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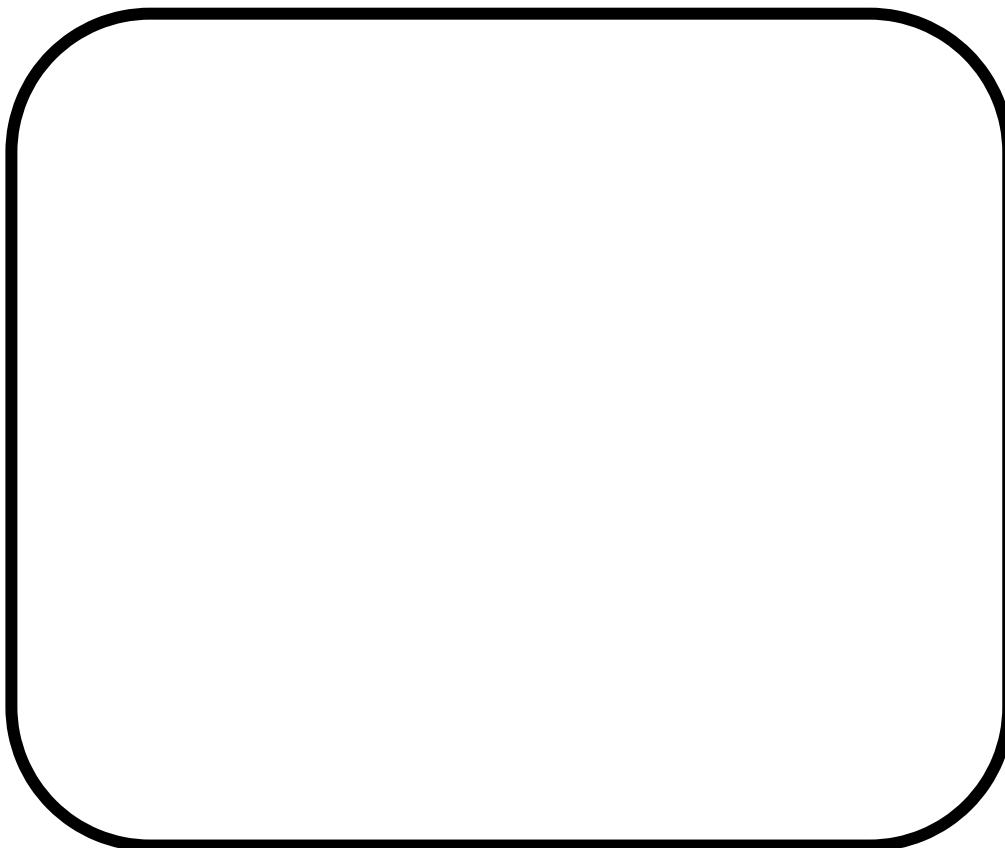
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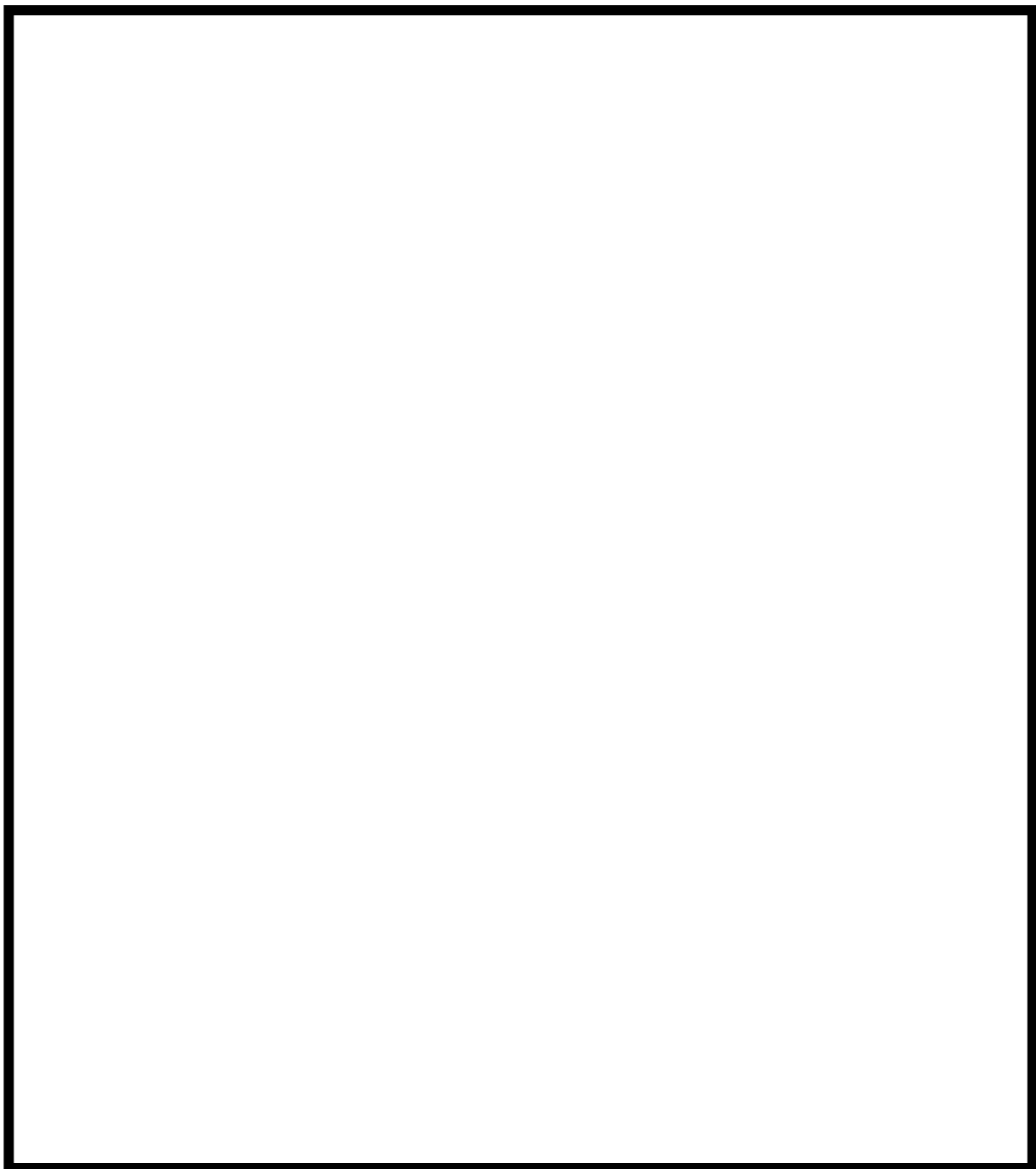
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Effect of Cassava Starch on Biodegradability, Mechanical and Swelling Characteristics of Styrene-Butadiene Rubber Vulcanizates

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ABSTRACT

Polymer composite are one of the most dynamic sectors of polymer industry which combine the properties of the individual polymers and extend the areas of applications of the different polymers. The properties of polymers like tensile strength, ductility, impact strength, abrasion resistance etc. can be improved by making composites with suitable reinforcing agents. Styrene Butadiene Rubber (SBR) is a general purpose multitalented synthetic rubber having high mechanical properties. Cassava Starch is a natural product and is used as the reinforcing agent. The studies show that SBR/Cassava Starch composite has better properties than that of pure SBR. The solvent resistance, mechanical properties and aging characteristics are studied.

Keywords: Composites, SBR, Starch

1. INTRODUCTION

Composites are materials that consist of two or more chemically and physically different phases separated by a distinct interface. The different systems are combined judiciously to achieve a system with more useful structural or functional properties non-attainable by any of the constituent alone [1]. Extensive studies have been conducted throughout the world during the few decades for getting new polymeric materials with specific properties for specific materials. Scientists have been trying to find out new materials for various applications. They have started concentrating on the modified forms like polymer blends, polymer composites, inter penetrating networks etc. So a deeper study of polymer composites has become a new and important challenge for researchers.

The interest in polymer composite research has been attracted by the fact that already existing polymers and some common substances that occur naturally or synthetically can be used in the composites fabrications. As a result, the costly development of new polymers via co-polymerization or polymerization of new monomers can be avoided. Subsequently, polymer composites have gained much interest and have now become a new branch of macromolecular science and engineering. Polymer composites are one of the most dynamic sectors of polymer industry. It is one of the easiest and most flexible methods to generate a new polymeric material for special properties. Composite materials are produced by combining properties of matrix materials and reinforcing agents and then extend its area of applications. The properties of polymers can be improved by this technique. In the context of eco-friendly materials, recyclability of the material is one of the major problems. Recyclability of the composites will lead to the cost effective products at the same time this is the remedy for the increased amount of waste materials. Green composites can replace all hazardous and waste producing counterparts.

Polymer composites have a long history and a great deal of research has been carried out on them. They are used in a wide range of applications. Particulate filling has been used extensively in the rubber industry to improve various properties because it is effective yet inexpensive. Many researchers have studied the development and characterization of various composite materials for the past few decades. Akil and Zamri [2] studied the dynamic mechanical properties of natural fiber reinforced composites. Special emphasis has been given to kenaf and jute fiber reinforced unsaturated polyester composites produced using the pultrusion method. Sonia et al. [3] examined celluloses microfibers reinforced poly(ethylene-co-vinylacetate) composites. Dynamic mechanical analysis of composites showed increased storage modulus and decreased stiffness and damping properties with cellulose microfibers (CMF) loading. Ahmed et al. [4] examined

the characterization of treated date palm tree fiber as composite reinforcement. Chemical and mechanical characterization study on date palm tree fibers is essential to be able to evaluate the behavior of these fibers as mutual reinforcement for polymer based composites. Gilfillan et.al.[5] studied the preparation and characterization of composites from starch and sugar cane fiber. Srithong kham et.al.[6] investigated starch/cellulose bio composites prepared compression molding. It was found that starch bio composites made from cassava starch and glycerol provided a good result on shape stability with relatively high modulus and tensile strength. Xiangwenzhou et al.[7] studied new fabrication and mechanical properties of SBR/Carbon nanotubes nanocomposite. Asish Malas et al.[8] studied the effect of expanded graphite and modified graphite flakes on the physical and thermo mechanical properties of SBR/Polybutadiene rubber. Rajasekar et al.[9] studied the development of compatibilizer SBR and EPR(ethylene propylene rubber) nanocomposites containing dual filler system. Gong et al.[10] studied the preparation and properties of the powder SBR composites filled with CNT_s by spray drying process. Shih et al.[11] studied the effect of peroxide cross linking on the structure and mechanical properties for SBS/PS/SBR foams composed of polystyrene (PS), poly(styrene-*b*-butadiene) diblock copolymer (SBR-1502), and poly(styrene-*b*-butadiene-*b*-styrene) triblock copolymer (SBS).

SBR is general purpose rubber produced from copolymer styrene (75%) and butadiene (25%). It is used in great quantities in automobiles and truck tyres as an abrasion resistant replacement for natural rubber. Also it is used in carpet backing, belting, flooring wire, cable insulation and footwears.

The present article deals with the preparation of SBR-cassava starch composites in different composition and study of the effect of cassava starch on biodegradability, mechanical and swelling characteristics of SBR composites. The aim of developing

composite materials by reinforcing polymers with suitable fillers is to achieve commercially viable products having unique properties at lower cost.

