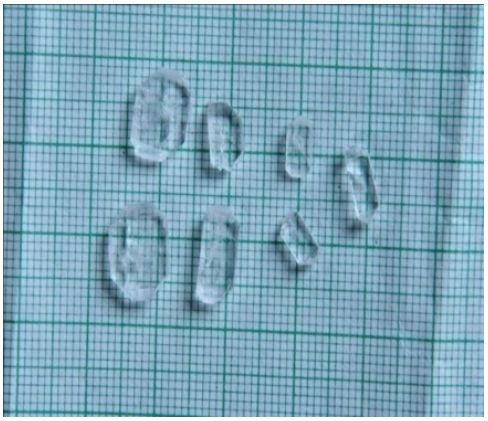

Fig:1 Photograph of L-lysine doped KDP crystals

3 Characterisation

The crystals were characterized by powder X-ray diffraction using Bruker D8 advance diffractometer with Cu K_α radiation (λ = 1.5418 Å). The composition of the doped sample was confirmed from EDAX spectrum. The absorption spectra of the doped samples were taken using JASCO UV spectrophotometer. The second harmonic efficiency of the doped samples were determined by Kurtz powder technique using Nd:YAG Q-switched laser beam The nonlinear optical properties were studied by the open aperture Z scan technique.

4 Results and discussion

4.1 Powder X-ray diffraction

The crystals were crushed into a fine powder and the powder X-ray diffraction was taken using the Bruker D8 advance diffractometer with Cu K_α radiation (λ = 1.5418 Å) . The powder XRD patterns of the doped samples are compared with that of KDP and displayed in Fig: 2.

From the powder X-ray diffraction studies of doped KDP crystals, the structure of the doped KDP crystals was determined by direct method and refined by Pawley method using Topaz version program using the single crystal X-ray data for pure KDP. The crystal data of KDP and L- lysine doped KDP are presented in Table.1. It is seen that both the pure and doped crystals crystallize in tetragonal crystal system with I42 d space group. There are slight variations in the lattice parameters of the doped crystal, compared to the pure one, due to the incorporation of the dopant in the pristine crystal, but has the same crystal structure as that of KDP.

Table.1 Powder XRD data of LKDP

Sample	KDP	LKDP
a	7.448(A°)	7.487(A°)
b	7.448(A°)	7.487(A°)
c	6.977(A°)	7.029(A°)
Space group	Tetragonal I42 d	Tetragonal I42 d

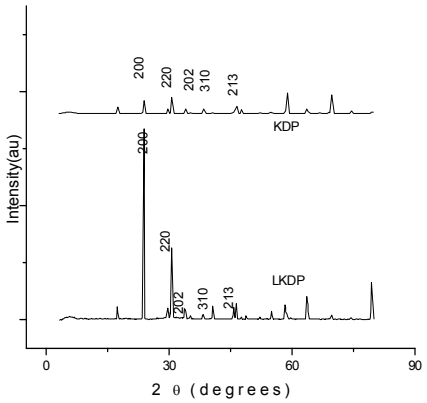

Fig: 2 Powder XRD patterns of LKDP

To confirm the constitution of the doped sample, the EDX spectrum was taken and is displayed in Fig:3.The spectrum shows the presence of the dopant, suggesting the formation of the sample.

4.2 UV-Vis absorption spectral studies

The absorption spectra of the doped samples were taken to know the absorption edge and transparency in the visible region. Crystals are transparent in the entire visible region with a strong UV absorption edge at 357 nm for LKDP. Fig:4 depicts the absorption spectra of the doped sample.

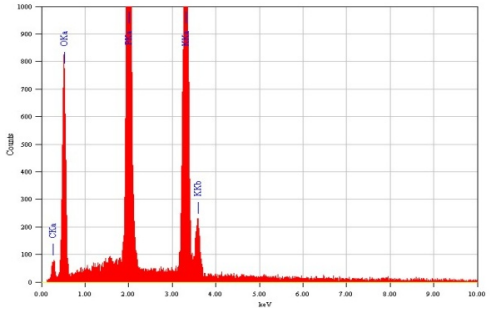

Fig:3 EDX spectra of LKDP

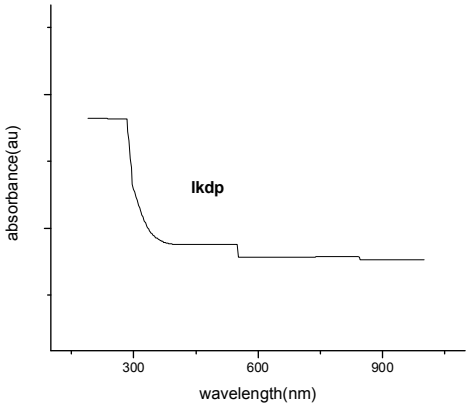

Fig:4 UV-Vis absorption spectrum

4.3 Second harmonic generation efficiency

The second harmonic generation efficiency of the doped samples were determined by Kurtz powder technique using Nd:YAG Q-switched laser beam. For a laser input of 4.2 mJ, the second harmonic signal (532 nm) the output is shown in Table 2. SHG efficiency for LKDP is found to be 1.3 times that of KDP. Thus doping KDP with aminoacids has enhanced the second harmonic efficiency significantly.

4.4 Open aperture Z scan technique

The nonlinear optical properties can be well studies by the open aperture Zscan technique. A Q switched Nd-YAG laser(532nm,7ns,10Hz) is used as the light source.The sample is moved in the direction of the light. The transmitted beam energy, reference beam energy and their ratio are measured simultaneously by an energy meter. The open aperture curve exhibits a normalized transmittance valley. The nonlinear absorption coefficient β is obtained by theoretical fitting for two photon absorption. β for LKDP $=4x10^{-10}$ m/W . The plot for the transmittance verses z axis in open aperture Z scan technique is shown in Fig: 5. It is inferred that doping KDP with L lysine has enhanced the nonlinearity. This obviously suggests the potentiality of the nanomaterial as optical power limiter.

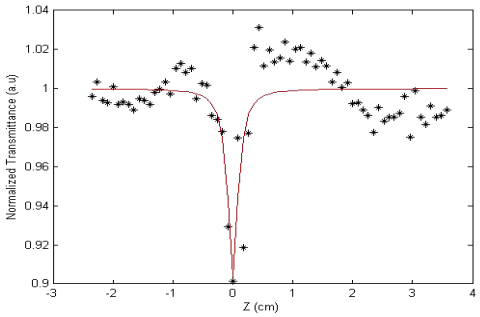

Fig: 5 Open aperture Zscan

5 Conclusions

Good quality nonlinear optical crystals of KDP doped with L lysine have been grown by slow evaporation technique. The crystals have been characterized by powder XRD,EDAX, UV-Vis absorption spectral analysis, SHG and open aperture z scan studies. Doping by the aminoacids have positively enhanced the optical properties especially the nonlinear optical properties. The doping has increased the SHG efficiency of the crystals to a large extent, thus putting forward the prospects for a harmonic generator and an optical limiter.

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MODIFICATION OF NATURAL RUBBER USING NOVOLAC RESINS FOR IMPROVED OIL AND AGE RESISTANCE

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Abstract

This work investigates the effect of addition of novolac resins of varying phenol: formaldehyde ratio into gum NR compounds. Novolac resins, in general, is seen to improve the tensile strength and tear strength of the rubber. There is in addition, a dramatic improvement in oil resistance and thermal ageing resistance of NR by the incorporation of novolac resins. The resins for the study were synthesized in the laboratory at various P/F ratios. But a direct relationship between P/F ratios and improvement in properties is not noticeable. Lower cure times are sufficient for the rubber in the presence of resin. Extraction studies prove that the resin is inextractable from the rubber. Summing up the presence of the resin as addressed to a considerable extent the limitations of NR, namely poor age and oil resistance.

Key words: Natural rubber, novolac resin, ageing resistance, oil resistance.

1. Introduction

Natural rubber is a low cost material with excellent physical properties such as resilience, high tensile strength, superior resistance to tear and abrasion, excellent tack and self adhesion. Natural rubber, being highly unsaturated, is easily attacked by oxygen, ozone and chemicals leading to degradation of polymer chains and deterioration of properties [1]. This limits its use in high temperature applications and hydrocarbon environments. Attempts have been made to improve the ageing characteristics of NR by compounding or by blending with rubbers that are inherently resistant to ageing [2].

The mechanical properties of crosslinked rubber undergo a marked change on heating with deterioration in elasticity and strength. The behavior of rubber when exposed to high temperatures is strongly influenced by the presence or absence of oxygen. More than half of the total change observed on ageing can be attributed to oxidation processes. Reaction with oxygen causes chain scission and crosslinking, After oxidation, a vulcanizate softens or stiffens depending on whether chain scission or crosslinking is more extensive [3].

Blending with different thermoset resins has been employed as a means for curing rubber as well as modifying the properties. The best known example for this is phenolic resin [4-7]. This study investigates blending of novolac resins with natural rubber for improvement of thermal ageing and oil resistance properties.

2. Experimental

2.1 Preparation of Novolacs

The novolac resins were prepared by reacting phenol with formaldehyde (1:0.5,1:0.7 and 1:0.9) in the presence of oxalic acid catalyst. The reaction mixture was heated and allowed to reflux at about 100^{o}C for 2-3 hours. When the resin separated from the aqueous phase the reaction was stopped. The resin was neutralized with sodium hydroxide, filtered, washed with water and vacuum dried.

2.2 Compounding and moulding of NR

NR mixes were prepared on a laboratory size two roll mill. The mixing was done according to ASTM D 3184-89 (2001). The rubber was masticated on the mill and the resin was incorporated into the rubber at various proportions (2, 4, 6 & 8 % weight of the rubber). Then the compounding ingredients were added in the following order: activators, accelerators, and sulphur. After mixing the stock was passed six times through tight nip gap and finally sheeted out.

Cure characteristics of the mixes were determined at 150^{o}C using Rubber Processing Analyzer, RPA 2000 as per ASTM standard, D 2084-01. Vulcanization to optimum cure time was then carried out in an electrically heated hydraulic press at 150^{o}C**.** The moldings were cooled and stored in a cool dark place for 24 hours prior to physical testing.

2. 3 Physical Testing

The vulcanizates were tested for different mechanical properties according to relevant ASTM standards. Ageing tests were carried out on cured rubber samples for 72 hours in accordance with ASTM 573-04.

3. Results and discussions

Curing studies indicate that for each mix cure time decreases with resin content up to 4% and increases slightly beyond 4% (Fig.1). One possible explanation is the imperfect dispersion of the resin at higher percentages which can lead to reduced interaction between rubber chains as well as between rubber chains and resin molecules. The inherent acidity of the resin can be another factor slowing down the crosslinking reaction. The interaction between the resin and the sites of unsaturation in the rubber chain is another possibility leading to increase in cure time at higher percentages of the resin.

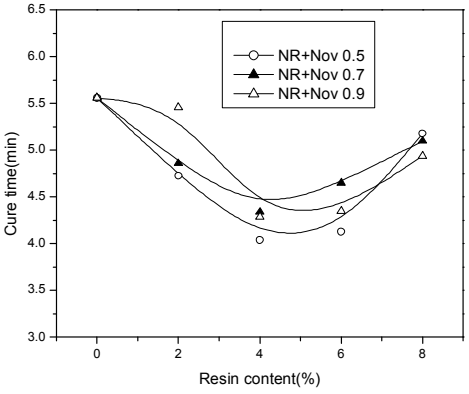

Figure 1 Variation of cure time with resin content of NR for different P/F ratio

Fig.2 shows the variation of tensile strength on addition of various percentages of novolac resin to the rubber. The resin has been synthesized with phenol formaldehyde ratio varying from 1: 0.5 to 1: 0.9. Each resin shows a maximum tensile strength at some percentage ranging from 2-6%. The novolac resin with phenol: formaldehyde ratio 1:0.5 shows the greatest improvement (~ 47% over virgin NR) in tensile strength at 4%. At this P/F ratio the number of benzene rings in the resin molecule will be greatest. Any interpenetrating effect between the rubber and the resin is likely to be maximum for this P/F ratio. Hence the better performance.

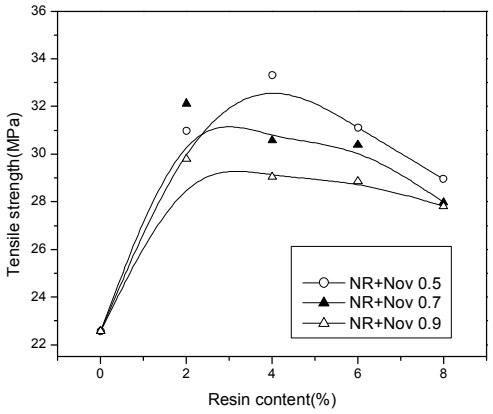

Figure 2 Variation of tensile strength with resin content of NR for different P/F ratio

Coming to tear strength (Fig.4) there is a general improvement in tear strength on addition of increasing amounts of resin. This might be due to better compatibility between the rubber and resin. The improved tear strength also points to interpenetration.

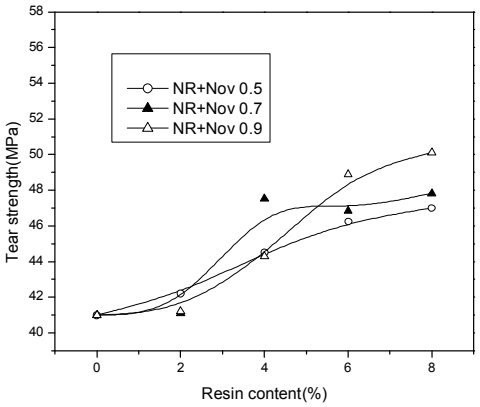

Figure 3 Variation of tear strength with resin content of NR for different P/F ratio

Figs. 5 and 6 depict the retention of tensile and tear strengths of different samples after ageing at 70°C for 72 hrs. In the absence of the resin the percentage retention of tensile strength after 72 hrs of ageing is only about 55%. On addition of resin this value increases steadily until at about 8% it is almost 100% of the original tensile strength. Similarly in the case of tear strength there is a dramatic improvement in tear strength retention at 2% resin. Although further increase is not substantial most samples show more than 100% retention of tear strength at 2%. The prolonged ageing process may help to make the crosslinking reaction of resin and/or chemical interaction between the rubber and the resin to go to completion. Hence the improvement in these two properties on ageing. Fig. 4 shows that the addition of resin dramatically reduces the percentage mass of oil absorbed over a 72 hour period. The presence of the resin in the crosslinked condition has made the rubber

less penetrable for oil. Moreover, the polar nature of the resin reduces the interaction between the rubber chains and oil.

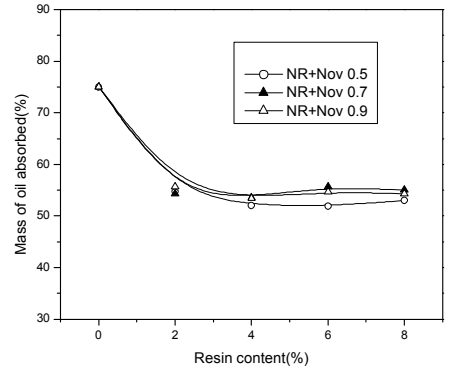

Figure 4 Variation of %mass of oil absorbed with resin content of NR for different P/F ratio

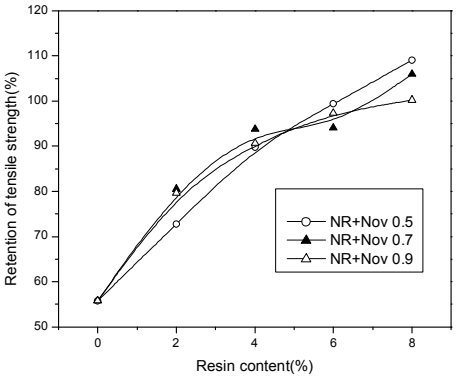

Figure 5 Variation of % retention of tensile strength with resin content of NR for different P/F ratio

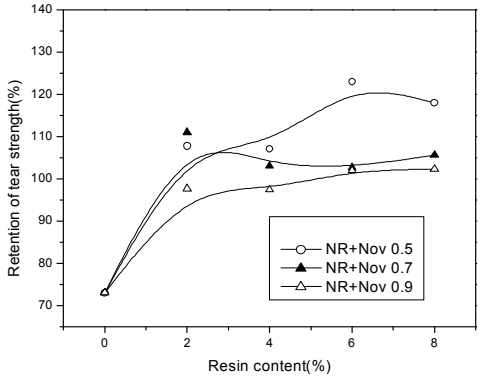

Figure 6 Variation of % retention of tear strength with resin content of NR for different P/F ratio

4. Conclusions

There is a general improvement in tensile strength and tear strength of NR on addition of different novolac resins although a correlation with P/F ratio is not readily noticeable in most cases. The age resistance of NR shows a clear improvement on addition of various novolac resins from the view point of tensile strength and tear strength after ageing. As low a percentage as 2% gives substantial improvement. The blending with the resin has considerably reduced the oil absorption of NR. Here again a 20-30% decrease is possible with only just 2% of resin. There is only a moderate increase of weight loss on extraction with acetone after adding various percentages of resin which indicates that most of the resin has been chemically incorporated into the rubber matrix.

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DETERMINATION OF INTERFACIAL TENSION OF NYLON6,66/EPDM BLENDS USING PALIERNE AND CHOI-SCHOWALTER METHODS

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Abstract

Melt rheological behaviour of nylon/EPDM blends has been investigated. The interfacial tension between the polymers is calculated from the storage modulus of the blends using Palierne model and Choi-Schowalter equation.Attempts were made to correlate the phase morphology with rheology.

Key Words: Blends, Rheology, Modeling

Introduction

Rheological studies are useful for optimising processing conditions and understanding the effect of various parameters on flow behavoiur of materials. Knowledge about the processability of a blend under high frequency is essential for the fabrication of articles of good finish and dimensional stability. Palierne model describes the linear viscoelastic behaviour of viscoelastic fluids. It has been shown to be very useful for predicting the rheological behaviour of the immiscible blends [1-7].

Experimental Materials

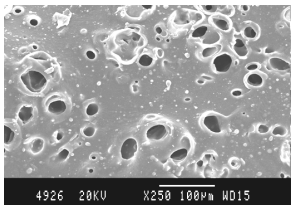
Nylon copolymer of melting point 148°C, EPDM with E/P ratio58/37.5wt%and Compatiblizer EPM-g-MA

Blend Preparation

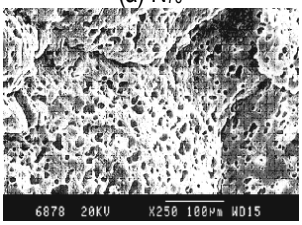
The blends were prepared in a Haake Rheomix at a temperature of 180°C and a rotor speed of 60 rpm for 11 minutes. The compatibilised blends were prepared by using the compatibiliser EPM-g-MA.

Morphology

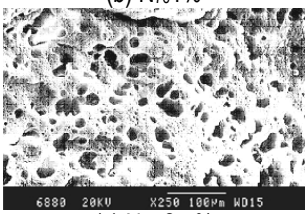
The morphology of the freeze-fractured cross-sections was examined using a scanning electron microscope, Jeol JSM-820. The samples were sputter coated with gold prior to SEM examination.



(a) N_{70}



(b) N_{70}1%



(c) N_{70} 2.5%

Figure1. Scanning Electron Micrographs of 70/30 blend containing different levels of EPM-g-MA (a) 0% (b) 1% (c) 2.5%

Palierne model -Theoretical basis

The Palierne model was used to determine the interfacial tension between the components [8], to determine the volume average radius of the dispersed particles, to calculate the sphere-size distribution from rheological data, to analyse the deformation of droplets under elongational flow. Palierne derived an equation for predicting the complex modulus of molten (emulsion type) blends (G_b^*), which is a function of the complex moduli of both phases G_m^* (for the matrix) and G_b^* (for the inclusions or dispersed phase) Palierne model has taken into account of the viscoelasticity of phases, the hydrodynamics interactions, the droplet size and size distribution and the interfacial tension of a multiphase system.

Jacobs et al. [60] developed an extended form of the Palierne model, written as,

$$G_b^* = G_m^* \frac{1+3\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}\nu(R)\,dR}{1-2\int_0^\infty \frac{E(\omega,R)}{D(\omega,R)}\nu(R)\,dR} \quad \ldots\ldots (1)$$

in which

$$E(\omega,R) = \left(\left[G_d^*(\omega)-G_m^*(\omega)\right]\left[19G_d^*(\omega)+16G_m^*(\omega)\right]+\frac{4\alpha}{R}\right) \quad ..(2)$$
$$\mathrm{X}\left[5G_d^*(\omega)-2G_m^*(\omega)\right]+\frac{\beta^I(\omega)}{R}\left[23G_d^*(\omega)-16G_m^*(\omega)\right]$$
$$+\frac{2\beta^{II}(\omega)}{R}\left[13G_d^*(\omega)-8G_m^*(\omega)\right]+\frac{24\beta^{II}(\omega)\alpha}{R^2}+16\beta^{II}(\omega)\frac{\alpha+\beta^I(\omega)}{R^2}$$

and

$$D(\omega,R) = \left[2G_d^*(\omega)+3G_m^*(\omega)\right]\left[19G_d^*(\omega)+16G_m^*(\omega)\right]$$
$$+\frac{40\alpha}{R}\left[G_d^*(\omega)+G_m^*(\omega)\right]+\frac{2\beta^I(\omega)}{R}\left[23G_d^*(\omega)+32G_m^*(\omega)\right]$$
$$+\frac{4\beta^{II}(\omega)}{R}\left[13G_d^*(\omega)+12G_m^*(\omega)\right]+\frac{48\beta^I(\omega)\alpha}{R^2}+32\beta^{II}(\omega)\frac{\alpha+\beta^I(\omega)}{R^2} \quad \ldots(3)$$

where, $G_b^*(\omega)$, $G_m^*(\omega)$ and $G_d^*(\omega)$ represent complex modulus of blend, matrix and dispersed phase, respectively. $\beta^I(\omega)$ and $\beta^{II}(\omega)$ are the complex interfacial dilation and shear moduli, respectively. $\nu(R)$ denotes the particle size distribution function while R, α *and* ω are particle radius, interfacial tension, and strain frequency, respectively. When the deformation of dispersed phase is small enough so that viscoelastic properties remain linear, we can set both $\beta^I(\omega)$ and $\beta^{II}(\omega)$ to zero. Graebling et al. [34] by assuming the particle size distribution to be narrow $\left(R_v/R_n \le 2\right)$ and interfacial tension to be independent of shear and interfacial area variation, simplified equation as:

$$G_b^* = G_m^* \frac{1+3\Sigma_i\varphi_i H_i(\omega)}{1-2\Sigma_i\varphi_i H_i(\omega)} \quad \ldots\ldots\ldots(4)$$

where

$$H_i(\omega) = \frac{(4\alpha/R_i)\left(2G_m^*(\omega)+5G_d^*(\omega)\right)+\left(G_d^*(\omega)-G_m^*(\omega)\right)\left(16G_m^*(\omega)+19G_d^*(\omega)\right)}{(40\alpha/R_i)\left(G_m^*(\omega)+G_d^*(\omega)\right)+\left(2G_d^*(\omega)-3G_m^*(\omega)\right)\left(16G_m^*(\omega)+19G_d^*(\omega)\right)} \quad \ldots(5)$$

in which, R_i and ϕ_i denote the i[th] particle fraction radius and the i[th] volume fraction of dispersed phase, respectively. The interfacial tension can then be estimated by fitting the experimental data to the Palierne model. Using (α) as fitting parameter, the best fit gives the interfacial tension.

Interfacial tension calculations

The interfacial tension can be calculated on the basis of the weighted relaxation spectrum ($\tau H_{(\tau)}$) with the relaxation time (τ) for nylon/EPDM blends. In order to get the

weighted relaxation spectrum the following equations were used:

$$G'_{(\omega)} = \int_{-\infty}^{\infty}\left[\left(H_{(\tau)}\omega^2\tau^2\right)\Big/\left(1+\omega^2\tau^2\right)\right]d(\ln\tau) \quad \ldots\ldots(6)$$

$$G''_{(\omega)} = \int_{-\infty}^{\infty}\left[\left(H_{(\tau)}\omega\tau\right)\Big/\left(1+\omega^2\tau^2\right)\right]d(\ln\tau) \quad \ldots(7)$$

the relaxation spectrum can be determined using Tschoegle approximation[61] as given in following equation:

$$H_{(\tau)} = G'\left\{\begin{bmatrix}\left(d(\log G')/d(\log\omega)\right)- \\ 0.5\left(d(\log G')/d(\log\omega)\right)^2\end{bmatrix}-\begin{bmatrix}(1/4.606)[d^2(\log G')/d(\log\omega)^2]\end{bmatrix}\right\}_{1/\omega=\tau/\sqrt{2}} \quad \ldots(8)$$

where ω is the frequency and τ is the relaxation time. It should be noted for neat polymer one will get one relaxation time where as for blends two τ (τ_1 and τ_2) will be there corresponding to the component polymers. The difference in the values ($\tau_1 - \tau_2$) was used to calculate the interfacial tension between the polymers in the presence and absence of compatibilisers. The interfacial tension (α) was calculated using two methods:(i) Palierne [29] (equation 8.11 and (ii) Choi-Schowalter [9] .

$$\alpha = \left[\frac{R_v\eta_m}{4\tau}\right]\left[\frac{(19K+16)(2K+3-2\phi(K-1))}{(10(K+1))-(2\phi(5K+2))}\right] \quad \ldots\ldots(9)$$

$$\alpha = \left[\frac{R_v\eta_m}{\tau}\right]\left[\frac{(19K+16)(2K+3)}{40(K+1)}\right]\left[1+\phi\left(\frac{5(19K+16)}{4(K+1)(2K+3)}\right)\right] \quad \ldots\ldots(10)$$

where η_m is the viscosity of the matrix, ϕ is the volume fraction of the dispersed phase, K is the viscosity ratio and is given as $K = \eta_d/\eta_m$ (η_d is the viscosity of the dispersed phase).

Table 1: Interfacial tension values of uncompatibilised nylon/EPDM blends

Blend	Interfacial tension (mN/m)	
	Palierne	Choi-Schowalter
N_{30}	13.03	14.21
N_{70}	17.46	20.33

The interfacial tension values of nylon/EPDM blends calculated from these equations are given in Table 1. In both cases, Palierne model gives lower values. It should be noted that in both methods, the blends show different α values. It is believed that the difference between the α values arises from the parameter R_v, which is derived from the phase morphology. Since both the blends are not dilute systems, the average particle size (R_v) contains contributions from interfacial tension as well as coalescence effect.

Table 2: Effect of compatibilisation on the interfacial tension of $N7_0$ blend

Blend	Interfacial tension (mN/m)	
	Palierne	Choi-Schowalter
N_{70}	17.46	20.33
$N_{70,1}$	0.637	0.714
$N_{70,2.5}$	0.318	0.356
$N_{70,5}$	0.792	0.888
$N_{70,10}$	1.166	1.307

Table 2 shows the effect of compatibilisation on the interfacial tension between the two components in N_{70} blends. On the basis of phase morphology studies it was concluded that addition of compatibiliser decreases the interfacial tension sharply up to CMC and beyond that a levelling off in interfacial tension occurs. Theoretical predictions of Noolandi and Hong, and

Leibler also supported this fact. So based on the phase morphology, we expect a sharp decrease in interfacial tension with initial addition of compatibiliser. It is obvious from the table that there is a very good correlation between the phase morphology and rheology. Addition of even 1wt% compatibiliser decreases α remarkably and this continues upto the CMC. Beyond CMC, the interfacial tension shows an increase at higher compatibiliser concentration.

Conclusions

In this work the interfacial tension of the blends in the presence and absence of compatibiliser was determined using Palierne and Choi-Schowalter methods. Both the methods were successful and gave reasonably good values. The interfacial tension drastically decreased with the addition of compatibiliser up to up to critical micelle concentration (CMC). It was also found that the minimum value was found at CMC.

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THE EFFECT OF DIFFERENT PRE-TREATMENTS ON SEED GENERATION IN *FLACOURTIA JANGOMAS* (LOUR.) RAECH

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Abstract

The paper entitled Seed germination in Flacourtia jangomas (Lour.) Raesch. has been done to analyze the reason for poor germination and to determine the treatment that promote maximum seed germination. In the natural habitat the seed germination is rare or almost nil. For the conduction of the experiment, nursery condition is applied. The seeds were subjected to pre-treatment such as mechanical scarification, acid scarification, hot water treatment, and chilling treatment. Only, mechanical scarification and hot water treatment gave result. None of the other treatment showed germination.

Key words: Flacourtia jangomas (Lour.) Raesch, Seed germination, Mechanical Scarification, Hot water treatment, After ripening period, Seed coat Dormancy

Introduction

India is very rich in its biodiversity. Along with the endogenous plants, the exotic plants also contribute a great deal in our plant diversity. *Flacourtia jangomas* (Lour.) Raesch. is one of such exotic plant which is seen in our country side and hilly areas. It is a medium sized evergreen tropical tree belongs to family Flacourtiaceae. The fruits of this plant are used as raw or in different recipes such as pickles, jams, etc. The plant contains different types of phytoconstituents such as phenols, flavanoids, etc. These has antidiabetic activity and is also involved in correction of altered biological parameters namely cholesterol and triglycerides. The leaves and bark are often used against diarrhoea, piles, weakness of limbs, bleeding gums, tooth ache, stomachitis, etc. Fruits are using in liver tonic and against rheumatism, skin disease, jaundice, tumors, etc. (Warrier et al., 1996).

Usually the plant is propagated by seeds. However, in natural condition, the seeds show very poor germination rate. A detailed study on the problem of germination is necessary for raising a good numbers of seedlings. Commonly, the germination of seeds is controlled by several factors such as water (Bradford and Somasco, 1994).), temperature (Kotowski, 1926), light (Ching Te May, 1972), dormancy (Hudson et al., 1997).

The seeds of *Flacourtia jangomas* have very hard and woody seed coat. In such seeds, one of the common causes of delay in seed germination is the blocking of water entry in to the seeds (Cavanagh, 1980). For germination to start the impermeable seed

coat must be rendered permeable. As the seed coat of *Flacourtia* is very hard, pre-sowing treatment of seeds are necessary for breaking the seed dormancy. So the objective of the present study is to analyze the reason for poor germination rate and determine the pre-treatments that promote maximum germination of seeds.

Materials and Methods

The study was conducted on seed germination of *Flacourtia jangomas* (Lour.) Raesch. in nursery condition. The fruits were collected from the plant at the month of December 2009 and 2010. The fruits were mechanically depulped to expose the seeds which were used for study. Bottom perforated polythene bags of dimension 14×16cm filled with potting mixtures were used. The potting mixture is prepared by mixing soil, sand and cow dung at 1:2:1 proportion.

The experiment was conducted from December 2010 to May 2011. The duration of experiment was 6 months. The healthy seeds were selected and thin, papery ones were discarded according to their morphological characters. Seeds of both 2009 and 2010 were made into groups of 16, each group contains 10 seeds. Then seeds were subjected to different pre-treatments.

Pre-Treatment Methods

1. Water soaking

The Ist set of seeds were taken and soaked in water for 1 week. Then sowed it in the polythene covers.

2. Mechanical scarification

The 2nd set of seeds was rubbed with sand paper and then soaked it in water for 24 hours and sowed.

3. Acid scarification

This was done by using concentrated 75% and 50% of H_2SO_4. The seeds were scarified with it in cavity blocks for specific time duration.

Table 1 Showing Acid treatment

Set of seed	Concentration of H_2SO_4	Time duration of treatment
3	98%	1 minute
4	98%	2 minute
5	75%	5 minute
6	75%	10 minute
7	75%	15 minute
8	75%	20 minute
9	50%	5 minute
10	50%	10 minute
11	50%	15 minute
12	50%	20 minute

After the treatment, the seeds were thoroughly washed in running water and sowed in polythene covers.

4. Hot water treatment

The 13th set of seeds was taken and kept it in the boiled water of 60^0 C for 1 hour. Then cooled and sowed it.

5. Stratification

The 14th and 15th set of seeds was placed in refrigerator for 48 hours and 2 weeks respectively. Then kept it in normal temperature for 24 hours and sowed in polythene covers.

6. Control

16th set of seeds were used as control.

OBSERVATIONS AND RESULTS

Seeds collected from the year 2009 and 2010 were used the germination study. For the conduction of the experiment, a total of 892 seeds were collected, 435 during the year of 2009 December and 457 in 2010 December. The seeds were light yellow in colour. They possessed very hard seed coat with many projections on the surface. Most of the seeds were thin and papery in nature. Others were thick and swollen. The thin and papery seeds were discarded. Only the healthy seeds were selected for the study. The percentages of healthy seeds were 39.8 in seeds of 2009 and 40.5 in 2010. (Table: 2)

Table: 2 Showing the percentage of fertile and sterile seeds collected during the year 2009 & 2010

Year	Total seeds	Healthy seeds	Percentage of Healthy seeds	Papery seeds	Percentage of papery seeds
2009	435	173	39.8%	260	59.78%
2010	457	185	40.5%	272	59.5%

The healthy seeds of 2009 and 2010 were divided into 16 sets. 10 seeds included in each set. Of this one set from each year kept as control. The remaining sets were subjected to different types of pre-treatments such as acid scarification, hot water treatment, water soaking treatment, mechanical scarification and stratification. After that the control and the pretreated seeds were sown in potting mixture taken in polythene bags.

The control and pre-treated seeds of 2010 showed no germination (Table: 4). Only the seeds collected in the year 2009 showed certain response. The control seeds of that year did not germinate. However certain sets of the pretreated seeds showed germination. Seeds treated with hot water showed 20% germination .The seeds germinated after 30 days in this treatment. The seeds mechanically scarified showed 30% germination (Table 3). It took about 30 days for the germination. The seeds treated with concentrated sulphuric acid showed no germination. Likewise the seeds subjected to scarification did not germinate.

The rate of germination was observed as very low or almost nil in the case of natural habitat. But, it show improved rate of germination in nursery conditions. From the experimental data it was observed that, only the seeds of 2009 gave rise to germination. None of the seeds of 2010 were germinated.

From the pre-treatment methods, only mechanical scarification and hot water treatment showed germination. In mechanical scarification, the germination percentage was 30% and in the hot water treatmentit was 20%. Pre-treatments such as acid scarification, water soaking and chilling did not show any germination and also seeds taken as control.

Table: 3 showing pretreatment of seeds collected during the year 2009

Treatment methods		Total Number of seeds	Number of seeds germinated
Acid Scarification	98% (1 minute)	10	-
	98% (2 minute)	10	-
	75% (5 minute)	10	-
	75% (10minute)	10	-
	75% (15minute)	10	-
	75% (20minute)	10	-
	50% (5 minute)	10	-
	50% (10minute)	10	-
	50% (15minute)	10	-
	50% (20minute)	10	-
Hot water treatment		10	2
Mechanical Scarification		10	3
Water Soaking		10	-
Chilling	2 hours	10	-
	48 hours	10	-
Control		10	-

Table: 4 showing pretreatment of seeds collected during the year 2010

Treatment methods		Total Number of seeds	Number of seeds germinated
Acid Scarification	98% (1minute)	10	-
	98% (2minute)	10	-
	75% (5minute)	10	-
	75% (10minute)	10	-
	75% (15minute)	10	-
	75% (20minute)	10	-
	50% (5minute)	10	-
	50% (10minute)	10	-
	50% (15minute)	10	-
	50% (20 minute)	10	-
Hot water treatment		10	-
Mechanical Scarification		10	-
Water Soaking		10	-
Chilling	2 hours	10	-
	48 hours	10	-
Control		10	-

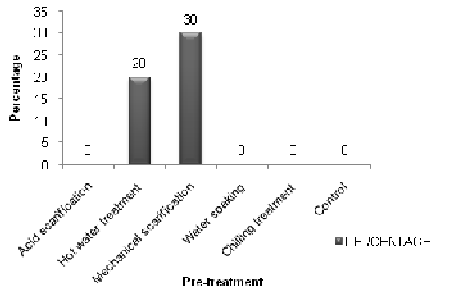

Chart showing Percentage of germination in different pretreatments

Discussion

Flacourtia jangomas (Lour.) Raesch. is an exotic tree showing low rate of germination. The knowledge about the germination rate of plant is very poor. The plant produces a large number of fruits and seeds. However, the germination rates of seeds in natural habitat are very low. From the collected seeds, nearly 60% of the seeds are thin and papery and only 40% seeds are healthy (table: 2).

In the present study, the seeds of *Flacourtia jangomas* (Lour.) Raesch. were subjected to different types of pre-treatment before sowing. Seeds collected during 2009 showing improved germination rate. None of the seeds of 2010 germinate during the experiment (table:4). Bewely and Black (1994) reported that certain plants require an after-ripening period to lose dormancy. The study reveals that the seeds at shedding may enclose an undifferentiated embryo. It may take several months for the production of mature embryo after shedding. Bhojwani and Bhatnagar (1974) reported similar type of embryo maturation in *Eranthis hiemalis*. The seeds collected in 2009 get an after-ripening period of about one year and during that time the embryo can attain maturity. Experiments with these seeds show certain percentage of germination. The seeds collected in 2010 have only the immature embryo and they do not get any maturation time. That is why the seeds are not germinated during the experiment.

From the result it is evident that the seed coat dormancy also plays a very important role in *Flacourtia* seeds. The seed coat is very hard and woody. Due to the presence of this impermeable seed coat, the water cannot enter into the seed, so the water potential get

reduced which is adversely affecting the germination process. Germination of most of the seeds is adversely affected by seed coat dormancy which is a kind of physical or exogenous dormancy (Sing, 1987). Control plot of 2009 seeds yielded no germination, indicating the fact that the seeds require pre-sowing treatments for good germination.

Scarification is the best way to overcome hard seed coat dormancy (Matthew Beckler, 2006; Umar et al, 2005). In the present study different sets of seeds are subjected to mechanical and chemical scarification. Out of this only mechanically scarified seeds show germination (table: 3). This may be due to the fact that mechanical scarification might have helped in physically breaking the impermeable layer in the seed coat, allowing water and oxygen to enter the seeds and permit the embryo to overcome mechanical restriction of surrounding tissues. This agrees with the results of Lopes et al., (1998) in *Caesalpinia ferra*. In the present study the mechanical scarification shows 30% germination.