2. MATERIALS

The synthetic rubber SBR and cassava starch were used for the study. The chemical dicumylperoxide(DCP-40%) was used as the free radical initiator and palm oil is used as the plasticizer. The solvents used for the experiment include dimethyl formamide and dimethyl sulphoxide. The formulation of different mixes used in the study is given in the Table 1. Mix A represent the gum sample without starch and mixes B, C, D and E contains 10, 20, 30, and 40 phr starch. SBR is masticated in a two roll mixing mill and other ingredients DCP, Palm oil, and Cassava starch are added successively. The compounded sheets were then cured in a hydraulic press at 160°C to the respective cure times obtained from rheogram.

Table 1 Formulation of SBR/Cassava starch mixes

Components (phr)*	Mix				
	A	B	C	D	E
SBR	100	100	100	100	100
DCP	0.5	0.5	0.5	0.5	0.5
Palm oil	1.25	1.25	1.25	1.25	1.25
Cassava starch	0	10	20	30	40

*Parts per hundred rubber

The mechanical properties tensile strength, elongation at break and modulus were carried out in a universal testing machine INSTRON 3365. Scanning Electron microscopy (SEM) is an important tool for observing the surface morphology of rubbers, the cause of crack initiation and the failure process in composite materials. The SEM observation was made using ISI-60 and Philips 500 (scanning electron microscopy). By interaction between

solvent and each of pure polymers it is possible to obtain information about the interaction between components in composites. The sorption and diffusion through polymer is controlled by factor such as polymer structure, its cross-link density, fillers, shape and miscibility of components as well as on the morphology of the systems¹². The direct involvement of micro-organisms in rubber can be studied by a method known soil burial test. Effect of soil burial on the rubber was primarily followed by quantitatively observing the change in their mechanical properties.

3. RESULT AND DISCUSSIONS

3.1 Mechanical properties

The mechanical properties tensile strength, elongation at break, modulus were carried out at a cross head speed of 500 mm/min by using dumb bell shaped specimens having thickness 3 mm. The variation of tensile strength with loading of cassava starch in SBR matrix is shown in Figure 1.

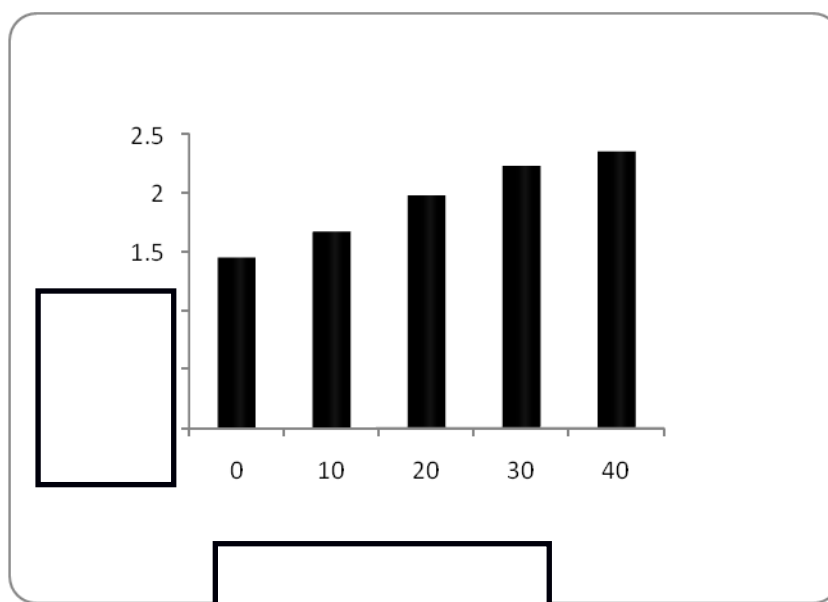


Figure 1. Tensile Strength of SBR/Cassava starch mixes

It can be seen from the figure that as amount of the cassava starch increase the tensile strength increases. Tensile values are increased due to the interaction between SBR and cassava starch. Tensile values reach an optimum value at 40g of starch in the composite.

The elongation at the break is the strain on the sample when it breaks. It is expressed in percentage. The variation of Eb with loading of cassava starch is given in Figure 2. From the result it clear that as the loading of cassava starch increases the elongation at break decreases. The decrease in elongation with increase in starch loading is attributed to the increased stiffness of the matrix.

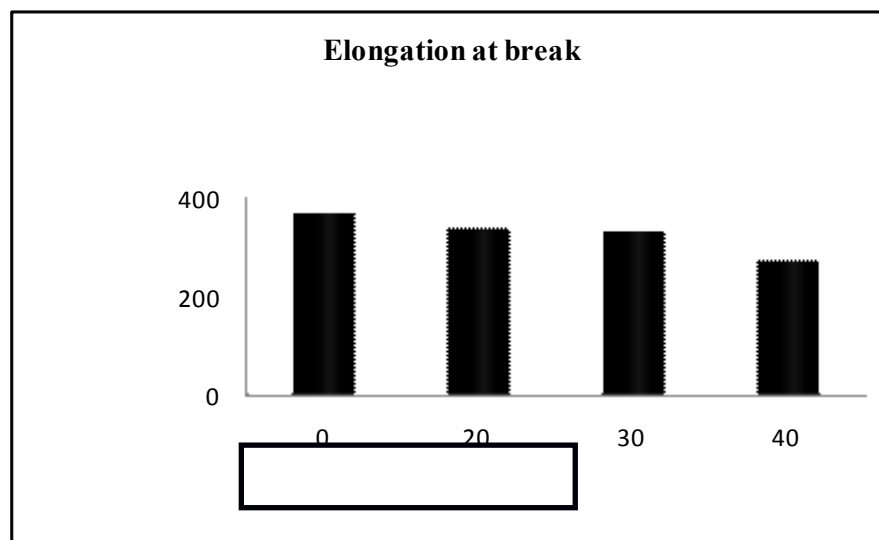


Figure 2 Elongation at Break of SBR/Cassava starch mixes

Modulus is measured as the force per unit area required to extend a rubber to a stated percentage of its original length e.g. 100%, 200%, 300% etc. The Figure 3 shows the variation of modulus at 100% of composite with starch loading. Modulus values of mixes increases with increase the amount of cassava starch and attain an optimum value at filler loading 40phr. The modulus is increased due to the increasing interaction between the SBR matrix and the reinforcing filler.

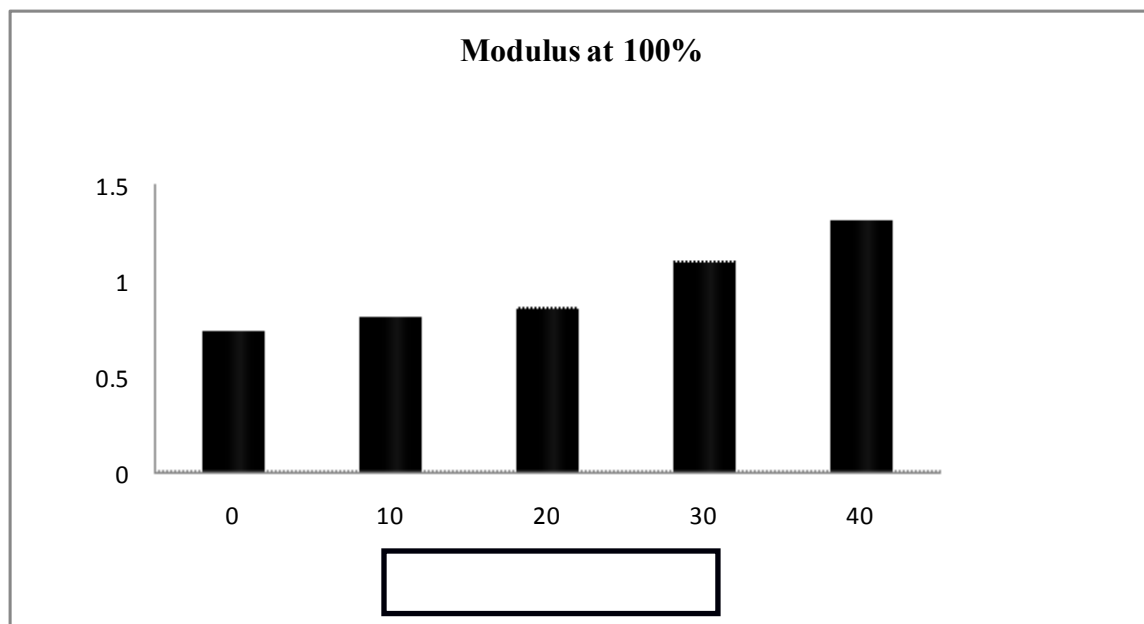


Figure 3 Modulus at 100% of SBR/Cassava starch mixes

3.2 Ageing characterization

Mechanical properties of the composite before and after ageing under soil burial were compared. The tensile test was conducted after the soil burial of SBR/Cassava starch sheets and detects substantial variation after one month. Figure 4 shows the comparison of tensile properties of the SBR/Cassava starch composite before and after the ageing. The figure shows that, tensile strength of composite is decreased after the soil burial test when it is compared to the tensile values of mixes before ageing. The tensile values decreased after the ageing, due to the degradability of cassava starch and the palm oil.

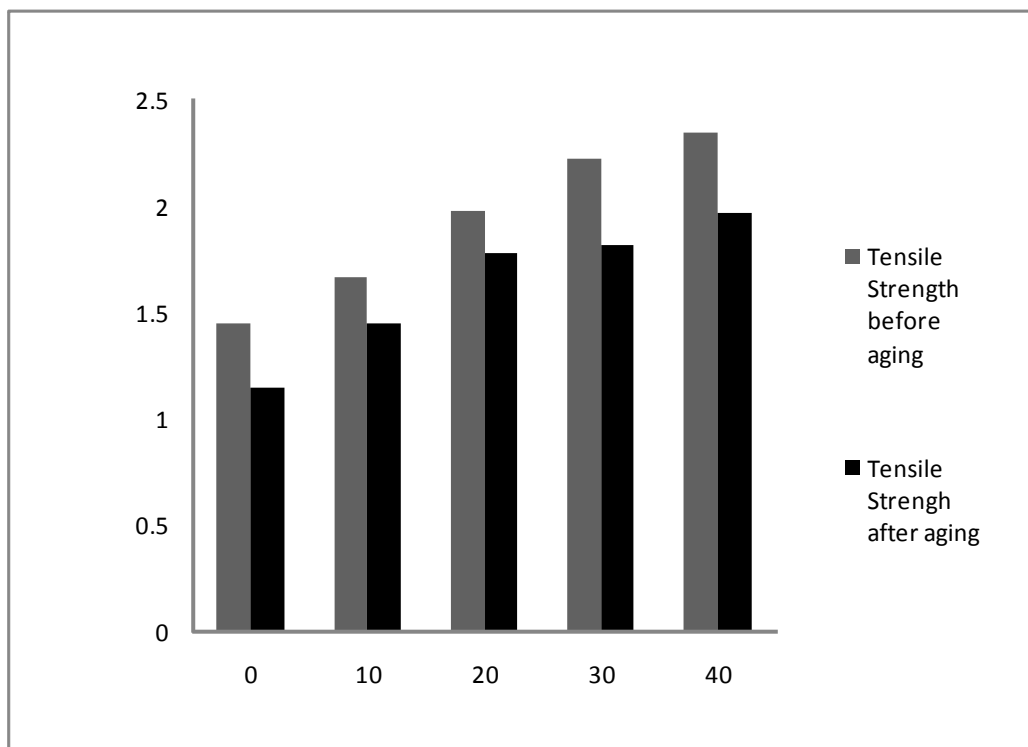


Figure 4 Tensile strength of SBR/Cassava starch mixes

The Figure 5 shows that variation of value in Eb in the SBR/Cassava starch mixes before and after ageing. From the Figure it is clear that the Eb value decreased after the ageing under the soil burial test.