The set of seeds which were subjected to acid treatment do not show any germination (table: 3 and table: 4).This is in accordance with the report of Seong et al., (1990) in which the pre-treatment of H_2SO_4 scarification decreases the germination percentage. The chemical may affecting the embryo and that may get destructed. So the acid scarification gives negative result.

Hot water treatment gives an improved germination rate. However the germination percentage is low. It is nearly 20% (table: 3). Kobmoo and Hellum (1984) proved that hot water treatment is the quickest, cheapest and simplest method to overcome seed coat dormancy. Hot water rendered seed coat more permeable, thus resulting in better germination.

Chilling treatment is also showing negative result. It may be due to the activity of low temperature, the embryo cannot withstand. The physiological and metabolic activity of embryo may slow down which may altering the germination process.

The present study reveals that the germination of *Flacourtia* seeds not only affected by immature embryo but also hard seed coat. Though the seeds collected during 2009 have attained embryo maturity they cannot germinate due to hard seed coats. When these seeds are subjected to pre-treatment, they give positive result. Mechanical scarification and hot water treatments are the best way to overcome seed coat dormancy in *Flacourtia jangomas (*Lour.)Reach.

Conclusion

The present study reveals that

- After-ripening period of the embryo and seed coat dormancy are the main reason for the low germination rate of the species.
- Seed coat dormancy can be overcome by pre-treatments such as mechanical scarification and hot water treatment

The described procedure proved that seed treatments are necessary to overcome dormancy in *Flacourtia* seeds. However, further experiments should also be conducted to draw a satisfactory conclusion regarding seed germination of *Flacourtia jangomas* (Lour.) Reach. since germination is influenced by various factors.

Acknowledgement

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LENGTH WEIGHT RELATIONSHIP OF *Dascyllus carneus* AT MINICOY ATOLL

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Abstract

In D. carneus the regression coefficient 'a' was small in all the fishes thereby indicating low fat content in the body. The 'b' coefficient was highest in indeterminates, and hence suggested that the growth was more in the younger ones. In the immature, mature, and spent fishes the growth for males were higher than females. As there was a difference in the growth pattern of the males and females, the linear equations were calculated separately and they are given below

For indeterminates	-	*W*	=	$0.0000018\ L^{3.16}$
For immature males	-	*W*	=	$0.0000049\ L^{2.90}$
For immature females	-	*W*	=	$0.00010\ L^{2.86}$
For Mature males	-	*W*	=	$0.000002\ L^{3.03}$
For Mature females	-	*W*	=	$0.00046\ L^{2.28}$
For spent males	-	*W*	=	$0.0000013\ L^{3.11}$
For spent females	-	*W*	=	$0.0000076\ L^{2.67}$

Key Words: *Minicoy Atoll, Length weight relationship, Immature, Mature, Indeterminates, Spent*

Introduction

Length-weight relationship was calculated with two objectives, firstly to obtain a formula for inter-conversion, and secondly, to analyse the type of growth pattern they follow. Separate length-weight equations were derived for the indeterminates, immature, mature, and spent.

A mathematical expression of both length and weight can be resolved so as to calculate an unknown variable from a known variable. According to Le Cren (1951) the length-weight relationship is useful to distinguish small taxonomic units. The regression coefficient is a parameter of the yield equation of Beverton and Holt (1957). David (1963) reported that there were also possibilities of the length-weight relationship turning out to be useful tools in the recognition of different stocks of the same species. The general expectation was that the weight of fishes would vary as the cube of its length (Brody, 1945; Lagler, 1952; Rounsefell and Everhart, 1953 and Brown, 1957). The actual relationship may depart significantly from this (Le Cren, 1951) as fishes normally do not retain the same shape on body outlines throughout their life span and the specific gravity of the tissue may not remain constant. Due to this the coefficient of regression of logarithm of weight on logarithm of length, depart from 3. In such cases, the value of the exponent 'b' in the parabolic equation may lie between 2.5 and 4 (Hile, 1936 and Martin, 1949).

Meticulous study was carried out on Length-weight relationship in different reef

fishes but it was found to be scanty for pomacentrids. The only available works are those of Kulbicki *et al.* (1993) for lagoon fishes of New Caledonia; Letourneur *et al.* (1998) which was an updated work presented by Kulbicki *et al.* (1993); Letourneur (1998) in reef fishes from Reunion islands.

Length-weight relationship in Indian waters on pomacentrids were reported by Pillai *et al*., (1985b) in *D. aruanus*; Mohan *et al.* (1986) in *C. caeruleus*; *A. triostegus* by Mohan and Pillai.(1988); Pillai and Mohan (1990) in *A glaucus*; Vijayamma (1997) in ornamental fishes of the reefs including pomacentrids.

Material and Methods

Length–weight relationship was determined by collecting data on length, weight and sex of the fish in different phases of its life. The specimen were wiped with an adsorbent cloth to remove the excessive moisture and extraneous matter adhering to the body of the fish, before noting its length, whole weight and sex.

The length-weight relationship of *D. carneus* w*as* estimated with 2053 specimens. Specimens were separated as indeterminate, immature male, immature female, mature male, mature female, spent male and spent female. They constituted, 125 indeterminates ranging from 7 to16 mm (TL), 362 immature males ranging from 16 to 30 mm (TL), 332 immature females ranging from 16 to 32 mm (TL), 404 mature males ranging from 28 to 72 mm (TL), 352 mature females ranging from 28 to 59 mm (TL), 261 spent males ranging from 33 to 71 mm (TL) and 217 spent females ranging from 35 to 59 mm (TL). The relationship existing between the length and weight can be calculated by the formula

$$W = a\ L^b$$

In this calculation 'W' is the weight of the fish 'L' is the length of the fish and a and 'b' are constants to be determined empirically from the data.(*i.e.,* initial growth index and regression constant respectively) and they are calculated from the formulae:

$$b = \frac{(N.S\ xy) - (Sx.Sy)}{(N.\ Sx)^2 - (Sx)^2}$$

$$a = y - bx$$

When expressed logarithmically the above equation becomes a straight line and can be written as: LogW = log a + b log L, which is linear relationship between 'W' and 'Y'. The parameters 'a' and 'b' were estimated by the method of Least Square (Snedecor and Cochran, 1967).

The data were analysed after classifying the fish into seven groups namely: indeterminate, immature male, immature female, mature male, mature female, spent male and spent female. The segregation was made according to the standard description given under 'Reproductive biology'. Since differences are expected between the regression equations for males and females they were studied separately and the data were subjected to analysis of covariance following Snedecor and Cochran (1967).

The regression of log length or log weight was first calculated separately for males and females of the samples and the data were pooled for arriving at a single formula.

Analysis of covariance (Snedecor and Cochran, 1967) was employed to find out whether the regression of different sets of variable differed significantly between males and females. The significance of variations in the estimate of 'b' for males, females and pooled data of this species from the expected value for ideal fish (3.0) was tested by the 't' test as per given formula:

$$T = \frac{B-3}{Sb}$$

where, $\frac{\sqrt{1/n - 2\,Sy^2 - (Sx)2}}{\sqrt{\Sigma}\ X^2}$

Results

The length-weight relationship of *D. carneus* estimated among indeterminate, immature male, immature female, mature male, mature female, spent male and spent female are as given below. The significance of the variation in the estimate of 'b' value from the cubic relation was tested by the't' test. The values of 'b','t', and their significance were given in Table 16.

Indeterminates

The length-weight relationship equation fitted for each of these categories were found to be:

Results

The length-weight relationship of *D. carneus* estimated among indeterminate, immature male, immature female, mature male, mature female, spent male and spent female are as given below. The significance of the variation in the estimate of 'b' value from the cubic relation was tested by the't' test. The values of 'b','t', and their significance were given in Table 16.

Indeterminates

The length-weight relationship equation fitted for each of these categories were found to be:

$W = 0.0000018\ L^{3.16}$

Log. W = -6.181 + 3.16. Log L, $r^2 = 0.977$

The scatter diagrams of length-weight relationship are presented in Fig. 15.

Immature

The results of regression analysis in the two sexes are given in the Table 17. Analysis of co-variance (Table 18) showed that the difference between the regression coefficients of the two sexes, was significant, hence the data were analysed seperately and equations obtained are:

Male

$W = 0.0000049\ L^{2.90}$

Log . W = -6.489 + 2.90 . Log. L, $r^2 = 0.95$

The scatter diagrams of length-weight relationship are presented in Fig. 16.

The 't' value was found to be significantly different; hence the growth was not isometric.

Female:

$W = 0.00010\ L^{2.86}$

Log . W = -4.101 + 2.86 . Log. L, $r^2 = 0.95$

Table 16. 't' values calculated for different maturity groups of *D. carneus*

Groups	Regression Coefficients	t' Values	Inference	Result
Indeterminate	3.16	8.18	Not significant	Isometric growth pattern not followed
Immature female	2.86	3.45	Not significant	Isometric growth pattern not followed
Immature male	2.90	0.49	significant	Isometric growth pattern followed
Mature female	2.28	3.25	Not significant	Isometric growth pattern not followed
Mature male	3.03	0.86	Significant	Isometric growth pattern followed
Spent female	2.67	12.47	Not significant	Isometric growth pattern not followed
Spent male	3.11	4.37	Not significant	Isometric growth pattern not followed

't' < 2.22 is significant at 5% level

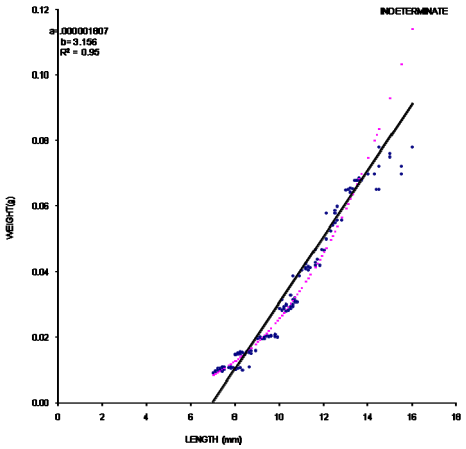

Fig.15. Scatter diagram showing relationship between log length and log weight in indeterminates of *D. carneus*

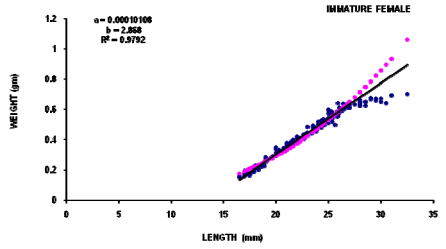

Fig. 16. Scatter diagram showing relationship between log length and log weight in immature females of *D. carneus*

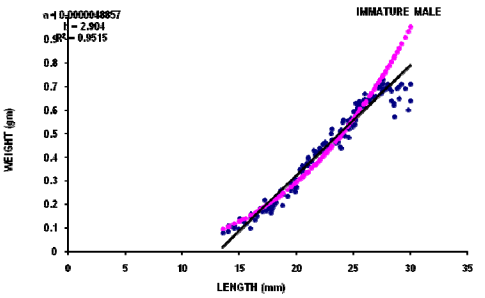

Fig.17. Scatter diagram showing relationship between log length and log weight in immature males of *D. carneus*

Table 17. Sum of squares and products of length-weight data of immature *D carneus*

Sex	$\bar{X}$	$\bar{Y}$	n	Sum of squares and product			a	b	Errors of estimate	
				S_{X2}	S_{XY}	S_{Y2}			df	ss
Males	3.09	.99	362	10.95	97.00	31.79	-6.489	2.904	361	5.539
Females	3.10	.96	332	7.74	20.60	57.38	-4.101	2.860	331	3.028
Pooled	3.10	.94	694	18.69	52.38	154.38	-5.469	2.789	693	8.932

X = Mean logarithmic length

$\bar{Y}$ = Mean logarithmic weight

a = Y- intercept

b = regression coefficient

S_{X2}, S_{Y2} = corrected sum of squares of length and weight respectively

S_{XY} = corrected sum of products of length and weight

df = Degree of freedom

ss = Sum of squares

Table 18. Analysis of co-variance of immature *D. carneus*

Source of variation	df	ss	MSS
Deviation from individual regression within sexes	693	8.932	0.013
Difference between regression	1	0.365	0.365
Deviation from total regression	694	8.961	0.013

F = 29.44, df = 1, 694, F at 5% = 3.84 F > 3.84 is significant at 5% level.

The scatter diagrams of length-weight relationship are presented in Fig. 17.

The 't' value was found to be significantly different; hence the growth was not isometric.

Mature

The results of regression analysis in the two sexes are given in the Table 19. Analysis of co-variance (Table 20) showed that the difference between the regression coefficients of the two sexes was significant. Hence the data was analysed separately and equations obtained are:

Male:

$W = 0.0000024\ L^{3.03}$

$\text{Log . } W = -6.240 + 3.03 \text{ . Log . } L,\ r^2 = 0.96$

The scatter diagrams of length-weight relationship are presented in Fig. 18

The 't' value was found to be significantly different; hence the growth was not isometric.

Female:

$W = 0.00046\ L^{2.28}$

$\text{Log . } W = -4.467 + 2.27 \text{ . Log . } L,\ r^2 = 0.94$

The scatter diagrams of length-weight relationship are presented in Fig. 19

The 't' value was found to be significantly different; hence the growth was not isometric.

Spent

The results of regression analysis in the two sexes are presented in the Table 21. Analysis of co-variance (Table 22) showed that the difference between the regression coefficients of the two sexes was significant, hence the data was analysed separately and equation obtained is:

Male

$W = 0.0000013\ L^{3.11}$

$\text{Log . } W = -6.13 + 3.11 \text{ . Log . } L,\ r^2 = 0.98$

The scatter diagrams of length-weight relationship are presented in Fig.20

The 't' value was found to be significantly different; hence the growth was not isometric

Female

$W = 0.0000076\ L^{2.67}$

$\text{Log . } W = -6.763 + 2.67 \text{ .Log } L,\ r^2 = 0.97$

The scatter diagrams of length-weight relationship are presented in Fig. 21

The 't' value was found to be significantly different; hence the growth was not isometric.

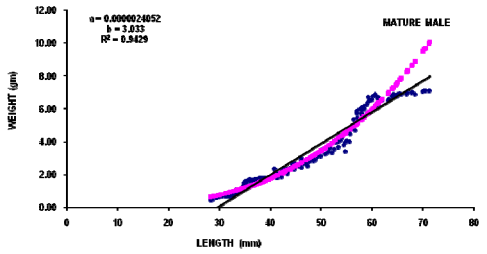

Fig. 18. Scater diagram showing relationship between log length and log weight in mature males of *D. carneus*

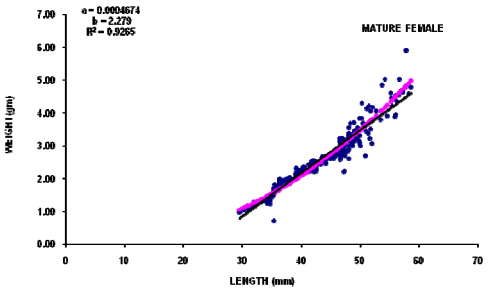

Fig. 19. Scatter diagram showing relationship between log length and log weight in mature females of *D. carneus*

Table 19. Sum of squares and products of length-weight data of mature *D. carneus*

Sex	X	Y	n	Sum of squares and product			a	b	Errors of estimate	
				S_{x2}	S_{xy}	S_{y2}			df	ss
Males	3.72	0.68	404	20.01	60.67	191.36	-6.240	3.033	403	7.695
Females	3.73	0.83	352	8.53	19.45	47.19	-4.467	2.279	351	3.027
Pooled	3.73	0.85	756	28.55	80.44	254.39	-5.598	2.809	755	4.064

X = Mean logarithmic length

$\overline{Y}$ = Mean logarithmic weight

a = Y- intercept

b = regression coefficient

S_{X2}, S_{Y2} = corrected sum of squares of length and weight respectively

S_{XY} = corrected sum of products of length and weight

df = Degree of freedom

ss = Sum of squares

Table 20. Analysis of co-variance of mature *D. carneus*

Source of variation	df	ss	MSS
Deviation from individual regression within sexes	755	14.064	0.019
Difference between regression	1	3.342	3.342
Deviation from total regression	756	14.04	0.019

F = 235.02, df = 1, 756, F at 5% = 3.84, F > 3.84 is significant at 5% level

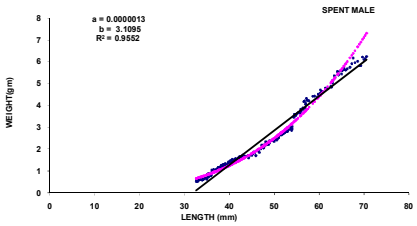

Fig. 20. Scatter diagram showing relationship between log length and log weight in spent males of *D. carneus*

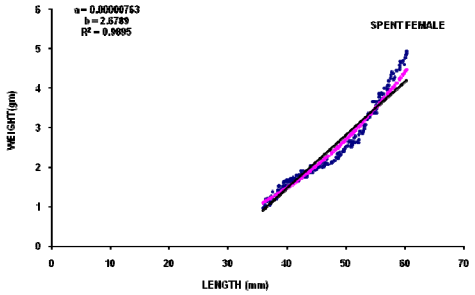

Fig. 21. Scatter diagram showing relationship between log length and log weight in immature females of *D. carneus*

Table 21. Sum of squares and products of length-weight data of spent *D. carneus*

Sex	X	Y	n	Sum of squares and product			a	b	Errors of estimate	
				S_{x2}	S_{xy}	S_{y2}			df	ss
Males	3.83	.68	261	11.52	35.84	113.56	-6.130	3.109	260	2.125
Females	3.84	.81	217	5.17	13.83	38.05	-6.763	2.678	216	1.047
Pooled	3.83	.74	478	16.70	49.78	153.72	-6.469	2.789	476	1.53

X = Mean logarithmic length

$\overline{Y}$ = Mean logarithmic weight

a = Y- intercept

b = regression coefficient

S_{X2}, S_{Y2} = corrected sum of squares of length and weight respectively

S_{XY} = corrected sum of products of length and weight

df = Degree of freedom

ss = Sum of squares

Table 22. Analysis of co-variance of spent *D. carneus*

Source of variation	df	ss	MSS
Deviation from individual regression within sexes	477	3.844	0.008
Difference between regression	1	0.672	0.672
Deviation from total regression	478	3.871	0.010

F = 100.83, df = 478, F at 5% = 3.84, F > 3.84 is significant at 5% level

Discussion

The present observation showed positive and negative correlation between length and weight in indeterminates, immature, mature and spent groups of *D. carneus*. No Previous reports on the length-weight relationship in *D. carneus* were reported from Indian waters. Comparitive studies were done by fishes of same genus , in *D. aruanus* , Pillai *et al.* (1985b) reported 'b' value as 2.481 for males and 2.807 for females from Minicoy; Kulbicki *et al.* (1993) obtained 'b' value of 3.04 (TL min. = 2.3 cm, max. = 9 cm) from Reunion; Letourneur *et al.* (1998) reported 'b' value of 2.64 (TL min. = 2.4 cm, max. = 6.5 cm) from New Caledonia; Murty (2002) reported 'b' value of 2.33 (TL min. = 1.3 cm, max. = 10 cm) from Lakshadweep. In the present study, the 'b' values for indeterminates, immature male, immature female, mature male, mature female, spent male and spent female were 3.156, 2.904, 2.868, 3.033, 2.279, 3.120 and 2.679 respectively. Therefore the previous recorded 'b' values for the closely related genus were in agreement with the present observations.

The results obtained in the present work is also compared with the results of several authors in different species of the genus. Vijayamma (1997) reported 'b' value for indeterminates, males and females as 3.03, 2.94, and 3.13 respectively in *D. trimaculatus*. In *D. reticulatus* she reported the 'b' value for the indeterminates, males and females as 3.54, 3.54 and 3.38 respectively. Letourneur *et. al*., (1998) obtained 'b' value as 2.74 for *D. reticulatus*. The 'b' values observed for *D. trimaculatus* is 2.75 by Froes (1998). The above studies are in agreement with the present observation.

According to Hile (1936) and Martin (1949) the value of the exponent 'b' in the parabolic equation usually lies between 2.5 and 4. Depending upon the value of 'b', fishes can be classified into three groups. Allen (1938) stated that if b = 3, the body form of fish at different length remains the same and hence isometric growth is observed. If b < 3 fish becomes more slender as the length increases. Growner and Juliano (1976) observed that b > 3 fishes grow stouter with increase of length and hence is allometric in growth. In reality, the actual relationship between the variables, length and weight, may depart from isometric growth, due to either environmental conditions or conditions of fish (Le Cren, 1951). Beverton and Holt (1957) stated that major deviations from isometric growth are rare. In the present study immature males and mature males show isometric growth as the 't' value is significant and 'b' value is equal to 3, but the indeterminates, immature female, mature female, spent male and spent females were not showing isometric growth as the 't' value showed insignificant values. Hence, it is in agreement with the above findings of different authors mentioning the reasons of deviation from the isometric growth pattern. It is true in majority of the fishes, the shape and density change with increasing age, which often causes the regression coefficient to depart from 3.

In fishes, generally the growth pattern follows the Cube Law (Lagler, 1952). Cubic relationship for fishes is valid when the fish grows isometrically. From the present

observation, it can be concluded that the Cube formula $W = a l^3$ will not be a proper representation of the length-weight relationship for *D. carneus* as the growth is not isometric in most of the groups.

Separate equations were formulated for the male and female of immature, mature and spent groups of *D. carneus* as the analysis of covariance showed a significant 'F' value. Pillai *et al.* (1985 b) formulated separate equation for the species. Similarly Vijayamma (1997) observed separate equation for sexes in *D. reticulatus* and *D. trimaculatus*. Mohan *et al.* (1986) in *Chromis caeruleus* and Pillai and Mohan (1990) in *Abudefduf glaucus* reported separate equations for both sexes. Hence the above works are found to be supporting the present study

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IMAPCT OF TWO COMMON EXOTIC SPECIES ON NATIVE FISH FAUNA IN PERIYAR LAKE IN PERIYAR TIGER RESERVE

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Abstract

Though Periyar Lake is enriched with different species of fish fauna, its number have been declining due to the impact of exotic species. Two most common exotic species in Periyar Lake are Oreochromis mossambica and Cyprinus carpio. Fishermen community was very fond exotic species because of its availability in any season. But these introduced fish fauna are a great threat to the native fish community due to their over production, habitat destruction and competition for food and space. Conservation of native fish fauna is the only solution to this problem. The present study was conducted in 1996 from January to December and it focuses on the impact of exotic species over native species.

Key words: Oreochromis mossambica, Cyprinus carpio, Periyar Lake, exotic fishes, distribution and species composition.

Introduction

The fish production from the inland water bodies are high and may reach as much as one third of that of the whole country including marine fisheries and contribute over half of the domestic supply (Sharma and Grover, 1982). Though the reservoir fishery has made much advancement in India it has made several adverse effects on the native fish fauna, existed before the construction of dams. One such adverse effect is introduction of exotic fishes into the reservoirs.

Exotic fishes are a great threat to native species. They exploit the feeding ground and space of native fishes. As they are sturdier than the latter the exotic species will succeed in the competition for food and space with the native species. *Oreochromis mossambica* and *Cyprinus carpio* have been introduced in India in 1952 and 1957 respectively from Bangkok (Jhingran, 1991). Alikunhi (1966), Alikunhi and Chaudhuri(1959) and Hora and Pillay(1962) have contributed valuable information on Common Carp Classic example of introduced fish causing habitat alteration or destruction includes an increase in turbidity by carp (Taylor *et al*., 1984). Freshwater fish species have been purposely and extensively transferred around the world. Only 10% of successful fish introductions have been unintended transfers (Welcomme1984). The main motivations for introductions have been aesthetical, recreational and to promote aquaculture (Allan and Flecker, 1993). According to Moyle and

Moyle (1995) introduction of exotic species was one of the reasons for depletion of aquatic biodiversity of the world.

Earlier information on the fish fauna of Periyar Lake comprised those of Chacko (1948), Abraham (1962) Zacharias *et. al.* (1996) and Arun *et. al .(*1996). The fish fauna of the lake today is dominated by exotic species such as the *Oreochromis mossambica* and *Cyprinus carpio* (Minimol, 2000). The native species of the lake caught by the fishermen in the order of priority were *Hypselobarbus kurali* and *Tor khudree*. *Hypselobarbus periyarensis*, *Heteropneustes fossilis*, *Barilius bakeri* and *Mastacembelus armatus* were also caught in lesser numbers (Minimol, 2000).

Study Area

The study area was Periyar Lake which spread an area of 26 Km^2 in Periyar Tiger Reserve with depth ranging from 46m to32m. The Periyar Lake had been formed by constructing a dam across the Mullaperiyar River by the erstwhile Madras Government in 1895. The lake is at an elevation of 900m.

Materials and Method

Fishes for the study were collected from the fishermen directly. Monthly observation was also done to get data on the distribution of fishes. For this two collecting centres of the fish catch were selected and the fishes were identified and counted for one year in 1996 from January to December. The data were pooled together for annual population estimates and catch proportion of these fishes.

Disribution of exotic and native fish in 1996

Distribution and species composition of these fishes were studied at Nellikkampetty and Anchuruli in Periyar Tiger Reserve. Since there was not much difference in the catches in these two fishing spots, the data were pooled for analysis and study.

Oreochromis mossambica was the dominant species of the lake with an annual catch of 15026 in the year 1996. The percentage catch was 65.34%. *Cyprinus carpio* showed a total of 3251 fish in the year 1996 and it came in the position in the annual fish catch. Its catch percentage was 14.14%. Other fish population comprised native fish species such as *Hypselobarbus kurali*, *Tor khudree*, *Hypselobarbus periyarensis*, *Heteropneustes fossilis*, *Barilius bakeri* and *Mastacembelus armatus.* The annual fish catch proportion of native fish came in the second position (4721) and the percentage catch was 20.53%. But when consider the population of individual native fish separately, this number was alarming. The total number of fish collected in this year was 22,998 **(Table 1& Figure 1)**.

Table1: Annual fish catch in the year 1996 in Periyar Lake

Sl. No.	Name of Fish	Annual Catch	Percentage
1	*Oreochromis mossambica* (Tilapia)	15026	65.34%
2	*Cyprinus carpio* (Common Carp)	3251	14.14%
3	Others	4721	20.53%
	Total	22998	

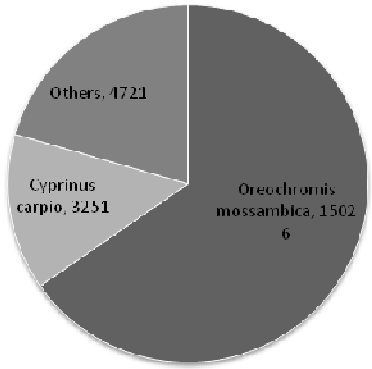

Figure 1: Total yield of fish in 1996 in Periyar Lake

Result and Discussion

In the Periyar Lake the dominant exotic species was *Oreochromis mossambica*. The number of *Oreochromis mossambica* caught, showed an increase of 15026. The rainfall affects the waterlevel in the lake and this in turn may affect production. When the water level increased, the fish production also increased, similarly when the water level decreased the production also is likely to be decreased. Though the production of native fish population showed little increase in its total number, the value should be given special attention. Because the number of other fish consisted of six native fish species. Therefore it should have been shown the greatest number than the other two exotic species and should have been in the first position. Instead the population of native fish fauna have shown only slight increase of 4721 numbers than the common carp and Tilapia have shown the greatest number. The total number of common carp was 3251. Tthe difference between the number of native fish population and common carp was only 1470. The percentage catch of *Oreochromis mossambica* was 65.34% and *Cyprinus carpio* was14.14%. The annual percentage catch of native fish fauna comprising six different species was only 20.53%.

The annual production of fish in Periyar Lake in 1996 showed increase in the exotic species such as Tilapia. *Oreochromis* had remarkable increase in its number than the others (15026). Common carp came in the third place (3251**)**. But this number should also be taken care of because when its biomass is considered it would outweigh all the other native species. The annual fish catch of six different native fish species was only 4721 numbers. In near future this number would be taken over by common carp because of its faster growth rate and its better adaptability to its habitat. Conservation of native fish should be done immediately to protect these fish fauna from extinction. Awareness on the indigenous fish species should be given to preserve our native fish wealth. Reviews of the effects of introduced species on natives generally agree that island or isolated faunas are most prone to risk of serious impacts (Usher, 1988). This is probably related to the increased levels of endemism evident in isolated areas as well as the more specialized niches typically occupied by endemic faunas (Crowl *et al*., 1992).

Suggestions

- Periodical observation and monitoring of the fish fauna in Priyar Lake should be carried out
- The number of Tilapias and Common Carp should be strictly controlled.
- They could be collected to the maximum level possible by repeated netting.
- Reintroduction Tor and carnivorous like *Channa striatus* should be tried.

Acknowledgement

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PHYSICO CHEMICAL STUDIES OF CHALAKUDY RIVER AT ANNAMALA, CHALAKUDY, ELOOR, MOOZHIKKULAM, AND KANAKKANKADAVU

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Abstract

Physico chemical characteristics of water of Chalakudy river were studied from Anamala to Kanakkankadavu, a stretch of 40 km. The duration of study was from April 2011 to August 2011. Five sampling stations were selected for study. The parameters under study were Temperature, pH, TDS, Electrical Conductivity, CO_2, Chlorides, Acidity, Alkalinity Dissolved oxygen, BOD, COD, Total Hardness, Calcium, Magnesium, Iron, Sodium and potassium. Temperature is close to the air temperature. Similarly pH showed an acidic trend. CO_2, Chloride, Acidity, Alkalinity, COD, Total Hardness, Calcium and magnesium were beyond the desirable limit. Whereas parameters like TDS Electrical conductivity, DO, BOD, Iron, Sodium, Potassium were found to be below the acceptable limit

Key words: Chalakudy river, Physico chemical parameters, Anamala, Chalakudy, Elavoor, Moozhikkulam, Kanakkankadavu.

Introduction

Due to increasing industrialization, urbanization and other developmental activities, most of our water bodies such as ponds, lakes, streams and rivers have become polluted. Today many rivers receive millions of litres of industrial effluents, sewage, domestic waste, agricultural and land drainage, etc. These effluents cause degradation of water quality (A.S. Rao et.al. 1999)

Chalakudy river is the 4th longest river is Kerala, India. The river flows through Palakkad, Thrissur and Ernakulam districts of Kerala. The total drainage area of the river is 1704 km^2. Out of this 1404km^2 lies in Keala and the rest 300km^2 in Tamil Nadu. The length of the river is 145.5km. It originates from Anamalai Hills of Western Ghats. The water in this river is used for water supply, irrigation, power generation, industry, navigation and aesthetic purposes. The domestic waste from the townships and human settlements is also disposed in the river. Due to the indiscriminate use of the river, the water quality has deteriorated considerably. the industrial activities in the river basin have significant impact on the quality of water in the down stream. The high incidence of coliforms is due to the activities of tourists at Athirappilly.

Water quality survey conducted by Kerala State Pollution control board revealed that high levels of faecal contamination is noticed in the river upto Aluva. The pH of the river water is found to be very low in the lower reaches of Udyogamandal industrial area indicating the impact of pollution due to industrial waste disposal. Excessive sand

mining from the river is affecting the water quality. Discharge of effluents from industries is affecting the water quality downstream of Eloor. Sewage and Sullage from major townships and run off from the rural community is causing pollution of the water upstream of Aluva. The environmental status and the water quality of Chalakudy river has been continuously changed (Padmalal et al. 2004, Chattopadhyay et al.2005). Babu & Maya (1997) made an earlier assessment of the drinking water quality around Kerala Chemicals and Proteins Ltd. (KCPL) at Kathikudam, Thrissur District. Water quality analysis of Chalakudy river near Kerala Chemicals and Proteins Ltd. (KCPL) at Kathikudam, Thrissur District, Kerala revealed that hydrographic parameters fluctuated with season and location. (Rincy Joseph and Tessy 2010).

The rapidly deteriorating health of the Chalakudy river due to factors such as catchment degradation, heavy sand mining, dams and the threat of further degradation due to new river based development projects is a cause of great concern. In this background, it has become an important social awareness activity to examine the quality of Chalakudy river water. The present study is an attempt to address the water quality status of Chalakudy river from Anamalai to Kanakkankadavu.

Materials and Methods

Samples were collected at 5 different sampling stations namely i) Anamalai, ii) Chalakudy, iii) Elavoor, iv) Moozhikulam, and (v) Kanakkankadavu. The distance between the two stations are approximately 10kms. Samples for analysis were collected during the premonsoon and post monsoon months. Water samples were collected in precleaned polythene containers from each of the five sampling stations and brought to labrotary for various physico chemical analysis. The samples were collected as composite samples. Analytical grade reagents, distilled water, and standard glass wares were used throughout this work. Various water quality parameters were determined using standard analytical methods 1988, 1974.

Temperature of water samples was noted using sensitive thermometer at the site itself. pH measured by using a pH meter (systronix PH meter MK VI) The conductivity meter directly measures the electrical conductivity. The unit is micro siemen / cm. TDS obtained by weighing the residue after evoporation (Trivedi & Goel, 1986). Free CO_2 determined by titrimetric method. Chloride estimated by volumetric titration with $AgNO_3$. Acidity by titrating the water sample with strong base such as NaOH, using phenolphthalin as indicator. Alkalinity determined volumetrically. DO estimated by winkler iodometric method. The amount oxygen concentration before and after incubation after 5 days at 20^0C was used to calculate BOD (APHA 1995). For measuring COD, the amount of $K_2Cr_2O_7$ consumed was determined and the amount of oxidisable organic matter calculated in terms of oxygen equivalent. Total hardness determined by volumetric titration (EDTA method). The

amount of calcium determined by titration with EDTA using Murexide indicator (APHA 1995; Golterman et. al., 1978)

Magnesium content detemined by calculating the difference between total hardness and calcium hardness. Total iron in water analyzed by colorimetric method (A I Vogel 1978). Sodium and potassium in the sample estimated by flame photometry.

Result and Discussion

The following are some of the observation from the study of the various water quality parameters (Table 1 and 2). The pH value of the sample varied between 4.94 to 6.9 during the pre monsoon and during post monsoon periods it was between 5.67 to 7.2 and was minimum in Kanakkankadavu. The range exhibits a slightly acidic nature of the samples. The world health organisation and Indian Council of Medical Research prescribed the limiting value of pH as between 6 and 8.5 for a sample of water to be used for industrial, agricultural and domestic purposes.

Temperature

The temperature of sampling stations ranged between 29.1 to 29.2^{0}C during pre Monsoons and between 20 to 28.1^{0}C during the Post monsoon. Temperature is a vital parameter for growth of organisms and plays an important role in the physico chemical behaviour of aquatic ecosystems (2011). The mixing of inflowing water and tidal influence plays an important role in the distribution of temperature. Processes like exchange of heat with atmosphere and any localized phenomena are also likely to influence the distribution of temperature. (Anirudhan, 1988). Present observation of surface water temperature in the study areas agrees with the observation of Kaul et al 1980 that surface water temperature usually remains close to the air temperature.

pH

The pH values of the samples varied from 4.94 to 6.9 during the pre monsoon and it was between 5.67 – 7.2 in the post monsoon and was found to be minimum at Kanakkankadavu. The range exhibits a slightly acidic nature of the samples. WHO and ICMR prescribed the limiting values of pH as between 6 and 8.5 for a sample of water to be used for industrial, agricultural and domestic purposes.

Electrical Conductivity

The Electrical conductivity ranges from 2 x 10^{-3} to 7x10^{-3} during the premonsoon period and is between 1.6 x 10^{-3} to 5.2x10^{-3} in the post monsoon period. The variation between the two seasons is not so significant. A rise in conductivity indicates pollution and it is very low in the present investigation.

TDS

The described limit of the total dissolved solids is 500mg/ltr. and the permissible limit is 2000mg/ltr. in the absence of alternate sources. According to WHO and Indian standards, TDS values should be less than 500mg/ltr. for drinking water. In the present study, the TDS values for all the samples

were too low and thus well below the acceptable limit and is insignificant as compared to the value suggested by WHO and Indian standards.

Fee CO_2

It was in the range of 3.925 – 5.99 mg/l during premonsoon and between 2.25 to 2.72 mg/l during the post monsoon. No significant seasonal variation is noted. But it was comparatively low. Typically surface waters contain less than 10ppm free CO_2, while ground water may have much higher concentration. Aquatic plant life, from phytoplankton to large rooted plants, depend upon CO_2 and bicarbonates in water for growth. The significant factor is that when O_2 concentration falls through degradation of organic wastes, the CO^2 concentration rises. The acceptable range of CO_2 for most finfish is less than 2 mg/l. The limit of CO_2 as per acceptable standards is 10mg/l for surface water and increase in CO_2 above this level indicates increase in pollution load (Koshy and Nair 1999).

Acidity

It was in the range of 8 – 18mg/l during pre monsoon and is between 9-20 mg/l during post monsoon. It showed an increasing trend. It gives a measure of effects of combination of compounds and condition in water. Acidity lowers dissolved Co_2 content, thereby reducing photosynthetic activity. The permissible limit of BIS value is less than 1 mg/l. Acidity is of little concern from sanitary or public health view point. Acid waters are of concern to industries because of their corrosive characteristics and the expense involved in removing or containing the corrosion producing substances (2009).

Alkalinity

It is the sum of compounds (mainly bicarbonates, carbonates, and hydroxide) in the water that tend to elevate the pH of the water the above 4.5. It is an important parameter involved in corrosion control. It was found to be in the range of 6-42 during the premonsoon and 8-47 mg/l during post monsoon. The alkalinity values of the water of the river in the studied stations showed an increasing trend. The acceptable range for most finfish is 20-200mg/l. For chemically treated water it shall be less than 120mg/l. (2009). The analysis indicated that the alkalinity is well below the acceptable limit all studied stations. Fluctuations in concentration during premonsoon and post monsoon seasons is not so significant in the present study.

Dissolved Oxygen

The investigation of dissolved oxygen revealed that the values lies between 7.8 – 2.2mg/l in the pre monsoon and 6.7 – 2.6 during the post monsoon. The minimum limit of dissolved oxygen for fresh water as per ICMR (1975) and ISI (1991) standards is 5 -6 mg/l. The tolerance limit for inland surface waters used as raw water and bathing ghats is 3mg/l. Except in one station water has higher D O value than the limiting value prescribed. The D O content satisfy the public water supply needs.