The Figure 6 shows that the values of modulus at 100% of all the SBR/Cassava starch mixes before and after ageing. It can be seen that the modulus values of composites at 100% are decreased after one month under the soil burial test due to the biodegradability of reinforcing filler and the plasticizer palm oil.

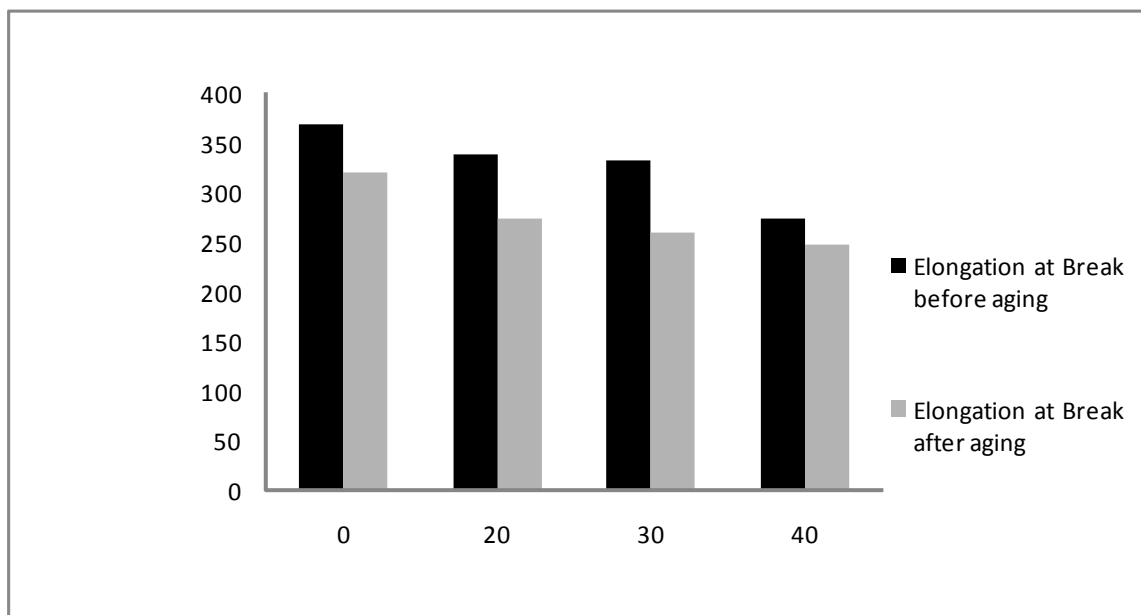


Figure 5 Elongation at Break of SBR/Cassava starch mixes

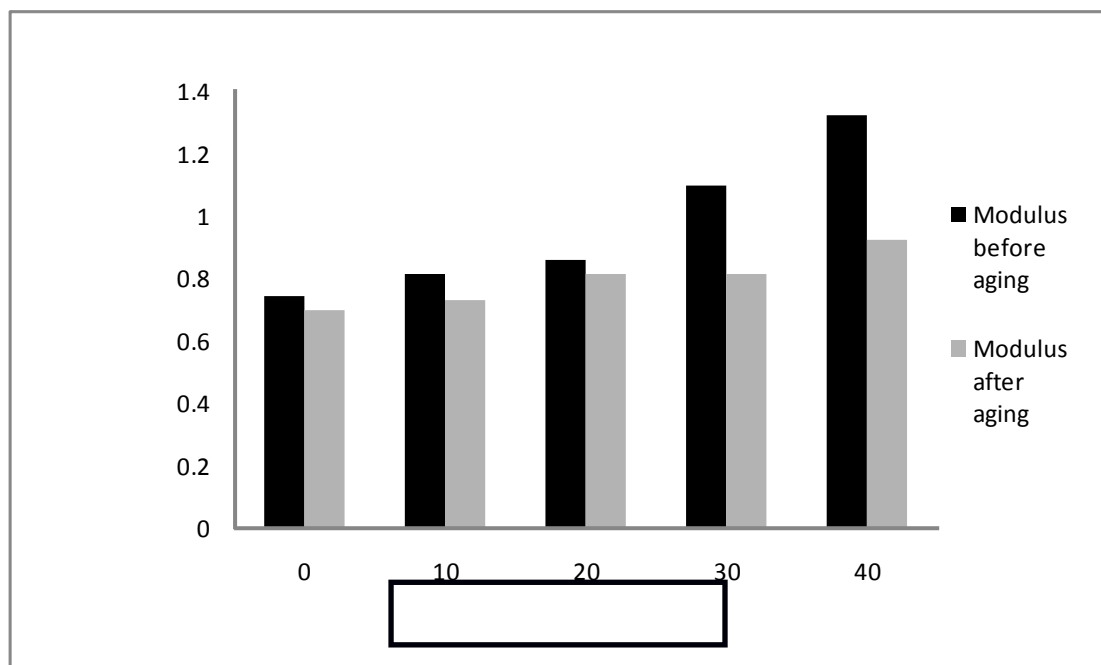


Figure 4.6 Modulus at 100% of SBR/Cassava starch mixes

4.3 Swelling characteristics

The swelling coefficients of SBR/Cassava starch composite in the solvents Toluene and Xylene are taken, and the values are tabulated in the Table 2.

Table 2 Swelling Coefficient of SBR/Cassava starch mixes

Mix	Swelling Coefficient in Toluene	Swelling Coefficient in Xylene
A	7.3946×10^{-3}	8.6579×10^{-3}
B	5.7706×10^{-3}	6.8928×10^{-3}
C	5.7616×10^{-3}	6.4995×10^{-3}
D	5.7342×10^{-3}	6.4754×10^{-3}
E	4.8815×10^{-3}	5.4953×10^{-3}

From the Table 2 it is clear that the swelling coefficients of composites decrease with increase in filler loading when toluene and xylene are used as solvents. Mix E, which contain optimum loading of starch (40phr) has been formed to have highest swelling coefficient value which indicates the maximum resistance to swelling in both toluene and xylene. The sorption behaviors of different SBR/Cassava starch mixes in toluene and xylene solvents at room temperature are shown in Figure 7 and 8.

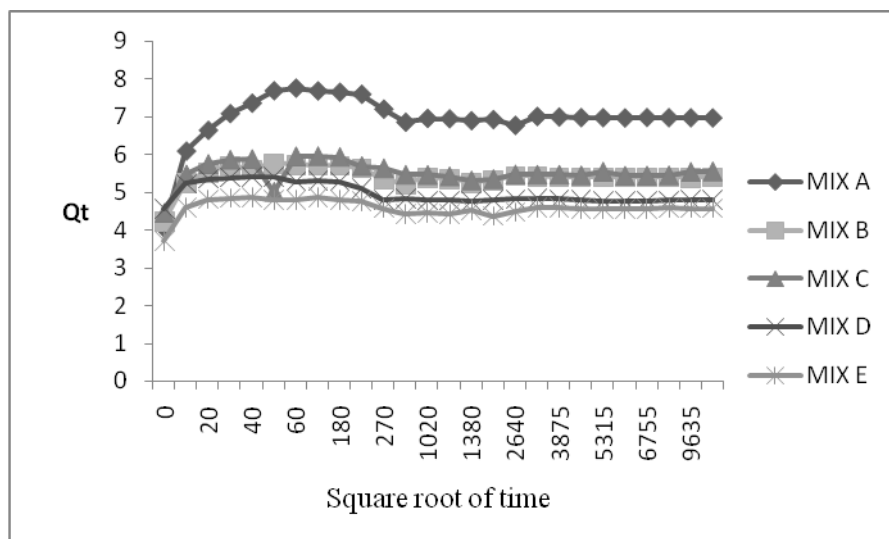


Figure 7 Mole percent uptake of Toluene by SBR/Cassava starch composite

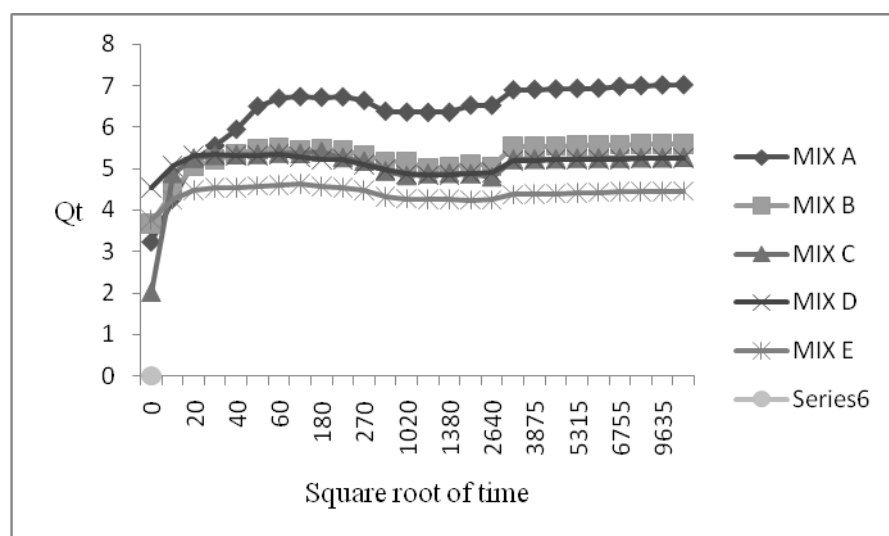


Figure 8 Mole percent uptake of Xylene by SBR/Cassava starch composites

3.4 Morphology of the composites

Molecular shape and arrangement of molecules in solid is important as these factors will determines the properties of polymers like crystallinity, branching, molecular weight,

cross-linking and polymer structure. The SEM photograph of gum sample (Mix A) and SBR/Cassava starch composite with optimum properties (Mix E) is shown in the Figure 9 and 10.