BOD

In the present study, the 5 day BOD value expressed in mg/l is 1.3 – 4.3mg/l in the pre monsoon and 1.2 – 4.2mg/l. in the post monsoon. No significant variation between the two seasons and it is within the limits. Typical natural waters has BOD value ranging from 0 – 8.5mg/l.

COD

COD test estimates the amount of a waste in terms of the total quantity of oxygen required for the oxidation of organic substances. The COD values measured varied from 12640 – 481620 in the pre monsoon and 10260 – 49480 mg/l. in the post monsoon season. Desirable limit is less than 10mg/l. and the permissible limit of COD is 750mg/l. No significant variation is observed between the two seasons. Conclusively it is proved that the river water is highly polluted.

Total Hardness

In the present study total hardness were in the range of 0.982gm/l. -6.39mg/l. during the pre monsoon and 0.692 to 6.56gm/l. in the post monsoon period. The desirable hardness for drinking water according to ICMR is 300mg/l. water containing hardness upto 60mg/l is referred to as soft and those containing 120 – 180mg/l. as hard. In the present study the limit of hardness is well above the permissible limit in all the studied stations.

Calcium

During the pre monsoon it is in the range of 30.24 – 69.66mg/l. and in the post monsoon it is in the range of 25.02 – 48.67mg/l. Even though it is an essential element for man, its high degree of consumption leads to health problems. The general acceptable limit of calcium in water is usually 75mg/l. whereas its maximum permissible limit is 200mg/l. (ICMR 1975).

Magnesium

The level of magnesium in the present study ranges from 90.3 – 1284mg/l. during the pre monsoon and 20.8 – 1268mg/l. in the post monsoon period. The U S public health has set 150.3mg/l. as the acceptable limit of magnesium in drinking water. So far no limit for aquatic application has been decided. In majority of the sample stations it is well above the acceptable limit. Not only that no appreciable variation in concentration is seen between two seasons. General acceptable limit of magnesium in water is usually 5mg/ltr, permissible limit is 100mg/ltr. (ICMR 1975) The value of iron varied from .002 – 022mg/ltr. in the pre monsoon and is .002 - .021mg/ltr. During the post monsoon period. Concentration above 1mg/ltr. impart a foul taste to water. In the present study concentration iron is much below the permissible range and no significant variation is observed between the two seasons. WHO recommends the maximum permissible limit of filterable iron in the drinking water as 0.3ppm and 1.0ppm respectively.

Chloride

Chlorides are available in all types of water. In the present study concentration of chloride Iron ranges from 1.2489 – 3.2428

gm/litre during the premonsoon and 1.148 – 3.2332gm/litre in the post monsoon. The prescribed maximum tolerance limit for chloride in drinking water is 600mg/litre. In the present study chloride content in all the stations are beyond the tolerance limit. High chloride content has deleterious effect on animals as well as in aquatic plants. It is one of the major anions to be found in water and sewage. Its presence in large amounts may be due to natural processes such as a passage of water through natural salt formations in the earth or it may be an indication of pollution from sea water intrusion; industrial or domestic waste. According to Durfur and Baker's classification where hardness is less than 75mg/l of $caco_3$, water is considered as soft (Adak et. al 2002).

Sodium

Sodium iron is ubiquitous in water. Drinking water usually contain about 50mg/ltr. Most water supplies contain less than 20mg/ltr., but in some countries levels can exceed 250mg/ltr. Saline intrusion, mineral deposits, sea water spray, sewage effluents, salt used in road for de-icing can contribute significant quantities of sodium to water. In addition, water treatment chemicals, such as NaF, $NaHCO_3$ and Sodium hypochlorite, can together result in Sodium levels as high as 30mg/ltr. Domestic water softeners can give levels of over 300mg/ltr. Excessive salt in take seriously aggravates chronic congestive heart failure and ill effects due to high levels of sodium in drinking water have been documented. In the present study sodium concentration ranged from 1.6 – 4.6mg/ltr. during pre monsoon and between 1.5 – 4.2mg/ltr. in the post monsoon and no significant variation observed between the two seasons.

Potassium

In water, potassium has no smell or colour, but may give water a salty taste. It is an essential nutrient for humans. Adverse health effects from exposure increased potassium in drinking water are unlikely in healthy people. No numerical canadian drinking water quality guideline exist for potassium. In the present investigation potassium concentration ranged from 1-5mg/ltr. in the pre monsoon and 0.05 – 2.6mg/ltr. during the post monsoon and significant variation was observed between the two seasons.

Table 1. Physicochemical parameters of water samples of Chalakudy river at five difference stations. Pre monsoon

Sl. No.	Parameter	Anamalai	Chalakudy	Elavoor	Moozhikulam	Kanakkan kadavu
1.	Temperature	29.1	29.1	29.2	29.2	29.2
2.	P^H	6.9	6.00	5.79	5.42	4.94
3.	Electrical conductivity	$2.1x10^{-3}$	$2x10^{-3}$	$4.2x10^{-3}$	$5.2x1^{-3}$	$7x10^{-3}$
4.	TDS	.047	.038	.182	.553	.618
5.	Free CO_2	4.215	3.925	4.235	5.157	5.99
6.	Acidity	8	9	13	16	18
7.	Alkalinity	7	7	6	25	42
8.	D.O.	7.8	6.7	6.2	4.4	2.2
9.	BOD	1.4	1.3	1.6	2.2	4.3
10.	COD	1264.0	1556.4	26540	32648	48620
11.	Total hardness	.982	2.34	5.80	6.39	4.92
12.	Calcium	30.24	32.56	40.76	50.76	69.66
13.	Magnesium	90.3	116.8	222.1	1168.0	1284.0
14.	Chlorides	540.7	780.6	1248.9	2839.6	3264.8
15.	Iron	.002	.009	.010	.016	.022
16.	Sodium	1.6	2.9	3	4.2	4.6
17.	Potassium	1	2.1	3.2	3.8	5

Table 2. Physicochemical parameters of water samples of Chalakudy river at five difference stations. Post monsoon

Sl. No.	Parameter	Anamalai	Chalakudy	Elavoor	Moozhikulam	Kanakkan kadavu
1.	Temperature	20	20	28	28.1	28.1
2.	P^H	7.2	7.00	6.30	4.24	5.62
3.	Electrical conductivity	$1.6x10^3$	$1.8x10^3$	$2x10^3$	$4.2x10^3$	$5.2x10^{-3}$
4.	TDS	.021	.030	.282	.542	.582
5.	Free CO_2	2.15	3.125	2.142	5.150	5.72
6.	Acidity	9	10	12	14	20
7.	Alkalinity	9	10	8	27	47
8.	D.O.	6.7	6.2	4.4	4.2	2.6
9.	BOD	1.2	1.4	1.8	2.6	4.2
10.	COD	10260	11540	24540	30629	49480
11.	Total hardness	.692	2.32	4.62	5.18	6.56
12.	Calcium	25.02	30.21	30.42	48.67	20.11
13.	Magnesium	20.8	40.3	170.3	1037.8	1268.0
14.	Chlorides	325.7	540.7	1248.9	2748.6	3232.8
15.	Iron	.002	.007	.010	.012	.021
16.	Sodium	1.5	2.3	3.2	3.6	4.2
17.	Potassium	.05	1.2	1.9	3	2.6

All the units are expressed in mg/ltr., except pH, temperature (^{0}C), conductivity (μmhos/cm), Chloride (gms/ltr.)

Conclusion

In the present investigation a physico chemical analysis of Chalakudy river from Anamalai to Kanakkankadavu were carried out. The study revealed that no significant variation in parameters were seen between the two seasons. Parameters like EC, DO, BOD, Iron, Sodium and Potassium were found to be below the acceptable limit. Whereas parameters like TDS, CO_2, Chloride, Acidity, COD, Total hardness, Calcium and Magnesium were beyond desirable limit. Temperature is close to the air temperature and pH showed an acidic trend. From the study it is revealed that the river is slowly but definitely get polluted. The main cause for this river pollution is due to the discharge of industrial effluence, agricultural run off, Sewage and Sullage from major townships, run off from the rural community, excessive sand mining. In addition the threat of further degradation due to new river based development project was a cause of great concern to the rapidly deteriorating health of the Chalakudy river.

In order that the Chalakudy river water becomes palatable, potable, suitable for industrial and civic purposes, it should be seen that the industrial effluents and sewage are properly treated and disinfected using proper scientific methods. These steps should be taken at the individual, industrial and district administration level, so that purified Chalakudy river water becomes fit for all purposes of industrial and human consumption. This being a social commitment concerned with everyone health and wealth, cannot be ignored for a long time. In this connection the activities of the Chalakudy Puzha Samrakshana Samithi which was born in 1986 need special mention. The Samithi members have been constantly involved in environmental education activities among students, women groups, Panchayath and Youth, all over Kerala, mainly focusing on conservation and participatory river restoration and management.

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NEST BUILDING IN ANTS – A COMPARATIVE STUDY

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Abstract

"The Nest Building in Ants – A Comparative Study" is the work purely based on thorough observation. The nest building is one of the most remarkable instances of social cooperation among lower animals. The study area chosen was a place in Malayattoor village, in Ernakulam district. The ants, Oecophylla smaragdina and Myrmicaria brunnea were selected for the study. A typical ant nest or colony is usually having a complex house pattern. Different kinds of ants construct their nests differently. However, weaver ants of species formicidae build nest in leaves. Ants in the species brunnea built their nests in ground. Among the two ants, Myrmicaria brunnea wasseen found making their nest in the soil faster than Oecophylla smaragdina . O.smaragdina took 6 to 8 days for nest building using leaves and pieces of twig. While M.brunnea took 5 to 6 days for building their nest. It was very obviously noted that number of workers involved in the process is more in M.brunnea family than Oecophylla smaragdina.

Introduction

Ants….. They live in a complex society. They have a caste system, they go to war, and they tend gardens. Ants have overrun the surface of planets. For every human there are 1,000,000 ants. Ants are a social insect that lives in large colonies and have developed complex system of communication. Ants are not only the gregarious creatures in the world. They have adopted a strictly hierarchical structure. Colonies, leaving some rare expectations, are founded on the coexistence of two separate castes, of different ranks. One hand they are the queens, whose sole function is to reproduce; and on the other hand, their daughters, workers, industrious and generally sterile.Weaver ants are obligately arboreal and are known for their unique nest building behaviour where workers construct nests by weaving together leaves using larval silk. (Hölldober,B& Wilson, E.O. 1990)

Once the colony is established and the queen has managed to get through her first year unaided, she can devote herself to her essential mission. She turns into a single egg laying factory, with a single job of ensuring reproductive future of the family. All the other jobs, the one on which depend the survival and the well being of the clan, are done by the workers. Demarcation never leads to dispute, each denizen of the nest, queen or

worker, having its designated function in an efficient division of labour.

Workers also act as architects and builders whose job is to construct nest, in accordance with the specifications of volume and structure required by each species and consistent with the size of their colony. The probability of a weaver ant worker joining the concerted effort is dependent on the size of the group, with workers showing a higher probability of joining when group size is large. (Deneubourg, J.L.,et.al., 2002) In myrmicaria species the underground nest vary from simple dug-out about twenty centimeters to nests comprising numerous passageways and many different rooms, which may lie four metres down. The ants move their house with respect to change in seasons to most favourable conditions for continuing their well being. The nomadic as they are, they build nest which are less elaborate than those of their previous.

Most of the ants live in nests or colonies, as ants are social animals. Ants are liked to live together. The small colonies are usually situated under stones, in stumps, logs, in leaves etc. Many of the larger colonies build on large amounts of earth, sticks and debris with complex system of galleries and chambers. A typical ant nest or colony is usually a complex house pattern. Different kinds of ants construct their nests differently. However, weaver ants of species formicidae build nest in leaves. Ants in the species brunnea built their nests in ground. Army ants built "live nests" of worker ants. Normally, there is one queen in a nest but there are sometimes several. Nests of Australian bull ants contain up to 600 ants, while some wood ants nests can house more than 300 million ants. Ants keep extending them in an easterly, direction in such a manner that only the extreme easterly, highest and most precipitous portions are inhabited by the insects. (TISSOT & LINDER,1969) The nature and characteristics of nests varies with the location selected. In the mountains, ants' nest is an elongated, almost regular form. Their direction is constantly from east to west. Their summits are more precipitous slope is turned towards the winter rise, their longer slopes in the opposite direction. (Humber, 1983)

The workers of the colony are very dedicated in performing several duties of which nest building is very important. "The worker ants will refurnish the upper parts of the nest by moving, in a more or less orderly fashion, the materials that it's made of. If the

structure has been damaged by the predators, the workers carry out the necessary repairs, using the larger twigs as a sort of roof framework on the inside and shifting the smaller woodwork to the top of the dome, setting them out in a layer several centimeters deep which will water-proof the nest."(Daniel Cherix)They have traditionally been used in biological control in Chinese and Southeast Asian citrus orchards from at least 400 AD. (Marco S. et.al 2005 and Van Mele, P. 2008) Many studies have shown the efficacy of using weaver ants as natural biocontrol agents against agricultural pests. (Van Mele, P. 2008)Studies indicate that the presence of *Oecophylla* colonies may also have negative effects on the performance of host plants by reducing fruit removal by mammals and birds and therefore reducing seed dispersal and by lowering the flower-visiting rate of flying insects including pollinators (Donald W. Thomas (1988) and Kazuki TSUJI 2004)

Observation and Result

Table 1 Different Stages of Nest Building in Showing the *O.smaragdina* for the completion of nest making

Days	stages of nest building
1ST	Ants concentrated at the tip of the leaf and aggregated.
2ND	Ants folded the first leaf.
3RD	Few more leaves were attached with the first leaf, Leaves are joined with the help of some secretions..
4TH	The leaves are connected together so that it appeared a leaf ball.
5TH	The nest was divided into chambers and galleries.
6TH	The nest making was completed.

Table 2 Different Stages of Nest Building in *M.brunnea*

DAY	STAGES
1	The ants were clumped at the base of the tree
2	The ants started digging soil around the tree
3	Underground compartments were made
4	The nest making was completed

STAGE I

STAGE II

STAGE III

Results

- The ant *Myrmicaria brunnea* built nest faster than *Oecophylla smaragdina.*
- *Myrmicaria brunnea* have more number of worker ants than *Oecophylla smaragdina*
- Summer season is more favorable for the nest making of ants.
- Both change their nest with respect to change in the climatic conditions.
- Repair works of the nest are done in case of damage to their nest due to predators attack or such.

Discussion

The Comparative Study on the Nest Building of ants in O.*smaragdina* and M.brunnea was selected. The ants were observed in Malayattoor village. It was interesting to note that the ants were very diligent. M.brunnea made their nest faster than that *O.smaragdina* as the number of workers were more in their group. Summer climate is favoured for the nest making of ants. Several chambers and galleries were built by the ants in their nests. They made separate spaces to store food and for laying eggs. The direction of ants nest building is from east to west. Worker ants are seen very active in nest building in both types. The workers of the colony are very dedicated in performing several duties of which nest building is very important. "The worker ants will refurnish the upper parts of the nest by moving, in a more or less orderly fashion, the materials that it's made of. If the structure

has been damaged by the predators, the workers carry out the necessary repairs, using the larger twigs as a sort of roof framework on the inside and shifting the smaller woodwork to the top of the dome, setting them out in a layer several centimeters deep which will water-proof the nest.M.brunnaeinvolve more members in the venture than O.smaragdina.

Conclusion

The comparative study on the nest making of ants, it was found that among the ants, *O.smaragdina* and *M.*brunnae; *M.*brunnae made their nest faster than *O.smaragdina*. The number of worker ants is more in *M.*brunnae when compared to *O.smaragdina*. The action of *M.*brunnea can cause the degradation of root of the tree.

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YOGA AS A SPIRITUAL SCIENCE – AN EVALUTION

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Introduction

Yoga is a Spiritual Science for the integrated and holistic development of our physical, emotional, mental and moral – spiritual aspects of being. The philosophy of yoga in partial and applicable in our day – to – day living. Yoga has been documented to normalize psycho-physiological function and recent advances in the field of research have shown that it has sound scientific basic.

Yoga is first and foremost a mokshasastra meant to facilitate the individual to attain the final freedom, liberation or emancipation. One of the important by products of the yogic way of living is attainment of health and well-being. This is brought about by right – use – ness of the body, emotion and mind with awareness and consciousness. This must be under stood to be as healthy a dynamicstate that may be attained in spite of the individual bija karma. That manifest as their genetic pre disposition and the environment in to which they are born. Yoga also helps after it has been attainable through disciplinedself-effort.

MaharshiPatanjali, the teacher of yoga, gives the clear definition to yoga-" *athayoganushasanam*"-'*atha*' implies now, the present moment. This change, this transformation, this silence must begin now.

The second sutra of the Samadhi pada-"*yogahchittavrittinirodhah*"-yoga is the cessation of the whirlpools of the subconscious mind. The third Sutra of the first Pada tells what the result of the endeavor will be "tadatrashtuhswarupevastanam"- the seeker is established in the form of its real being. In other words, the Sadhaka becomes what the truly is. One becomes established in one's essential form, which is Atman, Brahman, Shivam, the Purusha, the over soul. The characteristics of this essential form is "Sat-Chit-Anada". Sat means Reality or Truth, Chit means consciousness and Ananda means the Eternal bliss.

The first step of Yoga

The first step in Yoga is the awakening to consciousness from the deep slumber of animal consciousness. Patanjali lays out the eight necessary steps one must take once the awakening has occurred. In eight words he shows us how to live.ie: Yama, Niyama, Asana, Pranayama, Pratyahara, Dharana, Dhyana, Samadhi.

Yama- means control, restraining of the animal nature with all its self seeking,

survival, instinctive, behavioral patterns. So Patanjali tells us, the first step one must take up rise out of the animal nature and to begin constructing a truly human nature is to consciously reject all violence-Ahimsa, the great vow,which distinguishes man from beast. This is the first Yama. The remaining four Yamas are Satyam, Asteyam, Aparigraham and Brahmacharyam.

The second step in Yoga

The Niyamas are cultivation of consciousness, manas, that quality of existence which differeciates man from beast. The Yamas says no to the animal nature. The Niyamas say yes to higher, aware, choiceful living. In Yoga there are five Niyamas which are

Saucham- the first, is purity, cleanliness, a purity of character from which all animal traits or instincts have been eradicated: physically, mentally, emotionally. Soucham implies the purity of motivation. The motive is purely the desire to evolve towards higher states of being.

Santhosham- is a deep, profound understanding that every situation in which one finds oneself is exactly what one needs to progress on the spiritual path.

Tapas- is the fire of the discipline which burns out impurities and strengthens the will. Tapasya is the power to persist, to push through all obstacles with great cheerfulness. It is the ability to carry on the work when one wishes to give up. It is the ability to face horrendous challenges with skillful hands and a hapy heart.

Swadhyaya- is constant, every moment examination, an awareness that knows down to every nanosecond, exactly what one is doing, thinking, saying etc.

Iswarapranidhana- the fifth Niyama is Iswarapranidhana or submission to the will of God. Here is the most peculiar thing about Patanjali's wonderful codification, he says of this fifth niyama (II:45)

samadhisiddhiiswarapranidhanat

Samadhi is the fruit of total perfect surrender to divine will.