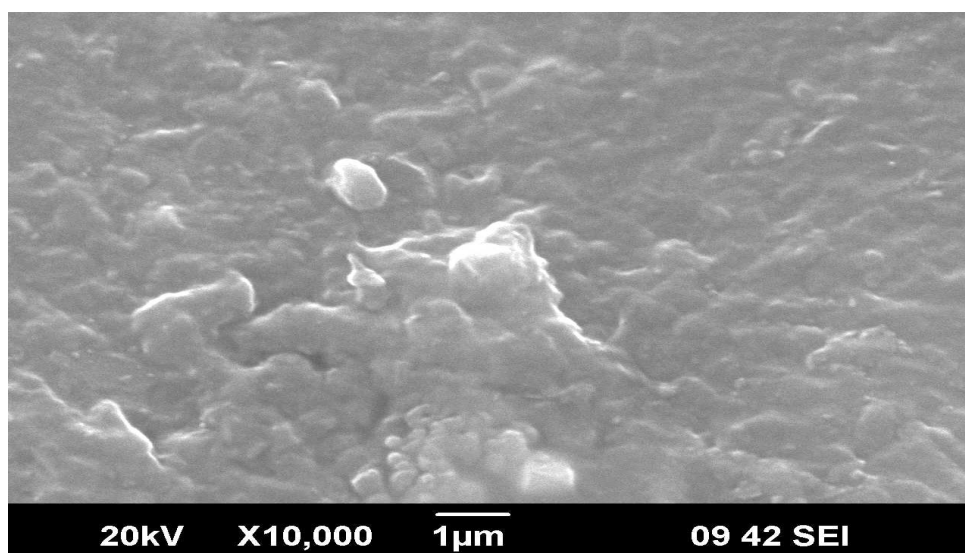


Figure 9 SEM photograph of Mix A

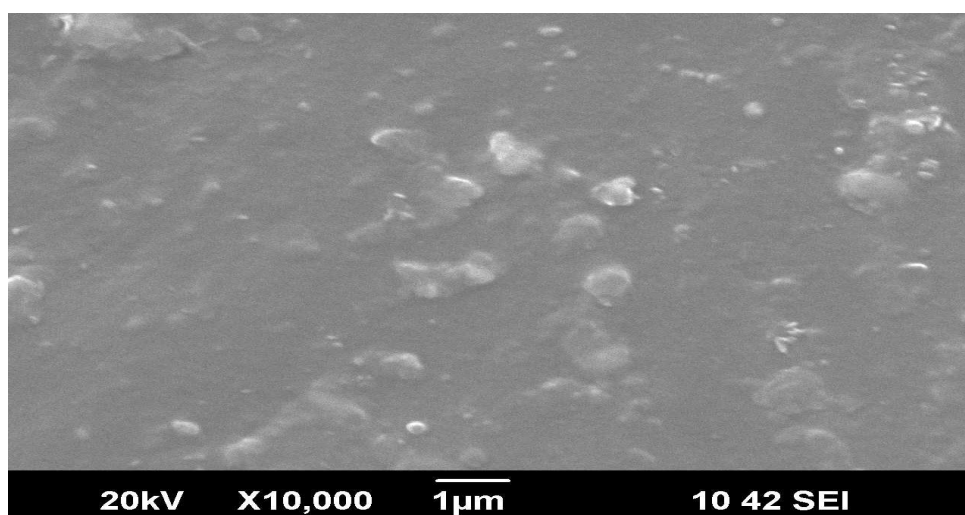


Figure 10 SEM photograph of Mix E

4. CONCLUSIONS

The mechanical properties of SBR/Cassava starch composites are better than that of pure SBR. The overall properties of SBR/Cassava starch composites were found to depend on the amount of filler, type of cross links and rubber-filler interactions. The studies show that with increase in the loading of cassava starch in SBR, the tensile strength increases progressively up to 40 phr loading. Tensile values increased due to the increase in interaction between SBR matrix and the filler. The tensile values decreased after the soil burial test for one month due to the biodegradability of cassava starch and palm oil. The swelling characteristics of SBR/Cassava starch composites have been studied using Xylene and Toluene as the solvents. The swelling coefficient values were found to be decreased with the filler loading in both solvent which indicated improved solvent resistivity.

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Development and Characterisation of Talc/Natural Rubber Nanocomposite

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ABSTRACT

Polymer nanocomposite is a multi phase solid material where one of the phases has one, two or three dimensions less than hundred nanometer. By appropriately adding nano particles to a polymer matrix we can enhance properties such as modulus, strength, and heat resistance etc. Natural rubber is a hydrocarbon polymer used mainly in automobiles. Talc is a mineral composed of hydrated magnesium silicate used in many industries such as paper making, plastic, paint and coatings, rubber, food, electric cable, pharmaceuticals, cosmetics, ceramics, etc. The present article aims at studying the reinforcing effect of talc on natural rubber by analyzing the mechanical, thermal and morphological characteristics of the nanocomposites. The applicability of these modified nanocomposite in products like sheets, bars, etc. are checked.

Keywords: composites, NR, talc

1. INTRODUCTION

Polymer nanocomposites represent a new alternative to conventionally filled polymers. Because of their nanometer size filler dispersion nanocomposites exhibit markedly improved properties when compared to the pure polymers or their traditional composites. These include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [1]. The methods for the

preparation of nanocomposites include in situ polymerization, solution and melt intercalation. Melt intercalation of high polymers is a powerful approach to produce layered silicate polymer nanocomposites. This method is quite general and is broadly applicable to a range of commodity plastics from essentially non-polar through weakly polar to strongly polar polymers.

Layered silicate polymer nanocomposites are processable using current technologies. In general two types of organic/inorganic hybrids are distinguished. Intercalated (polymer chains are diffused between the silicate layers preserving however some short range order of the latter) and exfoliated (in which the silicate layers of ca. 1 nm thickness are fully delaminated and dispersed in the polymer matrix)[2]. Nano scale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviors that are absent in the unfilled matrices. This effectively changes the nature of the original matrix such composite materials can be better described by the term genuine nanocomposites or hybrids. Some examples of such new properties are fire resistance or flame retardancy, and accelerated biodegradability.

Talc is a mineral composed of hydrated magnesium silicate with the chemical formula $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ or $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. In loose form, it is the widely used substance known as talcum powder. Talc is used in many industries such as paper making, plastic, paint and coatings, rubber, food, electric cable, pharmaceuticals, cosmetics, ceramics, etc [3]. Alexandre et al. [4] prepared a new type of materials, based on smectite clays usually rendered hydrophobic through ionic exchange of the sodium interlayer cation with an onium cation via various synthetic routes. Ke et al. [5] designed a study of polymer-layered silicate and silica nanocomposites. Polyamide is one of the earliest industrial polymers and one of the earliest engineering plastics. Okamoto et al. [6] studied the preparation, characterization, materials properties, crystallization behavior,

melt rheology, and processing of polymer/layered silicate nanocomposites. Hectorite and montmorillonite are among the most commonly used smectite-type layered silicates for the preparation of nanocomposites. Kiliaris et al. [7] presented the recent developments concerning the use of layered silicates (clay) for designing polymer nanocomposites endowed with enhanced flame retardancy. Emphasis was placed on the fact that the effect of layered silicates is beneficial mostly for retarding flame spread in developing fires, but not at the stage of ignition or in the case of fully developed fires.

Zhang et al. [8] prepared octadecylammonium montmorillonite/natural rubber/cis-1,4-polybutadiene (OMMT/NR/BR) nanocomposites by direct mechanical blending. The structure of these nanocomposites and the dispersion state of OMMT particles were evaluated by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Muller et al. [9] explained the influence of talc on the rheological, chemical, thermal and mechanical properties of polypropylene (PP)/talc composites during multiple re-extrusions. This mechanism caused an increase of rigidity whose intensity increased with the content of talc, and overcame the loss of rigidity due to the thermo-mechanical degradation of PP. The yield stress was stable for PP/talc 80/20 (20 wt.% talc) but increased for PP/talc 90/10 (10 wt.% talc) with the re-extrusion number.

Varghese et al. [10] provided the layered silicates, sodium bentonite (natural) and sodium fluorohectorite were selected in addition to a non-layered inert filler as reference material. The nanocomposites were prepared by compounding the dispersions of clays and other latex chemicals necessary for vulcanization. Gonzalez et al. [11] prepared of natural rubber (NR)/Na⁺ montmorillonite (MMT) nanocomposites in only one step by using poly(ethylene glycol) (PEG) has been investigated. PEG behaves as dispersing agent favouring the intercalation of rubber chains into the silicate galleries

and providing substantially improved clay dispersion. Intercalated/exfoliated miscible hybrids were observed by X-ray diffraction (XRD). Krishnamurthy et al. [12] prepared epoxy/clay nanocomposites using a diglycidyl ether of bisphenol A (DGEBA) epoxy and its blend with an epoxy functionalized hyperbranched polymer (HBP). The mechanical and dynamic mechanical properties of the nanocomposites were evaluated and compared with the corresponding matrix. Finnigan et al. [13] prepared hydrophilic layered silicate/polyurethane nanocomposites via twin screw extrusion and solvent casting. Evidence for altered polyurethane microphase morphology in the nanocomposites was provided by DMTA and DSC. WAXD results suggested that the appearance of an additional high temperature melting endotherm

Tabsan et al. [14] investigated the abrasion resistance and abrasion behavior of Montmorillonite (MMT) filled natural rubber (NR) vulcanizates. Cure characteristic results indicated that both pristine Montmorillonite (Na^+ -MMT) and organically modified Montmorillonite (OMMT) acted as accelerator for the vulcanization reaction of NR. The abrasion resistance of NR was improved by the addition of either Na^+ -MMT or OMMT. Bhattacharya et al. [15] studied different applications of polymer nanocomposites.

Stephen et al. [16] studied solvent resistance properties of nanostructured layered silicates filled natural rubber (NR). The morphology of filler dispersion in the rubber matrix was analysed from transmission electron micrographs. The extent of intercalation of polymer chain into the layers of silicates was estimated using X-ray diffraction technique. Valadares et al. [17] prepared nanocomposites of natural rubber latex and layered silicates by a mild dispersion shear blending process. X-ray diffraction (XRD) and transmission electron microscopy (TEM) show that clay particles are well dispersed in the dry latex and the platelets have a preferential orientation, forming translucent nanocomposites. Mechanical properties and swelling character are also studied.

The present article deals with the preparation and characterization of composite materials of Natural rubber (NR) with nanotalc. The effect of nanotalc on mechanical, thermal and morphological characteristics of the nanocomposites has been studied. The aim of developing composite materials by reinforcing polymers with suitable fillers is to achieve commercially viable products having unique properties at lower cost.

2. EXPERIMENTAL

Natural Rubber, Dicumyl Peroxide (DCP) used as vulcanizing agent and nanotalc were of commercial grade. The formulations of the mixes used in the present work are given in Table 1. A, B, C and D, and E represent mixes containing NR and nanotalc with dicumyl peroxide as vulcanizing agent. Mix A is the gum sample. B, C, D, and E are mixes containing 0, 2, 6, 8 and 10 phr of talc respectively.

Table 1. Formulation of NR composites

Components (phr)*	Mix				
	A	B	C	D	E
NR	100	100	100	100	100
DCP**	2.5	2.5	2.5	2.5	2.5
Nanotalc	0	2	6	8	10

* phr: parts per hundred rubber

** DCP: Dicumyl Peroxide

The composites were prepared by using a laboratory two roll mixing mill. Initially NR was masticated on the mill for 15 minutes followed by the addition of the ingredients. The nip gap, mill roll speed ratio and the number of passes were kept the same for all the mixes. The samples were milled for sufficient time to disperse the filler in the matrix. The cure characteristics of the mixes were measured by using a Goettfert elastograph rheometer. Vulcanisation of the mixes was done at 150°C using a hydraulic press having electrically heated platens to their respective cure times as obtained from the rheographs. The sheets were kept for 24 hours. Tensile properties of different mixes were examined using an Instron Universal Testing Machine (Model 4411; Instron Ltd. Buckinghamshire, U.K) at crosshead speed of 500mm/ min. The tensile tests were conducted according to the ASTM D 412-06A test procedures using dumb bell – shaped test pieces. The hardness (Shore A) of samples was measured by using Durometer (Modex India Pvt. Mumbai, India) according to ASTM 2240 – 86. Surface morphology of fracture surfaces of tensile bars of filler reinforced NR and Nanotalc composites were imaged using Hitachi SU – 6600 Scanning Electron Microscope.

3. RESULTS AND DISCUSSION

3.1 Cure Time Characterization

Cure time is defined as the time taken for a polymer to fully cure, undergoing a series of chemical reactions which allow it to set, harden and develop traits which will allow it to persist for weeks, months or years. Vulcanization is proportional to number of cross links formed per unit volume. Figure 1 shows the torque [Nm] vs time [min] graph of Talc/NR nanocomposite with variation in filler loading. Table 2 shows the cure characterization of Talc/NR nanocomposite.

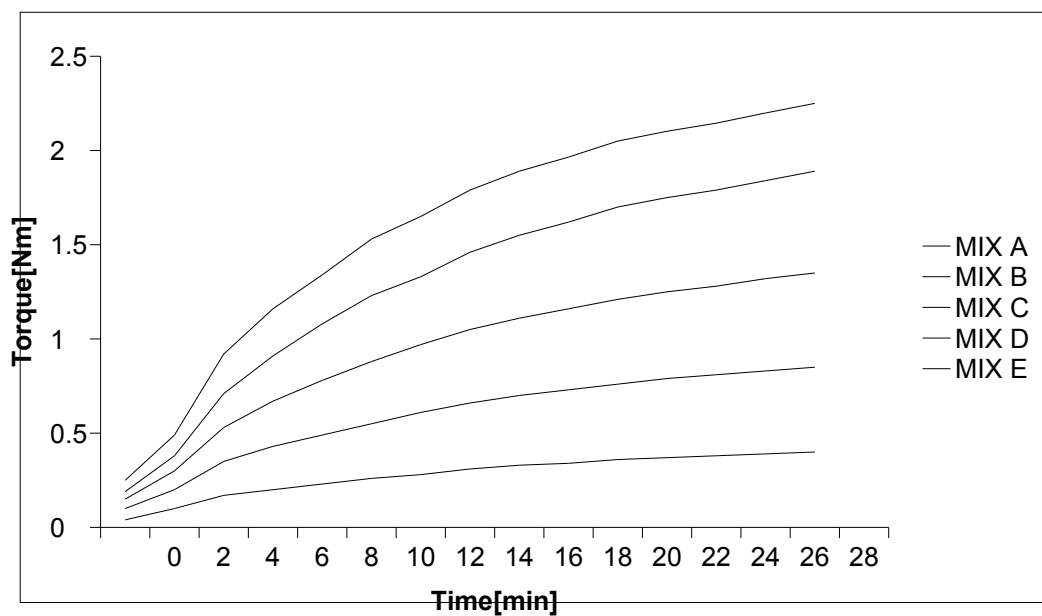


Figure 1 Torque vs time graph of Talc/NR nanocomposite.

Table 2 Cure characterization of Talc/NR nanocomposite

Mixes	Minimum Torque [Nm]	Maximum Torque[Nm]	Curetime [Min]
A	0.04	0.40	22.00
B	0.06	0.46	22.23
C	0.05	0.50	22.22
D	0.04	0.55	22.23
E	0.06	0.36	13.24

3.2 Mechanical Properties

The mechanical properties, ie; tensile strength, tear strength are carried out using UTM at a crosshead speed of 500mm/min by using dumb bell shaped specimen having thickness 2mm. Table 3 shows the mechanical properties of NR/Talc nanocomposite with amount of talc.

Table 3.2 Mechanical properties of Talc/NR nanocomposites

Mechanical properties	Mixes				
	A	B	C	D	E
Tensile strength(MPa)*	1.78	2.07	2.23	2.28	7.91
Tear strength(kN/m)*	17.38	19.42	19.76	20.86	22.50
Hardness	50	51	53	54	68

Tensile test was conducted in accordance with ASTM D 412-06 method. Specimen of dimensions 3mm width and 20mm length were used for analysis. Test was conducted at a constant strain rate of 10mm/min. Force was applied until the failure of the sample and load-elongation curve was obtained. Tensile strength=Ultimate load or load at break/cross sectional area. The variation of tensile strength with loading of nanotalc in natural rubber matrix is shown in figure 2.

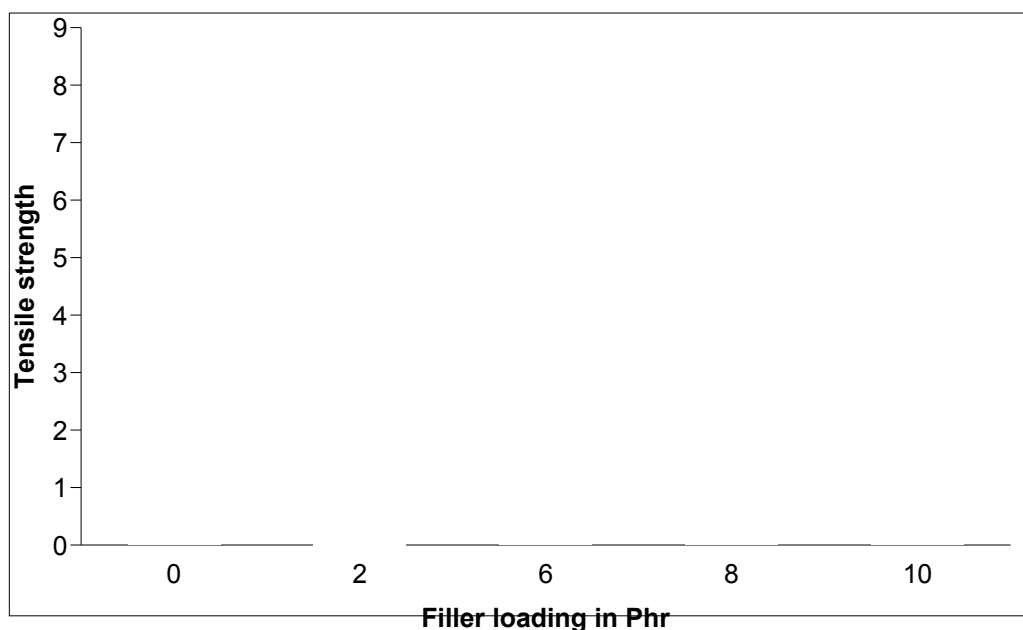


Figure 2 Tensile strength of Talc/NR nanocomposite with variation of filler loading

It can be seen from the figure that as amount of the nanotalc increases the tensile strength increases. Tensile values are increased due to the interaction between NR and nanotalc. Tensile values reach an optimum value at 10phr of talc in the composite. Tear test was conducted in accordance with ASTM D 412-06 method. Specimen of dimensions 3mm width and 20mm length were used for analysis. Test was conducted at a constant strain rate of 10mm/min. Tear strength is the force required to tear a specified test specimen divided by the specimen thickness. It is the amount of force needed to rip a particular sampling subject and to continue through it in a vertical axis. Typically used for testing of plastic film, plastic sheets and other rubber products, tear strength is calculated by force (in Newtons) divided by thickness (in millimeters, centimeters, inches, etc.): $\text{Tear strength} = F/t$. The variation of tear strength with loading of nanotalc in NR matrix is shown in figure 3.

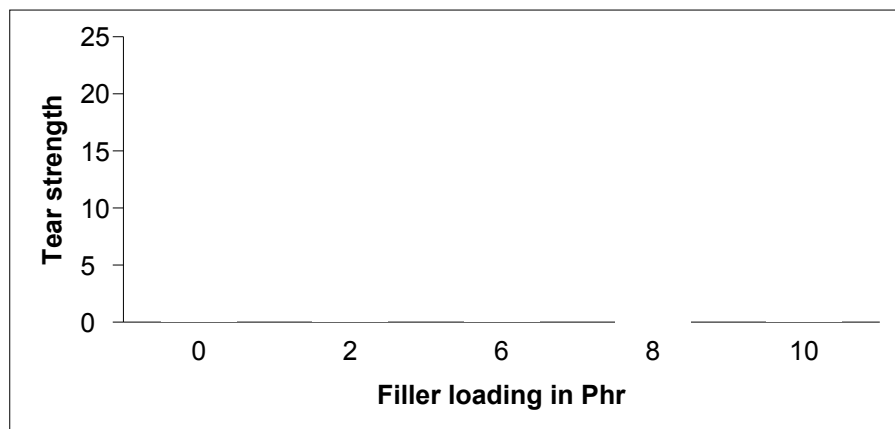


Figure 3 Tear strength of Talc/NR nanocomposite with variation of filler loading

Hardness is defined as the resistance of a material to deformation; particularly permanent deformation, indentation or scratching. Hardness of gum sample is 51. It increases to 68 loading of 10 phr. Variation of hardness with loading filler is shown in figure 4. When filler loading increases, hardness is also increases. It shows that filler phase adhere to matrix phase.

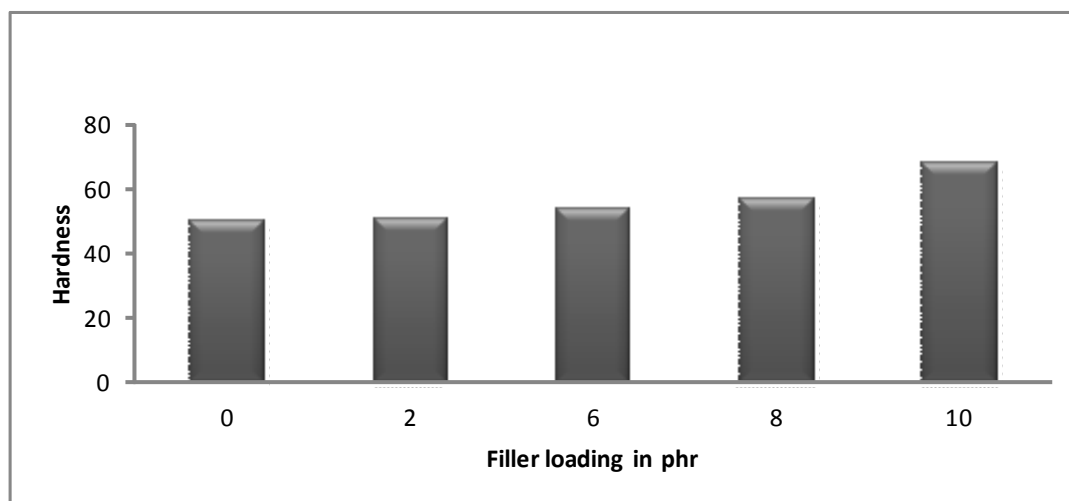


Figure 4 Hardness of Talc/NR nanocomposites with variation of filler loading

3.3 Thermal analysis

Differential scanning calorimetry is a thermo analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. Only a few milligrams of material are required to run the analysis.

Figure 4 shows the DSC curves of gum NR and nanotalc reinforced NR composites having filler loading 2, 8 and 10 phr. The DSC studies indicate that the filler filled systems possess higher glass transition temperatures (T_g) than the gum, which is due to the higher interaction between the filler and the matrix. Glass transition temperature of NR-talc nanocomposites of different composition is given in Table 4.

Table 4: Variation of T_g with filler loading

Filler loading in phr	$T_g(^{\circ}\text{C})$
0	-63.79
2	-65.73
8	-63.61
10	-64.27

T_g value of gum sample from DSC curve is -63.79 °C. T_g value increases drastically by addition of talc. The increment in T_g is due to the stiffness and rigidity provided by the filler. Figure 5 shows the DSC curves of gum NR (mix A) and nanotalc reinforced NR composites having filler loading 2, 8 and 10 phr (mix B, D and E) respectively.