If the Yamas and Niyamas are perfect , the mind enters in to a deeply still, perfect state. The cittavritti, the waves of the subconscious mind subside. That peace which passes understanding emerges. One becomes 'established in the state of one's true being'. The goal of Yoga is reached. This is called kriyayoga; the Yoga of living humanlife perfectly within the frame work of cosmic law, codified by Patanjali as the *panchayama* and *panchaniyamas*, five restraints and five observances, the first two steps on the path of *ashtangayoga.*

The six steps in Yoga

However, few can reach or sustain that state. Few can perfect Yama and Niyama. The rest of Sadhakas must go further. They must employ additional tools to construct that perfect silence,that perfect stillness.

The third step is Asana. The word 'asana' derives from the root 'asi' which means 'to be' Thus 'asana' means to enter in to one's true being. The qualitative aspect of heath in something that yoga and Indian systems of medicine have considered important for thousands of years. The definition of Asana given in the yoga sastra as- sthirasukham- implies this state of steady well being at all levels of existence (*sthiramsukhamasanam, - yoga darsana* .2:46) Patanjali tells as that through the practice asana, we can attain a state of well-being (yoga darsana:2:48)

The fourth step is pranayama-Controlling of vital energy by means of breath. The ultimate aim of pranayama is, 'to stop the breath', to silence the breath.'

Pratyahara-The fifth step, is transcendence of and silencing of sensual impression, detaching consciousness from sensual stimulus. This is silence of the senses.

By the time **the sixth step**, Dharana, is reached, the body, breath and senses will be silenced, made quiet and still. Conscious nessmay them be one-pointed and focused on a single point, a bindu.The mind in literally 'tied to one spot, onepoint'. Up to this point, the individual jiva is utilizing will power (icchasakti), power of discrimination and knowledge (Jnanasakti) and the power of action. (kriyasakti)to cultivate silence and stillness. There is a 'push' towards the goal a striving, an effort of will.

As the effort bears fruit; in **the seventh step**Dhyana and **eighth step** Samadhi, the push turns in to a pull and the Jiva is now pulled in to the state of highest silence and stillness. After intensive effort in the first six steps-restraint of emotional, animal impalses in yama; the conscious cultivation of human virtues in Niyama, control and deep awareness of body in Asana, stilling the body's natural restlessness; slowing; restraining, stopping the breath in pranayama; shuttingdown, closing, detaching from sensory stimulas in pratyahara; intense focus on one point which in worthy of worship in Dharma, after which there in nothing left to do.

From the seventh step onward, one 'must let go and be'. Thepush of individual effort become surrender of the pull to the Lord from Dhyana onwards. Dhyana is the beginning of the establishment in the state of mystic absorption.

What happens them?it is best to put it in the words of SriRamakrishna, The salt doll enters in to ocean. Who is left to describe the experience?

Yoga understands health and well-being as a dynamic continuum of human nature and not a mere 'state' to be attained and maintained. The lowest point on the continuum with the lowest speed of vibration in that of death whereas the highest point with the highest of vibration is that of immortality. For many, their state of health is

defined as that 'state' in which they are able to function without hindrance where as in reality; health is part of our evolutionary process toward, Divinity. The lowest point on the dynamic health continuum with lower speed of vibration may be equatedwith lowest forms of life and mineral matter while highest point with highest speed of vibration may be equated with divinity.

Qualities of mental health accerdey to yoga

Yoga not only considers physical health but also more importantly mental health. Qualities of a mentally healthy person (sthitaprajna) are enumerated in the B-G as follows.

Vita raga bhayakrodhah……–(BG. 2.56)- beyond the animal tendencies of passion, fear and anger.

Nirmamoniraharikarah……..– Devoid of possessiveness and egoism

Sthirabuddhirasammudo……. – firm in understanding and un-bewildered BG 5.20) and etc.

The catral I have of yoga is the golden mean , finding the middle path , a constet search for moderation and a harmonious homoeostatic balance. Yoga is the "unitiveimpulse" of life, which always seeks to unite diverse streams in to a single powerful force. Proper practice produces an inner balance of mind that remains stables and serene even in the midst of chaos. This ancient science shows its adherents a clear path to the 'eye of the storm" and ensure a stability that endures within, even asthe cyclone ragesexternally.

Maharshipatanjali tells us that we can going unexcelled happiness, mental comfort, joy and satisfaction by practicing contentment (*santosatanuttamahsukhalabhah*-yog:dars:2:42)

This link is quite apparent ones we think about it, but not too many associate the need for contentment in their greed for anything and everything in this material world.

Cousation of psychosomatic Disorders.

The root cure of disease as follows a yoga, a holistic, unified concept of oneness, is advaitam or non-dual in nature. It suggests happiness, harmony and ease-Dis-ease in created when duality or dvaitam arises in sees in the human mind-This loseconcept of duality has produced all conflicts of man'sdownfall.Yoga help return man to his pristine, whole nature.

All diseases, maladies, tensions, are many tensions of divisions of what should be man's complete nature, the atman or self. This is "ease" A loss of ease creates disease". Duality is the first insanity, the first disease, the unreasonable thought that "I am divert from the whole .... I am unique. I am me "The ego is a maniteration of disease. Only a distorted ego could feel along, suffer from "the lonely disease", in a universe, a cosmos totally filled with the self.

Yogic Perspective of Depression

According to the yogadarsanaco dified by MaharsiPatanjali, depression or rather daurmanasya is one of myth four viksepasahabhavan that are the man iteration that accompany the obstacls the yoga sadhana, the navaantaraya. The other sahabhavan are duhkha or suffering angamejayatva or tremors and svasaprasvasa or irregular respiration. (*dukhadaurmanasya-angamegayatvasvasaprasvasaviksepasahabhuvan* yog:dars:1:31)

When we analyze this sutra deeply we find that they are very truereflection of our inner state.

Duhkha orpainful sufferingat the physical, emotional mind mental level can drive us to despair. Suffering in an excellent trick our mind plays as very taw are capable of realizing what is really happening in the process of the evolutionary journey. The moment "supering"is left, most people give up, and the lower mind survives to fight another day.

Daurmanasya refers to dejection and despair. We must remember that depression is not just in the mind but has many physical aspects too. A state of depression in another tool by which, the lower mind tries to halt the spiritual progress of a sadhaka. However we must realign that the greatest teaching are offer give at moments of greats despair. The art and science of yoga understands that this may be the best "teachable" moment and have we find the highest teachings of the Bhagavat Gita and Ramayana

It is very important to say "A nervous breakdown is actually an opportunity for a spiritual break through it we can realize the positive implication". The teachings of the Yogavasista and the B.G which may be said to be the first and second recorded' "psychological counseling" sessions in human history were delivered when both lord Rama and Arjuna Respectively were at the depths of their depression. If we realize that this is indeed a window of opportunity for growth, success will come to us the soonest. But it we miss this golden chance, them even the divine will struggle to help us out of our own deep pit of self-pity.

Angamejagatva are the physical tremors of the body. The practice of asana helps as to attain to a state of physical control over our body. This enables us to go beyond the dvandva, the pair of opposites that are the cause of these tremors. Tremors are an externalized manifestation of internal imbalances of our emotions and mind. Imbalance at the higher level causes the imbalance in the neuro- chemical transmitters and psycho physiological pathways of the body, resulting in these physical tremors when confronted with such a frightening manifestation, many aspirants get scared whether they are harming themselves and stop their sadhana out of tear.

Svasaprasvasa refers to the irregularityin eating patterns. One of the main physical man transactions of mental and emotional upsets is the haphazardness of respiration. Ancientyogas contemplated this deeply and found that mental disturbances cause irregularity and instability of respiration. Though their jnanadrsti they realized that by stabilizing the breath, we can conversely produce a stability of emotions and mind. This knowledge is used even today in the practice of pranayama, This is one of the best examples of the numeroussomatic-psychic application found in the practices of hatha yoga, the physical science of balancing equal and opposite energies.

Yogic Methods to Attain and Maintain Health

The Science of yoga has numerous practical techniques, as well as, advice for proper life style in order to attain and maintain health and well being. Yoga works towards restoration of normalcy in all systems of the human body with special emphasis on the psycho neuro- immuno-endocrine axis.

In addition to its preventive and restorative capabilities,yoga also aims at promoting positive health that will help us to tide over health challenges that occur during our life time. Yoga has both a prevention, as well as, promotive role in the health care of our masses. It is also inexpensive and can be used in tandem with other system of medicine in an integrated manner to benefit patients.

The Science of Yoga

In the Science of yoga, body movement and breath must be synchronized. The breath pattern is important .Particularly in the use of Kriya or structural movements like suryanamaskara, The body is normally lifted on an incoming breath and lowered on an outgoing breath. Some of the breath patterns such as the bhastrikastrengthen the whole solar plexus area, as well as, the diaphragm, building up stamina while producing internal cleansing of organs and the blood stream. Kapalabhati is another dynamic technique that enable as to break out of the deep hole of depression by creating a sense of activation.

Suryanadi and vijayi pranayama can also help in activating those who need the activation for healthy well being.

The bandhatrayam as well as the asvini mudra are both a God-sent for those suffering from depression as they revitalise the entire psycho-neuro-endocrine system. The pranava and bhramari pranayama work towards create in an inner harmony that results in the attainment state of mental calmness.

The inherent message of Pranayama can be summarized like.

- There is an absolute and direct correlation between the way an organism breathes and its energy level.

- There is an absolute and direct correlation between the way a man breathes and the length of his life span.
- There is an absolute and direct correlation between the way a man breathy and state of mind and clearing of thought, which he enjoys.
- There is an absolute correlation between the way a man breathes and the quality of emotions which he experiences.
- There is an absolute and direct correlation between the way a man breathes and the subtlety of the thoughts, which pass through his mind.

Yoga which emphasizes the universal is a perfect foil to those human activities, which glorify the personal. In short it may be said that the practice of yoga as a unified whole helps the individual shift form a 'I'- tantric approach to a "we"-tantric approach.

Srimad Bhagavad Gita Says "*YogahKarmasuKausalam*" meaning there by that Yoga is skill in action. The real yogi, Immenselyconscious and aware at the physical, mental, and emotional level gains great control through that consciousness over all aspects of life thus developing a real skill in living. The yogi perform the needed action not for the sake of the fruits of that action, but because it is good and necessary todoso. Such an attitude of mind produces consummate skill in whatever action the yogi undertakes. Consummate concentration, consummate controls are all off shoots of good yoga sadhana.

The beauty of is that these abstract principles become concrete in the daily practice of the techniques available in the yoga system. Once the "Seed of yoga" finds fertile soil, these concepts grow naturally, slowly but surely taking root in all aspects of life.

(Yoga in still in action. "yoga n karmasukausalan). B.G : 2:50.

In short all aspects of yoga as a way of natural living can provide relief for many of the psyche somatic ailments affecting human kind today yoga has a step by step method for producing and maintaining perfect health at all levels of assistance. The social behavior in first optimized through an understanding and control of the lower animal nature (Pancayama) and development and enhancement of the higher human nature (Pancaniyama)

Conclusion

The dedicated practice of yoga, as a way of life is no doubt a panacea for problems related to psycho somatic, stress related physical, emotional and mental disorders and help us regain our birthright of health and happiness. It is only when we are healthy and happy that we can fulfill our destiny.

There are so many peoples have benefited by the life enhancing qualities of yoga as a way of life. Many of them were in the depths of despair and on the verge of committing suicide before they come to yoga. Today offer many years of sadhana coupled with the adoption of the yogic attitudes they have not only climbed out of the "deep self-made well" of depression but are guiding others too, some of the have become beacon lights to hundreds of their fellow human beings and are enabling them to come out of their shells and shine bright as stars. A lighted lamp gives off more light when it 'shares' itself by giving to other lamps thus on light ening the universe.

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CRITICAL THINKING IN HIGHER EDUCATION

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Educators have long been aware of the importance of critical thinking skills asvital outcome of student learning. More recently, economic trends worldwide increasingly demands individuals to be equipped with 21st century skills such as communication, creative thinking, collaboration, critical thinking etc. that are inevitably imperative in today's work places. The emergence of learning economy is expected to have profound implication for designing educational programmes for the future citizens and this necessitates education administrators and educators to be flexible, willing to try new ideas, responsible to design innovative curricula and employ evidence based pedagogical practices which are capable of promoting the required skills in the learners. Critical thinking has been claimed to be a primary goal of education and is among the prime skills that today's students will need as they move on to higher education and careers or later as a survival need.

The concept of Critical thinking

Critical thinking is essentially a decision making process and is sometimes misunderstood to mean to criticize or to point out weaknesses or to find fault. The word "critical" comes from the Greek word "kritikos" which means to question, to make sense of, and to analyze or the persons who have the ability to discern or decide. Different people have attempted to define Critical Thinking differently and the definitions have changed remarkably during the past years in breadth or inclusiveness.

Dewey (1938) defined critical thinking as reflective thinking which is thinking deeply and giving serious thought to a certain issue or task. According to Robert H. Ennis (1985) Critical thinking is reflective and reasonable thinking that is focused on deciding what to believe or do.

Facione & Facione (1996) in the Delphi report defined Critical thinking as purposeful, self-regulatory judgment which results in interpretation, analysis, evaluation and inference, as well as explanation of the evidential, conceptual, methodological, criteriological or contextual considerations upon which that judgment is based.

Duron, Limbach, and Waugh (2006) stated that critical thinking is the ability to analyze and evaluate information.

The review of literature on critical thinking reveals that there is no universal agreement

upon a definition for critical thinking and therefore a wide range of views exist as to what critical thinking is. The definition of critical thinking varies because of its abstract characteristics. Pascarella and Terenzini (2005) relate that most attempts to define critical thinking operationally focus on an individual's capability to accomplish some or all of several dimensions of critical thinking. Those dimensions include (a) identify central issues and assumptions in an argument, (b) recognize important relationships, (c) make correct inferences from the data, (d) deduce conclusions from information or data provided, (e) interpret whether conclusions are warranted based on given data, (f) evaluate evidence or authority, (g) make self-corrections, and (h) solve problems. Based on the definitions of critical thinking, it can be concluded that, the process of critical thinking, firstly, requires knowledge to think critically to solve a problem. Secondly, it requires cognitive abilities such as evaluating the premises and thinking deductively or inductively (Critical Thinking cognitive skills) and thirdly, it requires inclination and willingness to engage in critical thinking to solve problems (Critical Thinking dispositions).

Relevance of Critical Thinking

Critical thinking means carefully considering a problem, claim, question, or situation in order to determine the best solution. When a person thinks critically, he takes into consideration various sides of an issue, evaluates evidences, and imagines different consequences and the possible outcomes before he makes a decision. People proficient in critical thinking are often open-minded and mindful of alternatives, try to be well-informed, judge well the credibility of sources, identify conclusions, reason and assumptions, judge well the quality of an argument, including the acceptability of its reasons, assumptions, and evidences, can well develop and defend a reasonable position, ask appropriate clarifying questions, formulate plausible hypotheses; plan experiments well, define terms in a way appropriate for the context, draw conclusions when warranted, but with caution and integrate all items in this list when deciding what to believe or do (Ennis,2002). Hence development of Critical Thinking has become a promising strategy helping to increase efficiency of individuals.

Fostering of critical thinking skills among students is considered vital in all academic

disciplines in the democratic system of education and the teaching of critical thinking skills has been much emphasized by many educators. Early in this century, John Dewey (1938) pointed out that learning to think is the central purpose of education. To some scholars, including Michael Scriven (1985), training in critical thinking should be the primary task of education. Harvey Siegel (1988) also emphasize that Critical Thinking should be a part of educational system as youth deserve to be able to think critically, because Critical Thinking is becoming a necessary component of living life. Educators are not alone in recognizing the importance of critical thinking. The demands of employment in a global economy, the survival of a democratic way of life, and personal decision making in a complex and rapidly changing society require people who can reason well and make good judgments. Moreover, in our present society, making sound personal and civic decisions requires the ability to interpret and evaluate accurately the information imparted by media and other sources that often emphasize exaggeration and imagery. Hence for students, workers, and citizens, critical thinking is an essential tool for performing successfully in this complex and rapidly changing world. To sum up, it can be concluded that critical thinking is very essential for every individual because:

- It is a prerequisite for good citizenship, e.g. it has been suggested that there can be no liberty for a community that lacks the critical skills to distinguish lies from truth.
- People will be better equipped to compete effectively for educational opportunities, jobs, recognition, and rewards in our society if they can utilize their thinking abilities efficiently.
- The ability to think well contributes to a person's psychological well-being; good thinkers are more likely to be well-adjusted individuals.
- Human civilization is currently facing several exceedingly complex and threatening problems and skillful critical thinking is essential for making constructive judgments on these prime issues and
- Critical thinking is increasingly needed to perform effectively in the workplace.(Hager & Kaye,1992)

But despite widespread expressions of concern about developing critical thinkers, studies have shown that most educational programmes are neither challenging students to think critically nor helping them develop the reasoning abilities needed to deal successfully with the complexities of modern life. Our educational system continues to graduate students who do not reason well (Paul, 1992). Even a college education appears to have a limited effect on graduates' critical thinking abilities, including making reasonable interpretations of texts and formulating unbiased and well-reasoned arguments (Halpern, 1998). It is evident that while concern about critical thinking is widespread, effective instruction for critical thinking is not occurring on a broad scale. i.e. Even though Critical Thinking ability is highly valued in students especially in contemporary world yet many students are confused about what it means and how to develop it.

Teaching Students to Think Critically

Thinking is a natural process but, left to itself its development is often distorted and partial. The quality of our life and what we produce depends precisely on the quality of our thoughts and hence excellence in thought must be systematically cultivated. All students, regardless of presumed limitations in ambition or ability, have some degree of potential to think critically. Their capabilities to think critically are likely to be increased if they practice appropriate strategies and skills systematically and extensively in all subjects of the curriculum, and in a manner that is consistent with their cognitive development and prior learning experiences. This potential can be developed to the fullest by embedding critical thinking in the core curriculum at all levels of education. There are many teaching strategies used to help promote critical thinking. Costa (2001) mentions that generally there are four distinct categories of teaching strategies: Directive, meditative, generative and collaborative strategies.

- The directive strategy includes direct instruction and mastery of thinking skills. This is teacher centered – the teacher provides with most of the knowledge through different activities like drills.
- The meditative strategy is where the teacher acts as the facilitator and guides the students to become aware of their meta cognitive processes.

Activities are like making decisions through ethical disparities, guided by the teacher.

- Generative strategies are when there is minimal input from the teacher, and the students have to discover the knowledge/skills involved. Activities include research projects.
- collaborative strategies are the ones that encourage group work, be it promoting leadership or as a team player

Teaching students to think critically probably lies in enabling them to deploy the right type of thinking at the right time and this should mainly involve the three components- engaging students in dealing with tasks that call for reasoned judgment or assessment, helping them develop intellectual resources for dealing with these tasks, and providing an environment in which critical thinking is valued and students are encouraged in their attempts to think critically. Thus the academic system is probably the most effective way to educate the upcoming citizens of the nation to be skillful critical thinkers and proficient problem solvers in their lives. The increased emphasis of critical thinking on our education system will lead to the increased use of critical thinking at a societal level as well. With the accomplishment of the Critical Thinking curriculum, critical thinking would become an essential element in the general education of citizens rather than the privilege of intellectual or social elites. If so, opportunities for academic achievement, socioeconomic advancement, and effective citizenship will be spread more widely and equitably in our society.

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PEPPER EXPORT POTENTIAL OF KERALA AND THE FUTURE PROSPECTS IN THE NEW MILLENIUM

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Abstract

Spices are the grand gifts of nature to the mankind. Kerala is well known for the production of a variety of spices. The state is the leading producer and exporter of black pepper in India. In this paper an attempt is made to assess the export potential of Kerala in the export of black pepper and its future prospects in the new millennium.

Key Words: Spices, Black pepper, Export potential, Export direction, Export performance, Compound annual growth rate (CAGR).

India is known as the home of spices in the world from time immemorial. India has a tradition of cultivating different spices and has the capability to grow almost all the spices in the world. India grows about 52 spices, out of 109 spices listed by International Standards Organization (ISO). Among these, and 17 spices are commercially significant. These important commercial spice crops include pepper, cardamom, ginger, turmeric, clove, chilly, garlic, coriander, cumin, fennel, fenugreek, celery, ajwan, saffron, cinnamon, vanilla, nutmeg and mace. Among these, cumin, fennel, coriander, fenugreek, ajwan etc. are classified as seed spices. One or the other spices is cultivated in different states of the country. These spices play an important role in the economy of various states.

The availability of suitable climatic conditions has significantly supported the spices cultivation in different regions of the country. Among the various varieties of spices which are grown in India, spices such as pepper, cardamom, ginger and turmeric were originated here itself. Spices like chillies, clove, nutmeg and vanilla were introduced by the foreigners. India has the credit for producing a large share of high valued spices like pepper, cardamom, ginger, turmeric and nutmeg. The country is also the largest consumer of various spices also.

It is meaningful to quote the following words to understand the significance of Indian spices.

"Why did Vasco da Gama come to India?

Braving turbulent seas,

The Portuguese navigator,

Anchored at Calicut,

A tiny port at the Arabian Sea.

What propelled him to undertake the

Hazardous Journey?

The Indian Spices"

Objectives of the Study

The major objectives of the study were

1. To analyse the economic significance of pepper crop in the agricultural economy of Kerala.
2. To evaluate the export direction of Kerala black pepper.
3. To assess the export performance of various pepper exporting companies.
4. To know the straight line trend of pepper production in the state and its export since 2001.

Significance of the Study

Pepper cultivation in the state is mainly concentrated in districts such as Idukki, Waynad and Kannur. Idukki district is the main pepper producing centre with 50 per cent of the area and 60 per cent of production. The second leading producer of the crop is Wynad district with an area of 10 per cent and 11 per cent of production. Idukki and Wynad are the two districts, where pepper is cultivated as a mono crop. In the case of other districts it is cultivated as an intercrop. The share of Kannur district is 5.6 per cent in area and 6 per cent in production. Idukki, Wayanad and Kannur districts together contributed nearly 65 per cent of the total pepper area and 76 per cent of the production in the state. In the state more than 2.5 lakh farm families are cultivating pepper. In Idukki district more than 73 per cent of the farmers are cultivating pepper as a source of income.

Methodology

The study was conducted on the basis of secondary data. Trends in production and export of pepper, its exports and export earnings, direction of trade were studied by using secondary data. The main sources of secondary data were Spices Board, India, Cochin and the Department of Economics and Statistics, Trivandrum. Various issues of Economic Review, Spices Export Review, Annual Reports of Spices Board India and Annual Reports of the Cochin Chamber of Commerce and Industry, Cochin were also used for the study. The present study has made use of the data pertaining to 10 years i.e. from 2000-2001 to 2009-2010.

Tabular presentation and analytical technique was employed for estimating the trends and direction of exports. The compound growth rate with regard to production and export has been estimated on the basis of the semi-log or exponential function

$$\text{Log } Y = a + bT$$

Where Y = Production / Export

T= Time

'a' and 'b' are the parameters to be estimated

Compound growth rate = ((anti log b-1) x 100)

Spices Production in India-The Present Status

India is one of the largest producers of spices in the world. During the year 2008-09, India cultivated spices in 2.94 million hectares and produced 5.28 million tonnes of spices.

Area wise Cultivation

During 2008-2009, the total area under spices cultivation in the country was 29.40 lakh hectares. Total area under chilli was 8 lakh hectares which constituted 27 percentage of the total area. The area under cumin and coriander were 18 and 17 percent respectively. In the case of spices such as pepper, cardamom, ginger and turmeric were 16 per cent, 1 per cent, 5 per cent and 7 per cent respectively. The area under cultivation of cinnamon, ajwan, celery, tejpat, vanilla, clove and nutmeg were less than one per cent in area.

Quantity wise Contribution

Among various spices produced in India, chilli contributed 26 per cent of the total quantity followed by garlic (19 per cent), turmeric (17per cent), ginger (15 per cent) and coriander (8 per cent) during the year 2008-2009. The share of cardamom and pepper were 2 and 1 per cent respectively.

State wise Area and Production of Pepper-The Present Status

Southern states are the production centers of pepper in India. In recent years, India's pepper production is more or less stagnant around 50,000 tonnes mainly due to low productivity of aged and disease affected pepper plantations. Pepper is mainly cultivated in three states of the country, Kerala, Karnataka and Tamil Nadu. Once Kerala had the monopoly in the pepper production and more than 90 per cent of the produce was contributed by the state. But recently, the share of the state has shown a declining trend and the production of pepper in Karnataka has increased significantly. Coorg region is the production centre of pepper in Karnataka state. Even then, in 2009-2010 a major portion (55 per cent) of pepper production in the country was contributed by Kerala, followed by Karnataka (29.5) and Tamil Nadu (15.5per cent). The area under pepper crop in Kerala is around 88 per cent of the country's total. See table-1.

Table-1 State wise Area and Production of Pepper During 2009-2010 (Area in Hectares and Production in Tonnes)

State	2009-2010			
	Area	Share in per cent	Production	Share in per cent
Kerala	171489	88.40	29152	55.0
Karnataka	19706	10.16	15645	29.5
Tamil Nadu	2789	1.44	8238	15.5
TOTAL	193984	100.00	53035	100.0

Source: Spices Board

According to the data provided by the Directorate of Economics and Statistics, Kerala the total area under pepper in the state during the year 2009-10 was 171489 and the production was 42459 tonnes. If these figures are considered the share of the state should be 88 per cent in terms of area and 64 per cent in terms of production.

States Which Ranked First in the case of Spices Production, during 2008-2009

The production of spices and herbs is widely distributed in a number of Indian states. Southern states such as Karnataka, Kerala, Tamil Nadu and Andhra Pradesh are the major areas of spices cultivation. Table-2 shows the list of spices and its leading growers, ranked first in terms of production and the details regarding area under cultivation and the productivity.

Table-2 Major Spice Producing States in India

Item	Area(in Hectare)	Production (in tonnes)	Yield (Kgs/Hect)	Name of the state, Ranked First
Black pepper	175868	40641	231	Kerala
Cardamom(S)	41588	8550	206	Kerala
Cardamom(L)	23729	3675	155	Sikkim
Ginger	29092	273253	9393	Karnataka
Turmeric	61607	403228	6545	Andhra Pradesh
Nutmeg	16187	11249	695	Kerala
Vanilla		88		Kerala
Chilli	214000	766000	3579	Andhra Pradesh
Coriander	131140	155100	1183	Rajasthan
Garlic	41735	182500	4372	Madhya Pradesh
Cumin	259217	152845	597	Gujarat

Source: Spices Board

During the year 2008-09, Kerala reckoned the first place in the production of many spices such as pepper, cardamom (S), vanilla and nutmeg and mace. In the production of cloves and tamarind the position of the state was third. In the production of ginger and turmeric state's position were eleventh and twelfth respectively.

Status of Kerala in the Indian Spices Industry

According to the official data, the status of Kerala in the Indian spices industry during 2008-09 can be summerised as in table-3.

Table-3 Status of Kerala in the Indian Spices India

(Quantity in tonnes)

Item	Production	Share in %	Rank
Pepper	40641	88	1
Cardamom(S)	8550	78	1
Nutmeg mace	11249	99	1
Vanilla	88	52	1
Clove	73	7	3
Tamarind	20164	11	3
Ginger	23380	3	11
Turmeric	6292	11	12

Source: Spices Board

Significance of Pepper in Kerala's Economy

In the present day, agricultural production in Kerala is mainly focused on cash crops. The predominance of cash crops is considered as a unique feature of Kerala's agricultural economy.

Kerala is famous for black pepper from olden days. Pepper popularly known as black gold holds a prime position in the spices economy of Kerala. The agro-climatic conditions prevailing in the state are suitable for the cultivation of pepper. Kerala is the

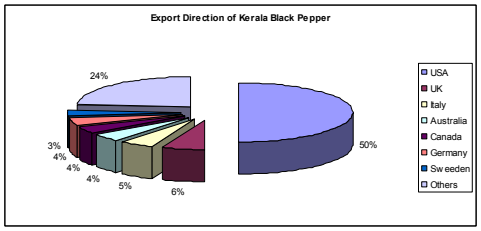
leading producer of black pepper in the country. It is believed that black pepper originated in Kerala. Pepper is a plant of humid tropics requiring adequate rainfall and humidity.

During 2009-2010 the state continued to hold the monopoly in pepper production by producing 40641 tonnes of pepper in an area of 175868 hectares of land and it is considered as the king of Kerala's spices. Kochi and Sulthan Bathery are the primary markets for black pepper in Kerala. The products developed from pepper broadly fall into four categories: black pepper, white pepper, green pepper and oil and oleoresin of pepper. Kerala exports pepper to more than fifty countries across the world.

Export of Pepper from Kerala According to Destination during 2009-2010

Pepper export from Kerala, through Cochin Port find its way to nearly 50 markets all over the world. However, during 2009-10, USA shares around 50 per cent of the total export. Important other markets for Kerala pepper were U.K (6 per cent), Italy (5 per cent), Australia (4 per cent), Canada (4 per cent), Germany (4 per cent) and Sweden (3 per cent). Export direction of Kerala pepper is given in figure-1

Figure-1 Export Direction of Kerala Pepper



Zone wise Performance of Exports of Pepper from Kerala, during 2009-2010

A zone wise an analysis of export performance shows that American zone stands first in the case of import of pepper from Kerala. Fifty-five per cent of our total export of pepper was directed towards American zone. USA is the largest importer of this zone. Canada is the second largest importer. The European Union is the second important zone with a share of 26 per cent of our export quantity of pepper. The UK, Germany and France are the leading markets in this region for the black pepper of Kerala. East Asia zone comes third in terms of import of pepper from Kerala, contributed to 9.5 per cent. Japan and Taiwan are the two important markets in this zone. The details of the analysis are furnished in table-4.

Table-4 Zone wise Export of Pepper from Kerala
(Qty in Tonnes.)

Zone	Export Quantity	Share in Per cent
America	9170.56	54.86
European Union	4382.37	26.22
CIS Countries	253.11	1.51
East Asia	1585.96	9.49
West Asia	354.22	2.12
Africa	173.40	1.04
Australia &Oceanic	734.67	4.40
Others	61.19	0.37
GRAND TOTAL	16715.48	100.00

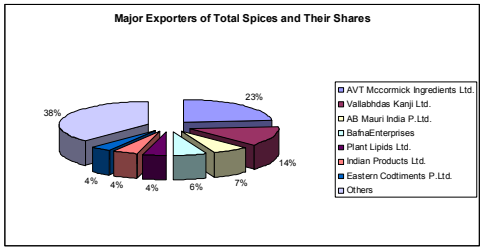
Source: Office of the Cochin Chamber of Commerce and Industry

During the year 1990 more than half of the country's pepper export was to the former USSR (57.42 per cent). At that time the export to USA was only 13 percent. Around 70 per cent export was to these countries. After the disintegration of the USSR and liberalised world trade practices, India has lost the former USSR market. Recently USA has emerged as the major importer of Indian pepper. During 2009, around half of the pepper export of the country was to USA (50.26 per cent) and the share of Russian Federation was only less than 2 per cent. Since the year 2001, USA is the single largest importer of Indian Black pepper.

Leading Pepper Exporting Companies and Their Export Performance

Among the top twenty five exporters of black pepper in India, nine exporters were from Cochin Region and eleven from Kerala as a whole. These Cochin based exporters alone contributed 83.45 per cent of the total export of black pepper from India. The leading pepper exporting companies through Cochin Port were Bafina Enterprises (18.2 per cent), AVT Mc cormic Ingredients Ltd. (17.4 per cent), AB Mauri India Pvt. Ltd. (14.3 per cent), Indian Products Ltd. (12 per cent), Nishant Exports (9.1 per cent), Vallabhdas Kanji Ltd (7.7 per cent), Harmony Spices Pvt. Ltd.(6.4 per cent), Kishore Spices Company (4.8 per cent), Lucid Colloids (1.4 per cent) and other companies export share was 8.8Per cent. The export share of the major pepper exporting companies is given in figure-2.

Figure-2 Leading Exporters of Pepper during 2009-2010



Compound Annual Growth Rate (CAGR) of Production, Export and Export Value of Pepper during the Period 2000-2001 to 2009-2010

During the year 2000-2001 the area under pepper cultivation in the state was 2.02 lakh hectares and the production was 60929 tonnes, with a productivity of 301 kg per hectare. In the year 2009-2010, this area came down to 1.71 lakh hectares and the production fell down to 40641 tonnes. The mean quantity of production accounted as 59490 tonnes. The Compound Annual Growth Rate (CAGR) of production in this period was negative and it was -5.11 per cent.

The export quantity of pepper from Kerala during 2000-2001 was 19073 tonnes, which has declined to 16715 tonnes in 2009-2010. In the case of export value of pepper, the foreign exchange earnings were Rs.33562.76 lakhs, which has also declined to Rs.25538.85 lakhs. For the overall period,

the mean quantity of export was 18402 tonnes. During this period, the CAGR of export quantity and export value realised were 2.83 per cent and 7.08 per cent respectively. The results of the linear trend analysis are furnished in table-5.

Table-5 CAGR of Production, Export and Export Value of Pepper

Variable	Linear Trend Line	R2	CAGR
Production	Y= -0.0228 x + 4.8951	0.3259	-5.11
Export	Y= 0.0121 x + 4.1798	0.0725	2.83
Export Value	Y= 0.0297 x + 4.1196	0.1251	7.08

The graphic illustrations of trends in production, export and export value of pepper in Kerala during the period 2000-2001 to 2009-2010 are given in figure-3, figure-4 and figure-5 respectively.

Figure-3 Trends in Production of Pepper in Kerala Since 2001

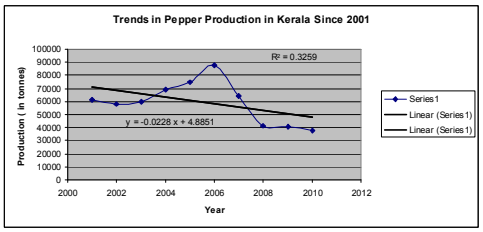


Figure-4 Trends in the Export of Pepper from Kerala Since 2001

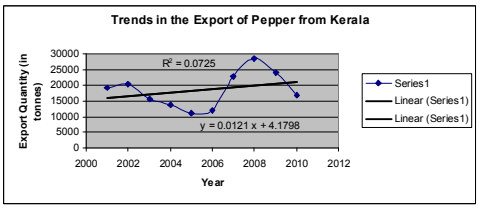
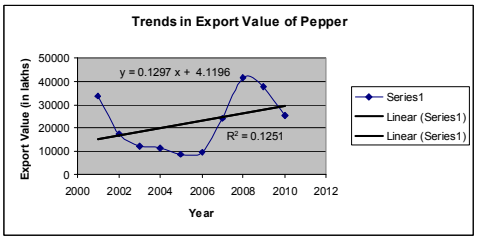


Figure-5 Trends in the Export Value of Pepper Since 2001



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FEMINISATION OF WORK AND RURAL DEVELOPMENT IN KERALA

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In Kerala, rural sector depicts a recent trend of development. It is nothing but the feminisation of manual work. Feminisation of work refers to a rise in female labour force participation and a relative fall in men's employment. It is observed that the rural sector in Kerala debits the trend of feminization during the post globalization period. However the policy makers are not so bothered about this positive trend of development. Therefore it may be interesting to examine the performance and prospects of feminization in rural Kerala.

Female job opportunities are linked to primary sector, traditional industry, poverty alleviation schemes and self-help group activities in rural sector. Therefore the present study examines the strength of female participation among the activities mentioned above.

In Agriculture

A recent study in Kasargod district reveals the feminization of workforce in agriculture sector. The study shows that work and labour market outcomes in the district significantly deviated from the rest of the State during the period of agrarian distress. It is found that there is a significant rise in employment rates especially among women in Kasargod district. Feminisation also proved by the proliferation of women workers in casual employment and elementary occupations. This represents a modern trend of feminization in the agriculture sector in Kerala.

Self Help Groups –The Kudumbashree Mission

A self-help group is a small group of people that all suffer from the same condition or addiction and work together as a supportive group to overcome the condition/ addiction together. The involvement of Self help groups in social and economic development become the major development strategy adopted by the UDF government in Kerala. The major self help group involvement in rural Kerala is nothing but the Kudumbashree Mission. The mission aims at the empowerment of women, through forming self-help groups and encouraging their entrepreneurial or other wide range of activities. It represents the best example for the feminization of rural employment. 99% of the kudumbashree units are organized by females.

Kudumbashree focuses on rural economic development through self employment, food security, health, creative potential development etc. Major poverty alleviation programmes of

kudumbashree are practically implemented through the following:-

a) **Linkage Banking:-** The bank linkage programme has helped NHGs (Neighbourhood Groups) to augment their existing resources collected through thrift. The cumulative amount that has been lent to NHGs was Rs. 13446.27 lakh in 2011.

b) Lease land Farming:- Under this programme 25062.88 hector wasteland was brought under cultivation.

c) **Strengthening of Balasapha, Balapanjayath and Holistic child health**:- In 2011, the formation of 50618 number of Balasaphas across the State has been completed with a membership of 878826 children, which led to cultivating creative potential in children.

d) **Micro Enterprises:-** It is enhancing the economic empowerment and employment opportunities for the poor women. An amount of Rs. 37.69 lakh had been provide as subsidy to 525 individual enterprises and an amount of Rs. 1236.28 lakh had been disbursed as subsidy to 2198 group till 2011.

e) **Akshaya:-** The main objective is to rehabilitates the entire destitute families of the State by providing them with basic minimum needs, improved health, education and literacy levels and to enhance the social and economic status b by empowering them. Women are the beneficiaries of this programme. The cumulative number of destitute families assisted under the programme till 2011-12 is 73827.

In short the kudumbashree mission represents the feminization of rural employment by evolving primary, secondary and tertiary sectors of the rural economy.

MGNREGS (Mahatma Gandhi National Rural Employment Guaranty Scheme)

The major poverty alleviation/ employment guaranty scheme implemented in Kerala is nothing but the MGNREGS. It ensures 100 days of guaranteed wage employment in a financial year to every household whose adult members volunteer to do unskilled manual work. Daily wages under the scheme is Rs. 150 irrespective of gender differences. This scheme mandates 33% of participation of women. However in Kerala 92% of the total workers seeking employment under this scheme are women. This is evident from the following table.

Women Participation in MGNREGA Scheme

State	Percentage of women participation
Kerala	92
Tamil Nadu	80.52
Rajasthan	71.32
Andhrapradesh	59.26
Jammu and Kashmeer	4.22
Chattisgarh	52.27
Tripura	52.0

Source: Ministry of Rural Development, Government of India

In all other States, not mentioned in the table, the share of women remained below 50%.