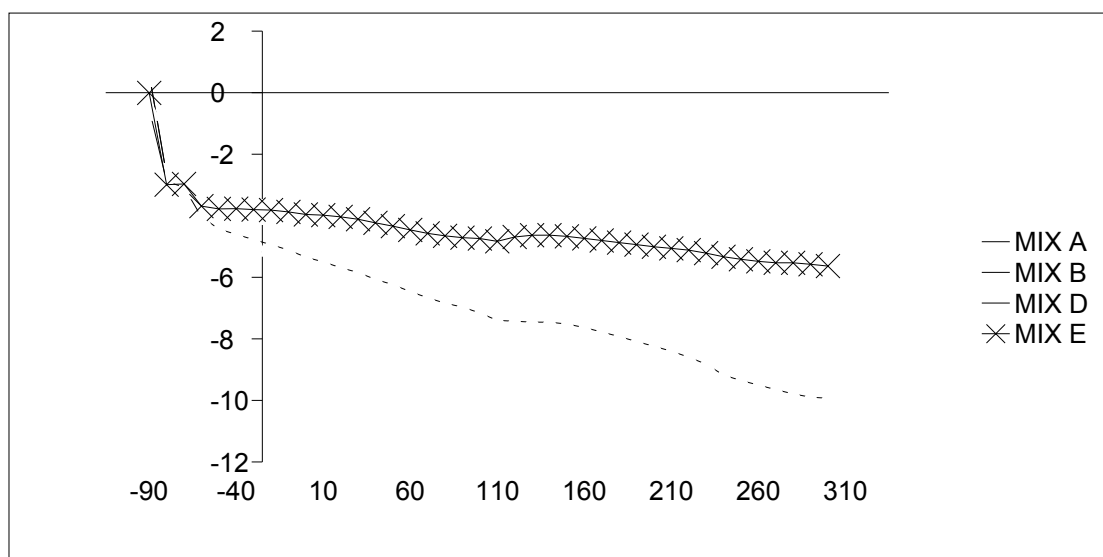


Figure 5 DSC curve of Talc/NR nanocomposite

3.4 Surface morphology

Molecular shape and arrangement of molecules in solid is important as these factors will determine the properties of polymers like crystallinity, branching, molecular weight, crosslinking and polymer structure. Figure 5 (a) and (b) shows the SEM image of gum sample. Figure 6 (a) and (b) shows the nanotalc/NR composite at 10 phr filler loading. The figure shows the particles have globular like structure. The black particles in the photographs represent NR rubber and the particle seen in white are the nanotalc and the

chemical DCP etc. The figure also shows the interaction between the NR matrix and the reinforcing filler nanotalc .

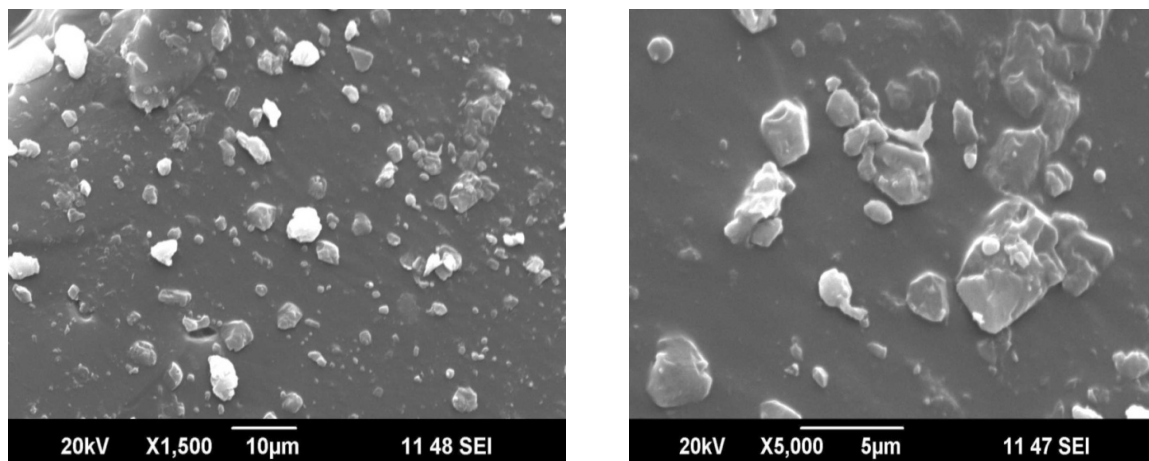


Figure 5(a) The SEM image of gum sample. Figure 5(b): shows the SEM image of gum sample at a higher magnification.

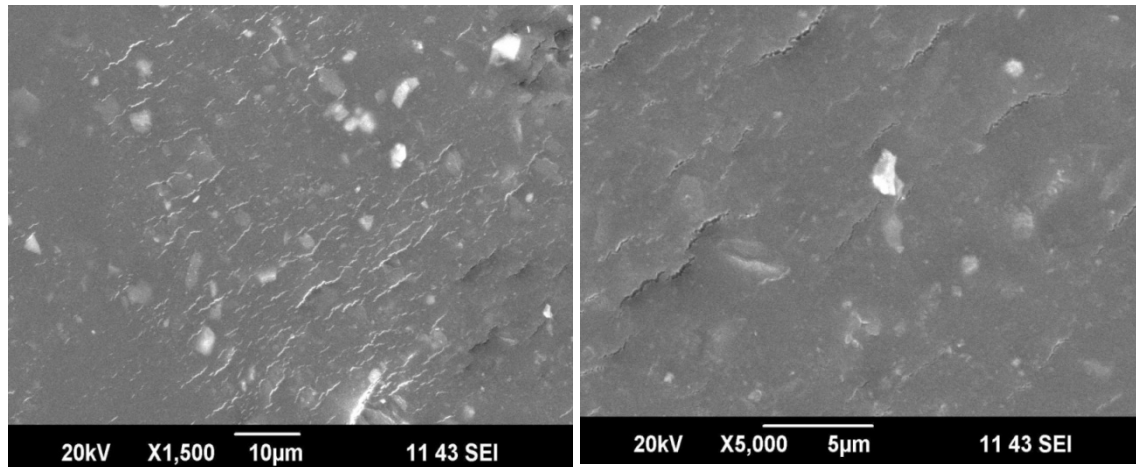


Figure 6(a): The SEM image of 10 phr of filler loading. Figure 6(b): The SEM image of 10 phr of filler loading with a higher magnification.

4. CONCLUSION

The studies showed that with increase in the loading of Nanotalc in NR, tensile strength and tear strength increased progressively up to 10Phr filler loading. The increase in these mechanical properties is due to the increase in interaction between NR matrix and the filler. Hardness also was found to be increased. The thermal properties studied by Differential scanning calorimetry indicated an increase in T_g with increase in filler loading. The SEM result of composites indicated the miscibility of the components of the system. The overall properties of NR/talc starch composite depend upon the different kinds of cross links and rubber-filler interactions.

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Thermal and Mechanical Characterization of Acrylonitrile Butadiene Styrene-Coir Fibre Biocomposites

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ABSTRACT

Biocomposites are materials comprising one or more phases derived from a biological origin. Natural fibers such as wood fibers or non-wood can be made as reinforcements in polymeric matrices to prepare bio composites. Coir is a natural fiber extracted from the husk of coconut and used in products such as floor mats, doormats, brushes, mattresses, etc. Acrylonitrile Butadiene Styrene (ABS) is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. The present article deals with the development of composite materials from acrylonitrile butadiene styrene and coir fibre. The effect of coir fibre on mechanical and thermal properties of resultant composites is studied as function of fibre loading. Mechanical properties of these composites show strong interaction between fiber and ABS even without using any coupling agent.

Keywords: *Composites, ABS, Coir*

1. INTRODUCTION

Composites are combinations of materials differing in composition where the individual constituents retain their separate identities. They are superior to those of the individual component it include and those constituent give mechanical strength and stiffness to the material. Bio composites are materials comprising one or more phases derived from a biological origin. Natural fibers such as wood fibers (hardwood, wood dust and softwood) or non-wood fibers (e.g., wheat, husk, jute, sisal, coir and flax) can be

made as reinforcements in polymeric matrices to prepare bio composites .Coir is the fibrous material found between the hard, internal shell and the outer coat of a coconut. Coir fibers are non abrasive, eco-friendly, biodegradable and insoluble in organic solvents and also have good mechanical properties, low density, hydrophobic behavior and low cost. Coir has more life compared to other natural fibers due to its high lignin content. Coir fiber showed very high interfacial adhesion under dry conditions. Coir fibers are more efficient and superior in reinforcement performance when compared to other reinforcement composites. However, the main limitations of coir fibers are high moisture content. It can be controlled with chemical treatment. These characteristics make coir fibers a suitable material to be used as a high structural reinforcement in polymer composites. Composites reinforced with coir have low density and recyclability and these can be manufactured at low costs. These composites are eco friendly and biodegradable. ABS (Acrylonitrile butadiene styrene) is a terpolymer made by polymerizing styrene and acrylonitrile in the presence of polybutadiene. ABS is amorphous and therefore has no true melting point. Acrylonitrile butadiene styrene materials can be processed by any of the standard thermoplastic processing methods. The most important mechanical properties of ABS are impact resistance and toughness. The present article deals with the development and characterization of biocomposites of ABS with coir fibre.

The main reasons for the increasing popularity of bio composites or natural fiber composites (NFCs) are the availability and consistent quality of a wide range of fibers, and their environmental friendliness. It can be controlled with chemical treatment. A large number of experiments have performed with natural fiber reinforced polymeric composites all over the world.

Nitinat and Kasama [1] examined mechanical properties and flammability of sisal polypropylene composites. The flame retardancy of sisal polypropylene composites can be enhanced by the addition of Magnesium hydroxide and zinc borate without sacrificing their mechanical properties. Threepopnatkul et al. [2] conducted experiments on effect of surface treatment on performance of pineapple leaf fiber- polycarbonate composites. The modified pineapple leaf fibers composite was used to enhance mechanical properties of the composite. Chanakan et al. [3] studied the materials and mechanical properties of pretreated coir based green composites. The pretreatment of the coconut coir plays an important role in the physical, mechanical and thermal properties of the coconut coir green composite.

Ku et al. [4] conducted study on the characteristics of silk fiber reinforced biodegradable plastic. It has been found that flexural modulus of the composites increased with the use of silk fiber reinforcement while their tensile and flexural strengths decreased. Mukherjee and Satyanarayana [5] showed in their investigation of banana fiber with polyester composites without weathering test that the specific modulus of the composites is 2.39 which are of the same order as that of glass fiber plastics. Harish et al [6] investigated the mechanical properties of coir fiber composites. Scanning electron micrographs obtained from fractured surfaces were used for a qualitative evaluation of the interfacial properties of coir/epoxy and compared with glass fiber/epoxy. These results indicate that coir can be used as a potential reinforcing material for making low load bearing thermoplastic composites. Kasama and Nitinat [7] examined effect of glass fiber hybridization on properties of sisal fiber- polypropylene composites. Lima et al. [8] studied the effect of alkali treatment on structure and mechanical properties of ABS/bamboo fiber composites. Bakkal et al. [9] studied the possibility of reinforcement of low density polyethylene composites with cotton fibres and tested the changes in

mechanical properties of the composite upon multiple recycling. Budrun Neher et al [10] investigated the surface morphology and structural characterization of palm fiber reinforced Acrylonitrile Butadiene Styrene(PF-ABS) composites.