Traditional Industries and Female Employment

Traditional industries in Kerala give employment to more than 5 lakhs of people. The sex wise analysis of employment in traditional industries represents female domination. The following table proves the same.

Table-2 Sex wise employment in traditional industries

Industries	Female (Percentage)	Male (Percentage)
Cashew	95	5
Coir	85	15
Fisheries	68.5	31.5
Handloom	83*	17*
Khadi & Village Industries	25.4	74.6

Source: Economic Review, *Primary data collected from central Kerala

The table shows that most of the traditional industries except khadi & village industries represent female domination. Traditional industries are concentrated in rural parts of Kerala. Therefore, strong female participation of these industries indicates a new paradigm of rural development through feminization of work.

Reasons behind the feminization of work

High female literacy, strong movements of women organizations, political awareness, participation of women in local governments, presents of self-help groups etc. strengthened women empowerment in Kerala. This empowerment enhanced feminization of job in rural Kerala. Therefore feminization and women empowerment are interrelated. However a strong indirect, though neglected, reason behind feminization of job (i.e. a relative fall in men's employment) may be discussed here.

In the midst of high literacy and a number of movements against liquor consumption, Kerala is edging towards one of the largest consumers of alcoholic beverages in the world.

Taxes on alcohol are a major source of revenue for the State government. More than 40% of revenues for its annual budget come from liquor sales. Revenues from alcohol to the state's exchequer have registered a 100% rise over the past four years.

The increased liquor consumption in Kerala is evident from Table-3

Table-3 Liquor Sale during Onam Season in Kerala

Year	Sales (Crore)	Growth rate (%)
2008	110	--
2009	132	16
2010	155.61	15.17
2011	236	34.06
2012	286	17.48

Addiction to liquor in Kerala is strongly indicated by the consumption of liquor during the Onam season. The above data represent a steadily increasing trend of consumption.

Increased liquor consumption by men in rural Kerala resulted in reluctance of manual work and distortion of income from family budget. This created rural poverty though the labour income has increased considerably in Kerala. This manmade poverty may be the reason that enhanced feminization of job. This positive transition should be noted and evaluated seriously by the policy formulators.

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SRE NARAYANA GURU'S CONCEPT OF EDUCATION

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The Guru wanted educationists of his time and all the time to frame the academic curricula for both elementary and higher levels which can promote 'Sreyas' (spiritual freedom) as well as 'Preyas' (worldly prosperity) which are essential for man. The education as visualized by the Guru covers all disciplines of Self-realization and material well-being .Actually the Guru set the model of such an education by establishing an English school at Varkala, Kerala, along with the installation of sarada, Goddess of learning in the Sivagiri Mutt there. The Guru started a Sanskrit school and the Advaita Ashram at Alwaye. The Guru wanted to start a " Sarvamatha Padhasla" at Sivagiri where all religions could be studied with love and due respect. After the "all religions conference", the Guru laid the foundation stone for this Padhasala at Sivagiri in September 1925.

The present system of education in our schools and colleges is defective because it gives importance to physical and intellectual aspects only. No importance is given to spiritual values. The result is that only the physical and intellectual faculties are developed. Because of the total deprivation of spiritual and ethical principles, the spiritual faculty, the most important one, is not developed. Students are not uplifted into the world of high morality and they are not illuminated by the light of divine inspiration. The glorious achievements of modern education are just like shining soap bubbles which are very beautiful to look at, but there is nothing inside them. Students have noknowledge of moral and spiritual laws governing the life of man and their inter course with others. Modern education gives students information on different subjects, but does not produce men of character. Mere acquisition of scientific and technical know how develops superiority complex in students and makes them very proud. They have no love for fellow beings. They fail to look equally towards all irrespective of caste, creed or religion. They do not cultivate divine virtues such as love, kindness, sacrifice, self-denial and forgiveness, instead of being broad minded and liberal, they are narrow minded and selfish. They are in the grip of enticing effects of false glamour's. They become cannon fodder to the wicked ambitions of sadistic demons. They are mad after material comforts and wordly pleasures. They are least concerned about the evil systems such as the caste system in society. They have no strength and courage to demolish the narrowing walls of the caste system.

The Guru, one of the rare greatest souls, gained mastery over the Self and enjoyed the peace of self-realization. According to one school, the aim of education is to equip the pupil with the ability to win his bread and other material comforts. According to another school, education aims at only spiritual development in the pupil. The Guru's approach was different and unique. The Guru was neither a hater of the phenomenal world nor a voter of the same to the exclusiveness of the spiritual side. The Guru gave importance to both material and spiritual education. The Guru considered both complementary and contributory to each other. The Guru harmonized idealism with the realities of life. The type of education initiates the pupil into a life of noble aspiration and sacred values. It eradicates the gross nature and animal instincts in the pupil, thereby transforming him into a noble soul. He will have a sense of oneness with his fellow beings and a sense of responsibility towards others which he values above his own interests. This kind of education develops the pupils potentialities , and refines and elevates his mind.

According to the Guru, spiritual education makes the pupil know the real nature of his Self which will lead to the realization of the Universal Self. Such a pupil can never do any harm to his fellow beings and he can include in his happiness their happiness. Spiritual education will have ethical discipline and spiritual culture as its foundation. It cultivates fellow feeling and brotherhood. The Guru wanted the pupil to approach and understand all religions with equal respect and reverence. It is very interesting to not that the view of the Guru on education reflect in the UNESCO report of 1982. The report entitled " Learning to be" admits that the aim of education is the all round development of the pupils spiritual and material potentialities , thereby producing a complete man.

It is our ignorance which prevents us to get over the dichotomy between matter and Spirit(God). A true spiritual education will help pupils to recognize the relationship between Spirit and matter. Then they will not look down upon matter and all the problems the material life presents and shun spirituality as a lesson in escapism. Spiritual education will prepare them to face life armed with a greater faith and an outlook which are integral. Their recognition of the problems of life will not depend completely on their appearances. They will be able to delve deep into them and see the play of hidden forces behind them. They will be able to grow spiritually through taking the hurdles presented by life. It is high time the people belonging to different religions understood the Guru's concept of one God and this awareness will make them put an end to conflicts in the name of gods, which have been frightening the whole world and destroying the people's peace of mind.

GLOBALISATION

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The word "Globalization" denotes an idea of "One world – One nation especially in respect of all human economic activities: One economy for the whole world is a wonderful idea. Here all the nations try to eradicate all hindrances to trade and economic activities so that all articles, goods or commodities services, etc are made available easily all over the world in the right time.

Pre- globalization period:- After the Russian Revolution, cretaine nations adopted communism or socialism as a way of economic system. Some of such nations are USSR,China,E.Germany, Yugoslavia, Czechoslovakia,Poland, Guba,Vietnam etc, In. such nations, the "State" owns, controls and manages the whole or the lionshare of the economic activities like production, price-determination, consumption, distribution, exchange, public finance, transport, communication etc,Countries like India adoptyed"Mixed Economy": as an economic system which is also aimed at " Democratic Socialism" ie Socialism through democracy. India adopted and introduced a lot of socialistic measure like public sector and strict controls over the private sector, nationalization programmes especially in the field of banking sector, rationing system in the field of essential food products, pricing , licensing and other controls in respect of manufacturing and other industries etc,.But it is said that all over the world these activities resulted in the economic backwardness (India may be an exception), poverty, economic injustice and the destruction of economic freedom. But India could achieve much economic development. But in the 1980s and 1990s, the idea of "Free maket economy" began to grow in almost every socialist or communist country. It resulted in the strong movement of the people to eradicate the evils of communism.

PRESENT SITUATION

At last 14 nations out of 18 achieved freedom. They established democratic governments in their nations. Even,China, the existing largest communist nation, also participated in this movement. This situation encouraged the growth and development of "Free market economy" all over the world. By this time several international agreements, between nations were made. GATT is the most important among them. All these paved the way for the introduction of "Globalisation" thought.

INTERNATIONAL AND INTERNAL INVESTMENTS

India has also to participate actively in this movement. We also signed the GATT

Our public sector undertakings in spite of serious and long-term efforts, showed a very poor" show because of inefficiency, consecutive heavy losses, red-tapism, undue political interference etc. Investments in the important economic activities became vcery poor. Because of strict controls by way of acts like MRTP Act licensing system etc, our capital became very shy. This affected our growth. The present day economic system failed in giving sufficient employment opportunities to millions of our youth. It is said that the poor people became poorer and the rich became richer.

HOW GLOBALISATION IS BEING INTRODUCED IN INDIA

In India, our government is every particular to introduce globalization measures very carefully. For this, we introduced economic libera-lisation programmes in almost every field of economic activities. We encouraged private participation in several industrial activities. The Government is every careful to retain the available employment opportunities to a great extent.

AREAS OF INVESTMENTS:

International Trade:

1. Exports:- The government gave much importance to our export programmes. Industries producing export products ie, .Export- oriented industries are being given encouragements. These encouragements are in the form of several tax or customs duly, concessions etc. New item like computers,electronic products technical know how etc are included in the list of export.
2. Imports: Several duties on imports were either lifted or ourtailed. Now the industry is requiring costly and rare raw materials can be imported. Now we are able to import any necessary costly raw materials or sophisticated machinery without much difficulty.
3. Automobiles: With the help of the new collaborations, now we get ample resources, technical help etc,.We can find good market for automobiles spares etc internal and external.
4. Transport: Our development in respect of all types of transport means is tremendous. Production has been increased and now we can meet the increased demand in this respect.
5. Roads and their development: Investment in roads- new and the development of old ones is also very valuable.
6. Communication: India witnesses tremendous progress in respect of information technology. This is of course, with the help of the vast development achieved in respect of the development of electronics science and software and hardware computer engineering. Communication or IT development is a subject of study in the modern education system

7. Education: The old and out of date systems of education have been undergoing vast changes. Internet facilities , and computer education at all levels achieved progress. Modern education in respect of information technology, management science, engineering etc, have been accelerating globalization.
8. Airways, Aeronautic engineering etc, are developing with greater speed, of course with the help of modern highly sophisticated technical know hows.
9. Railways: Indian railways also try to develop by adopting modern techniques and better customer services.
10. Industries: Computerization and the use of upto date techniques and science, easily available imported technical know-how etc are the results of globalization .In respect of industries, we invite global investors on a large-scale. In the field of even the key industries, the government welcomes private participation. Indian and Global investors are invited to invest money in the following categories of industrial field, which generate large scale employment opportunities:-

1) Computer & Electronics 2) IT, 3) Tourism and Travelling 4) commerce and banking 5) Service industries 6) Education and other infrastructure

Role of Kerala: Just like other states especially A.P., Karnataka etc, Kerala State also organized a Global Investment Meet recently. The State Govt. submitted several projects for consideration. The major ones are in respect of " State Express Highways: Electrical and electronics industries , tourism, infrastructure etc. The Prime Minister announced Rs. 10,000/- crores investment programmes. The participants in the "GIM" and the State Govt. could agree with the common cause and could enter into certain important agreements of investments of large size.

All these will create employment opportunities on a large scale and will pave the way for speedu economic progress.

AGREEMENT FOR GLOBALISATION AND GLOBAL INVESTMENTS:

1. Overal economic development: Investment in the various fields of our economy will definitely improve our economic condition. We can expect increased production at all levels, improved distribution and increased standard of living of the people in general.
2. Increased services: The customers at large will get better after sales services at cheaper rates. They get better education regarding the articles or services. They get better banking and other commercial services.
3. Efficient operation: Programmes of investments in re-orgnisation of

industries expansion and moderisation will increase the operational efficiency. This is highly beneficial to the people large. This is due to lower cost of increased production and lower or reasonable prices will attract the people to buy.

4. Increased educational facilities are being offered especially in the field of computer, electronic information technology, modern Scientific management etc.
5. Importing technical know how: Out liberalized international trade policy encourages the import of technical and scientific know how which is essential for any developemtn.
6. Mobilization of Capital Indian and foreign capital) This is the most important objective. Without capital investment, we cannot expect a speedy economic progress . So, we always welcome Indian and Global investors to invest money and capital in various economic activities.
7. Creation of new employment opportunities: Large scale and medium scale industries will be the result of large-sale investment. This will create thousands of employment opportunities directly.
8. Development of several allied industries, service industries etc is another outcome.This will create several indirect opportunities of employment.
9. Expansion of Marker: We can expect considerable increase in production at all levels and this will expand the market India can get more competitive strength in the foreign market. This will improve exports and foreign exchange earnings.
10. Best quality products at cheaper rates: This is an objective of any investments. Now any management (investor) has objectives of their investment projects 1) Reasonable profit,2) Reasonable wealth,3) Reasonable return on investment (ROI) and 4) Social objective ie, social welfare. These objective can be achieved only with the help of quality production and reasonable prices. This will increase the living standards
11. Most efficient institution of resources: Investment in several industries require resources ie, in Men, Money, Materials etc on a large scale.Their efficient utilization will lead to economic progress.
12. Electricity: Industries require electricity. They will be allowed to generate electricity by operating their own power plants.(solar, Thermal etc).
13. Increased Tax revenue: The Government can also expect more revenue out of “Profit-Tax” sales tax, income tax etc.

14. Role of commercial banks : Banks and other financial institutions will have a more important role in such a situation .Money, banking and credit facilities will have to be extended and expanded in the new situation.
15. Transport Development at all kevels is essential for the speedy movement of men and material to production or service centers and to the consuming centers.
16. Development in the field of communication, information technology etc will be immensely valuable.
17. Living standards: We can achieve the ultimate objective of improved living standard of the people in general.

ARGUMENTS AGAINST GLOBALISATION

Globalisation or Global investment may not be an unmixed blessing. It has certain disadvantages also.

Some of them may be briefly explained a s follows:-

1. Uncontrolled Investment: Once all liberalization programme is introduced, it paves the way for uncontrolled investments. This may create unhealthy competition in the economy and lead to industrial failures.
2. Over capitalization: In such a situation capital may not be efficiently utilized or there may be wastage of capital.
3. Unwanted production: Because of cut: throat competition there may be attempts to produce more and more to achieve economics of large scale production. At last this may lead to over-production.
4. Generation of power-in the private sector: This is criticized on the ground that power is a very important factor of production and this should be in the hands of and under the control of "State Monopoly".
5. Scarcity of Materials : Every one knows that the supply of materials is limited in any field.Such materials may not be used carefully.Conservation of the nation's scarce materials is needed. But this may bot be possible.
6. Uncontrolled Imports: Globalisation paves the way for uncontrolled imports. Liberalized import policy and lack of proper restrictions on import will affect the Indian industries especially weak industries.
7. Uncontrolled Foreign Capital: Globalisation envisages the import of foreign capital. Uncontrolled inflow of foreign capital may invite economic troubles like over investment, over capitalization, wastage of capital, acute and cut-throat competition, business and industrial failures etc in the long – run This will again rate and aggravate our unemployment problem

8. Neglect the principle of "Production according to Need "The investor always tries to maximize profits" Reasonable rate of return" principle may be ignored. This attitude of global investors will lead to "produce not according to need but for rich profits" alone.
9. Home industries may suffer: Multinational industries are always stronger than our weak home industries .Development of new global investments may affect the home industries .Development of new global investments may affect the home industries adversely.
10. "Run-after Global investors"- More and extra care of such new projects may lead to the negligence of our poor home, traditional small and cottage or village industries. This may affect the poor mass adversely.

Remedies: Certain remedies may be suggested to overcome the above.

1. Introduction of some reasonable control on investment.
2. Watch the progress of investments and verify at regular intervals whether the funds have been effectively and efficiently utilized.
3. Control of production to avoid over production and cut-throat competition.
4. Supervision of the new electricity power plants, operated by private sector.
5. Introduce clear policy of conservation of scarce materials.
6. Imports should be controlled .Introduce "anti-dumping" policy
7. Encourage foreign capital investment only in the most essential fields.
8. Encourage the policy of "Production according to need" by proper planning.
9. Special care to protect and modernize the weak home industries.

To conclude, we can say that globalization, should be welcomed in the best interest of the nation. Great care should be taken to a avoid its evils.

PRESENT SITUATION IN FDI IN RETAIL INDUSTRY

India also entered in to the "ASIAN" Agreement along with a large number of Nations. This also will smoothen international trade. In 2012, the Central Government also passed a resolution, inviting Foreign Direct Investment (FDI) in medium and small scale and retail trading. The anticipated employment opportunities generated by this touch about 17 lacs. It will be definitely a great achievement in solving our unemployment problem. It will also attract a lot of new products.

INTERNATIONAL CONTAINER TRANS-SHIPMENT TERMINAL, KOCHI (THE NEW GATE WAY OF INDIA'S INTERNATIONAL TRADE)

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The Kochi International Container Trans-shipment Terminal (ICTT), locally known as Vallarpadam Terminal, is a container trans-shipment facility which is part of the Kochi Port Trust. It is the one and only trans-shipment port in India, and is located in Kochi, the 'Queen of Arabian Sea'. Trans-shipment means the shipment of goods or containers to an intermediate destination, then moves to another destination.

It is constructed in three stages, the first phase of the terminal was commissioned on 11 February 2011. It can handle cargo up to one million TEUs (Twenty- foot Equivalent Units) per annum.TEU refers to a 6.1*mt* intermodal container, which can be easily transferred from one mode of transportation to another ie.Ship,train and truck. Through the completion of third phase, the terminal will be able to handle 4 million TEUs of cargo per annum. The terminal is now being operated by Dubai Ports World (DPW), which will operate ICTT for 30 years, after which the control will come back to the Kochi Port Trust. (This is called as BOT i.e Built, Operate and Transfer). This biggest project was formally launched with the laying of the foundation stone by Mr. Manmohan Singh, the Prime Minister of India in 2005

ICTT is the largest single operator container terminal in India and the first in country to operate in a Special Economic Zone (SEZ). The terminal gave another golden feather to the 'Queen of Arabian Sea', Kochi. ICTT reduces India's dependence on foreign ports to handle trans-shipment. It transforms Kochi into a centre of shipping world. With the advantage of the right location, an efficient and cost effective reach to the markets in India as well as the proximity to the major sea route, ICTT is set to revolutionize the future of global trade.

The ICTT is a Public Private Partnership (PPP Model) project being developed by DP World, along with Kochi Port Trust. The Kochi Port has invested over Rs.1500 crore on road, rail connectivity and dredging of the channel. Container capacity handled for international and domestic traffic stood at 9.1 million TEU in 2008 and is expected to reach 21 million TEU in 2014

The major advantage of ICTT is a growing immediate hinterland. South India's container market has accounts for close to 2 million TEUs. The absence of a hub port in

India has resulted in a significant share of containers leaving an Indian port going through a feeder, with trans-shipment and mainline movement causing additional delay. This result in a 40-50 hours delay as containers are transshipped through ports such as Colombo, Singapore, Dubai and Salah. Now the importers and exporters in South India receiving direct calls, which will reduce their logistics cost and time. It will also generate opportunities for coastal feeder movement of containers, as ICTT will be an alternative transshipment hub for Indian cargo.

Now ICTT is growing in its all respects. A considerable change has taken place as regards the volume of cargo handled at ICTT. There has been a growth of 11 per cent during January-March 2013, when compared with the corresponding figures of the previous year. The frequent strikes had tarnished the goodwill of Kochi among the international shipping fraternity. To put it briefly, ICTT can be considered as a new gateway of India's international trade scenario.

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