2. EXPERIMENTAL

ABS used is SD-150W Injection Moulding grade. Coir fibre was obtained from local source. The compounding ingredients used were of laboratory grade. Table 1 show the formulations of mixes used in the present work. A, B, C, D and E represent mixes containing ABS and coir fiber. Mix A is the virgin sample. B, C, D and E represent mixes. The coir is immersed in 5% KOH and stirred well. It was kept at room temperature for 48 hours. After that it was washed and dried in sunlight. Then it was cut into 3mm length. The correct balance level of time and concentration of the treatment ensures the optimum mechanical properties. The composites were prepared by using an extruder. Initially ABS was masticated on the extruder for 3minutes followed by the addition of the ingredients. The nip gap, extruder speed ratio and the number of passes were kept the same for all the mixes. The samples were extruded for constant time to disperse the fibers in the matrix and injection moulded.

Table 1: Formulation of ABS composites(phr*)

	A	B	C	D	E
Acrylonitrile butadiene styrene(ABS)	100	100	100	100	100
Coir fiber	0	50	100	150	200

*parts per hundred rubber

Measurement of mechanical properties like tensile strength was done by universal testing machine and hardness by durometer. The thermal analysis was done by differential scanning calorimeter and thermo gravimetric analyser. Moisture content analysis was done by systematic analyser.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of ABS-Coir Fiber Composites

The mechanical properties are determined by stretching standard test pieces at a constant rate using a tensile machine. Mechanical properties of ABS-Coir fiber composite is shown in Table 2. The variation of tensile strength with loading of coir fibre is shown in Figure 1.

Table 2 :Mechanical properties of ABS-Coir fiber composite at various fiber loading

Sample	Tensile Strength (Kg/Sq.Cm)	Elongation (%)	Hardness
ABSF0	428.8	23	46
ABSF5	438.6	24	47
ABSF10	442.4	26	51
ABSF15	448.2	29	54
ABSF20	449.8	31	56

It is observed that the tensile modulus increases from 428.8 to 449.8 with the addition of 15 wt % coir fiber filler. This shows that the fiber surrounds the matrix region and the stiffness given by the filler withstands the deformation of the composite hence increase in modulus. This shows that the composite has better strength compared to stretching or pulling of specimen. The strength of the composite is mainly dependent on the bonding between the filler and matrix as well as weakest section of the composite. As the amount of coir fiber increased in the composite, the tensile strength also increases. The reinforcing effect of coir fiber is reflected here. It shows that there is good interaction between coir fiber and ABS matrix. It also indicates that most of the fibers are oriented in longitudinal direction.

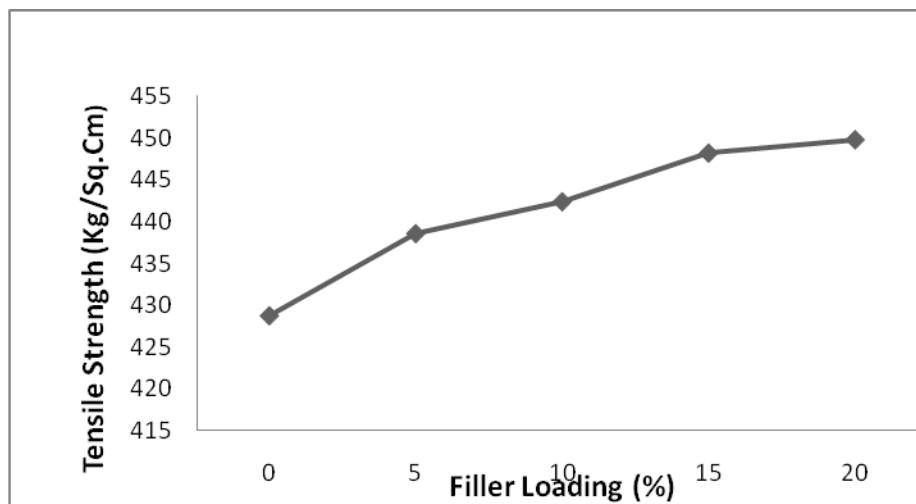


Figure1. Variation of tensile strength with loading of coir fibre

The variation of elongation with loading of coir fibre is shown in Figure 2. From the figure we can understand that, elongation increases with loading of fiber.

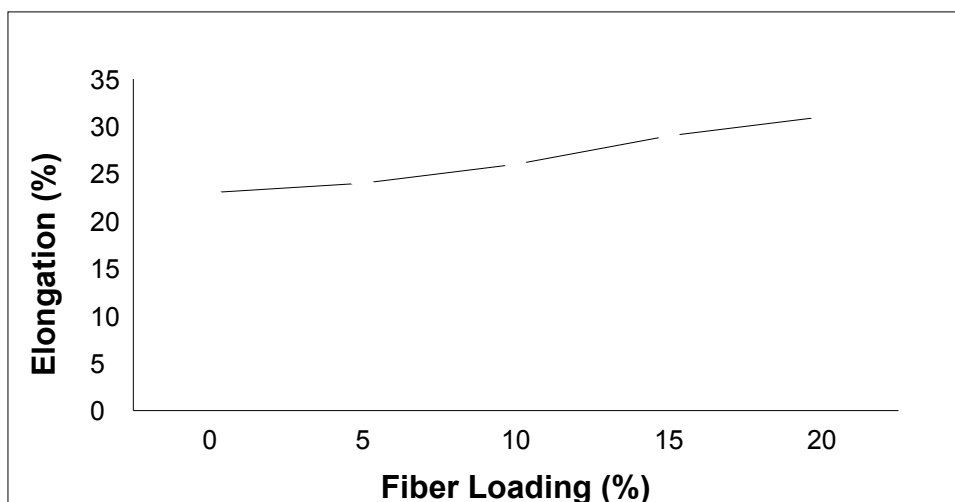


Figure 2. Variation of Elongation (%) with loading of coir fiber

The variation of hardness of the composites with loading of coir fibre is shown in Figure 3. It can be seen that hardness increases with fibre loading. It shows that fiber phase adhere to matrix phase to some degree. The incorporation of surface treated coir fiber increases the modulus of ABS plastics slightly. The slight increase in hardness is

due to the increase in surface roughness of exposed surface treated coir fiber. The increase is small because, coir fiber being hygroscopic and moisture absorption results in the wetting of already hygroscopic ABS surface.

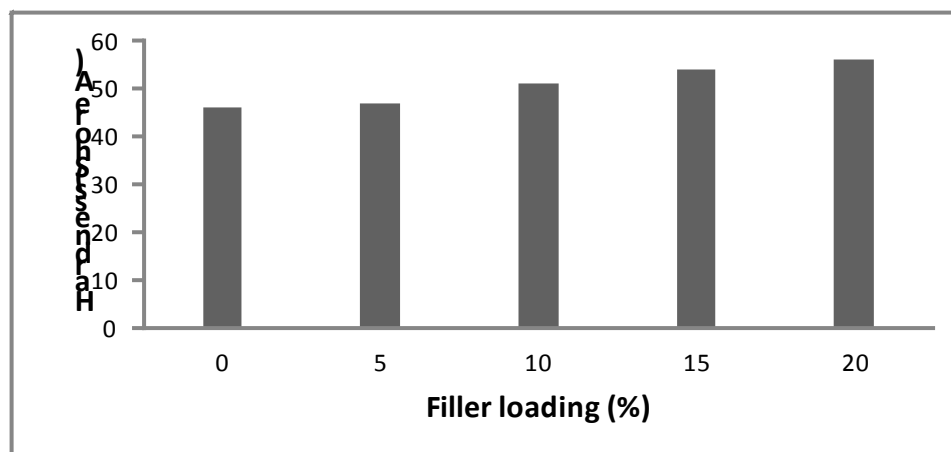


Figure 3. Variation of Hardness with loading of coir fiber

3.2 Thermal Properties

Figure 4 shows the DSC curves of composites having fiber loading of 0, 5, and 20 phr.

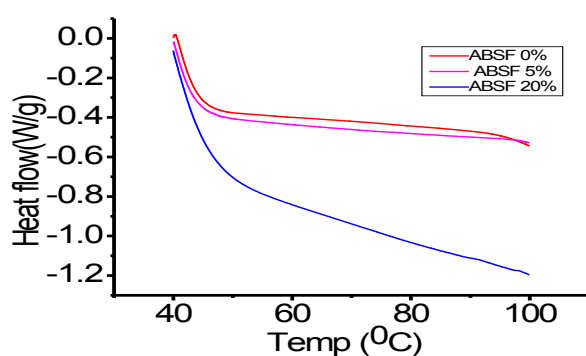


Figure 4. Variation of Tg with loading of coir fiber

Glass transition temperature of coir fiber reinforced ABS composites is found to increase with fiber content. This increase may be due to the reinforcing effect of fibers which may restrict the internal Brownian movements of ABS polymer chains. The coir fiber can act as a nucleation centre which results in the crystallization at slightly higher temperatures. Figure 5 shows the TGA curves of ABS and coir fiber reinforced composites having fiber loading 0 and 20 phr.

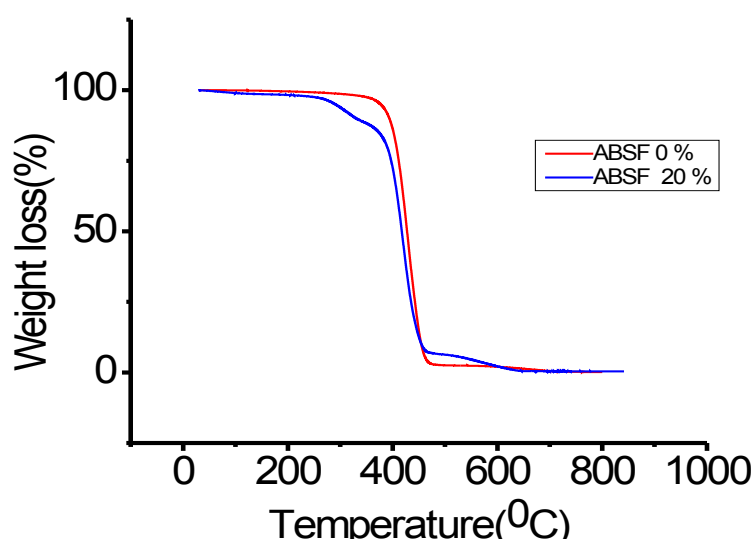


Figure 5. Variation of Weight loss with Temperature

The thermal degradation of ABS varies due to changes in molecular weight, component ratio of acrylonitrile, butadiene and styrene, etc. These factors affect the decomposition of ABS. The degradation of ABS found that the evolution of butadiene commenced at 340°C and styrene at 350°C, while the evolution of acrylonitrile began at 400 °C. The slight weight loss for ABS-Coir 20% is due to moisture expulsion. The first major weight loss is due to the decomposition of hemicelluloses starting at around 300°C. The final weight loss is due to the decomposition of crystalline cellulose present in

coir fiber which is followed by degradation of ABS, which will happen between 340 °C to 450 °C.

Heat deflection temperature is a relative measure of a material's ability to perform for a short time at elevated temperatures while supporting a load. The test measures the effect of temperature on stiffness. It is defined as the temperature at which a standard test bar (5x1/2x1/4 inch) deflects 0.010 inch under a stated load of 66 psi when heated at the rate of 2°C per minute. It is observed that incorporation of coir fiber into ABS matrix increases heat deflection temperature, which is shown in Table 3 and in Figure 6. The increase in the HDT is due to the reinforcing effect of surface treated coir fiber with ABS matrix.

Table 3 : Variation of HDT with fiber loading

Sample	HDT (°C)
ABSF0	84.7
ABSF5	86.2
ABSF10	91.3
ABSF15	98.8
ABSF20	102.2

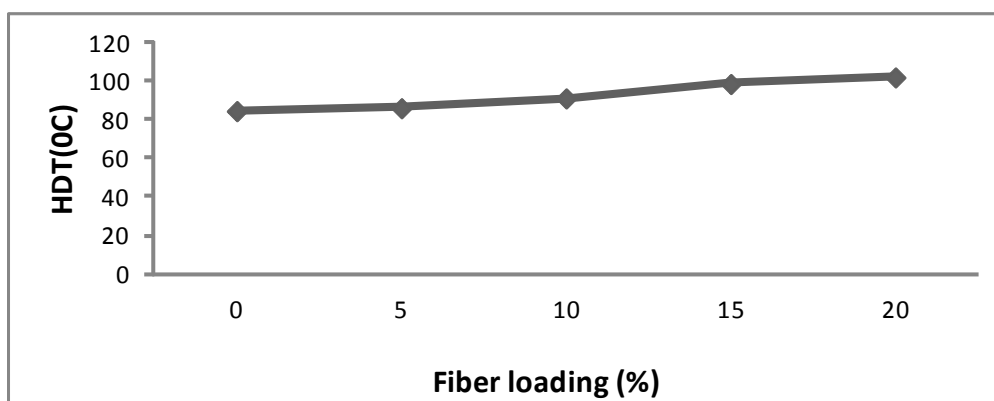


Figure 6. Variation of HDT(°C) with loading of coir fiber

4.3 Moisture Content Analysis

The moisture content analysis was performed using Mettler Toledo HE 53 moisture analyser. The result shows that percentage of moisture content increases with increasing filler loading which is shown in Table 4 and in Figure 7.

Table 4: Moisture Content of ABS-Coir fiber composite at various fiber loading

SYSTEM	% MOISTURE CONTENT
ABSF0	0
ABSF5	0.26
ABSF10	0.37
ABSF15	0.57
ABSF20	0.98

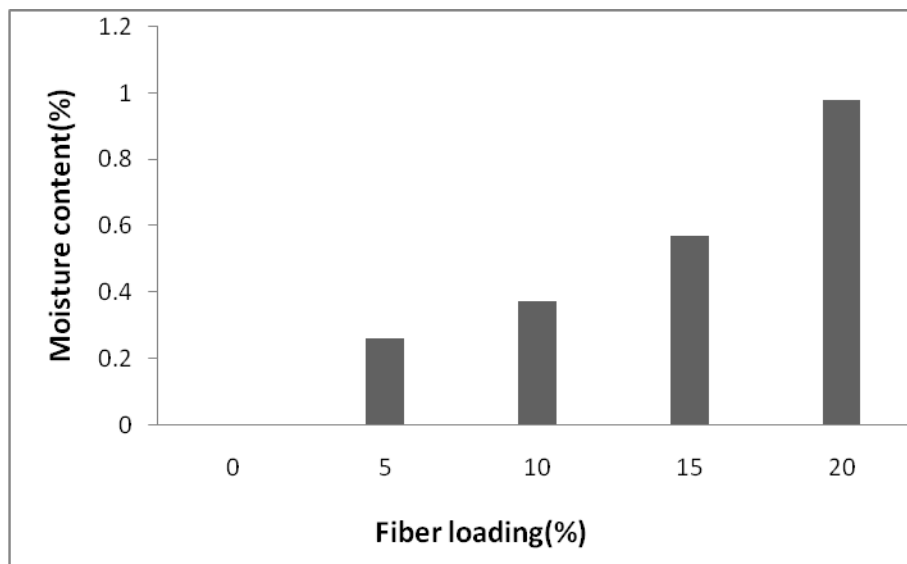


Figure 7. Variation of moisture content with loading of coir fiber

4. CONCLUTIONS

ABS has ability to be injection moulded and extruded which makes it useful in manufacturing products such as musical instruments. Composite materials are prepared in which ABS is reinforced with coir fiber. From the study of coir fiber composite, it is found that coir fiber can act as a reinforcing agent in ABS. Relatively small percentage of coir fiber results in an increase in tensile strength, hardness and increase in elongation. Differential scanning calorimetric studies show that incorporation of coir fiber increases the T_g of composite material.

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Biomedical Application of Ethylene Vinyl Acetate-Graphite Composites

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ABSTRACT

Ethylene vinyl acetate copolymer (EVA) is a polar copolymer used for application requiring flexibility, toughness, stress-cracking resistance and adhesion to coatings, co-extruded film and laminates. The present article deals with the development of composite material from EVA and synthetic graphite for biomedical application. Mechanical and electrical properties of composite are studied and the hemolytic activity of composite against human erythrocytes was analyzed. The graphite powder can act as a reinforcing agent in EVA. Mechanical properties of these composites show strong interaction between EVA and graphite powder. The electrical properties such as dielectric strength and conductivity of composite increased with incorporation of graphite in EVA. Study of haemolytic activity against human erythrocytes in EVA/graphite polymer composites showed inhibition of human erythrocytes.

Keywords: EVA, graphite, composites

1. INTRODUCTION

Within a short span of time, polymeric materials have witnessed considerable growth in the field of material science. Versatility of polymers is such that they have replaced natural substances like wood, cotton, metal etc. Polymer materials are equipped with better physical and mechanical properties than many of their natural counterparts and thus play a key role in the field of high technology. Polymer alone could not provide enough

strength for structural applications. Reinforcement is needed to provide strength and rigidity. Filler is needed to provide strength, thermo-mechanical properties and reduce cost. Polymer matrix composites are very popular due to their low cost and simple fabrication method. Polyethylenes are the largest volume family of commercially important thermoplastic polymers. They have variations in the molecular structure due to branches and polar functional groups (polar copolymers). Polar copolymers usually exhibit lower crystallinity and yield strength. They are used for application requiring flexibility, toughness, stress-cracking resistance and adhesion to coatings, co-extruded film and laminates. One such a polyethylene copolymer contains vinyl acetate and is known as ethylene vinyl acetate copolymer (EVA). They are randomly structured polymers which offer excellent ozone resistance, weather resistance and excellent mechanical properties. EVA is one of the most widely used polymers for cable insulations. It is also frequently used as a long lasting life plasticizer to improve the mechanical and processing properties of PVC. EVA is abundantly available as a plastic, thermoplastic elastomer, and rubber depending on the vinyl acetate content in it.

Graphite is a natural form of carbon characterized by its hexagonal crystalline structure. Graphite has unique physical and chemical properties, which facilitate its use in the high-tech industrial sector. Graphite can provide innovative solutions to long-standing industrial problems. The present article deals with the development of composite material from EVA and synthetic graphite for biomedical application.

For the past few decades, several researchers are investigating with the characterization and application of many composite materials. Ethylene vinyl acetate (EVA) reinforced with graphite has a long and successful history of innovation in medical packaging, medical devices, and pharmaceutical applications etc. Pang and Weng[1] investigated the preparation of expandable graphite composite under the auxiliary intercalation of Zinc sulfate and its flame retardancy for ethylene/vinyl acetate

copolymer. Longchao et al. [2] studied the flammability characteristics and synergistic effect of hydrotalcite with microencapsulated red phosphorus in halogen-free flame retardant EVA composite. The results obtained by comparing the flame retardancy of hydrotalcite with magnesium hydroxide (MH) and aluminium hydroxide (AH) for their EVA composites showed that hydrotalcite has higher flame retardant effect than MH and AH at the same loading level. Thaher et al. [3] introduced a novel graphene-based chemiresistor gas sensor for nitrobenzene vapor detection. A molecularly imprinted polymer (MIP) containing the cavities compatible with nitrobenzene molecules was synthesized using methacrylic acid and vinyl benzene as the functional monomers. The imprinted polymeric particles were mixed with graphene to produce a nanocomposite chemiresistor gas sensor. Feng et al. [4] investigated the flame retardancy and thermal degradation of EVA composite with efficient charring agent. Xianru et al. [5] studied on orientation in EVA/Fe₃O₄ composite hot-melt adhesives. The result of peel test indicated that peel strength of composite adhesive increased as Fe₃O₄ content increased when particle size was 3.665 µm but the tackiness of composite adhesive decreased as Fe₃O₄ content increased when particle size was 0.426 µm. Mehdi et al. [6] studied the effect of processing method on the properties of multifunctional exfoliated graphite nanoplatelets/polyamide 12 composites. Dikobe and Luyt [7] observed that wood fibre (WF) influenced the melting temperatures and crystallization behaviour of EVA in EVA/WF composites. The EVA part of the composite crystallized fairly normal, even though the crystals were not as perfect as expected. Luyt et al. [8] studied EVA-sisal fibre reinforced composites, and found that Young's modulus increased remarkably with an increase in the sisal fibre content.

Shao-xin et al. [9] prepared oriented graphite/polymer composite sheets using natural, crystalline flake graphites as raw materials, polyvinylbutyral as binders, polyethylene glycol and dibutyl phthalate as plasticizers by a tape-casting method at room

temperature. Sengupta et al. [10] studied the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites.

2. EXPERIMENTAL

The raw materials are used in these studies were EVA-460 (DuPont™ Elvax® 150), Graphite (Graphite India private limited B) and Phosphate buffer saline solution. Table 1 show the formulations of mixes used in the present work. The composites were prepared by using a laboratory solution casting and melt mixing.

Table 1: Formulation of mixes

Samples Code	Amount of EVA (g)	Percentage of Graphite
EVA/G0%	1	0
EVA/G1%	1	1
EVA/G5%	1	5
EVA/G10%	1	10

The hardness of the samples was measured as per ASTM D2240 standards using a shore A type durometer (Modex India Pvt. Mumbai, India) having a pressure foot, and indenter and a scale reading from 0 to 100. In vitro haemolytic activity was performed by spectrophotometer method. A volume of 0.5 ml of the cell suspension was mixed with 0.5 ml of the sample. The mixtures were incubated for 30 min at 37°C. Then it is centrifuged at 1500 rpm for 10 min. The free haemoglobin in the supernatant was measured in UV-Visible spectrophotometer at 540 nm. Phosphate buffer saline and distilled water were used as minimal and maximal haemolytic controls. Each experiment was performed in triplicates at each concentration. The level of percentage haemolysis by the sample, calculated according to the following formula:

$$\% \text{ of haemolysis} = \frac{A_t - A_n}{A_c - A_n} \times 100$$

Here A_t is the absorbance of sample, A_n is the absorbance of the control (saline control), A_c is the absorbance of the control (water control). In figure 3.3 shows that image of haemolytic activity against human erythrocytes. The electrical properties like dielectric constant, conductivity and resistivity was measured by using impedance analyser.

3. RESULTS AND DISCUSSION

3.1 Mechanical properties of EVA-Graphite composites

Variation of hardness with loading graphite is shown in Table 2 and Figure 1.

Table 2: Variation of hardness with graphite loading

Loading of graphite (%)	Hardness (Shore A)
0	14.44
1	16.36
5	20.82
10	22.86

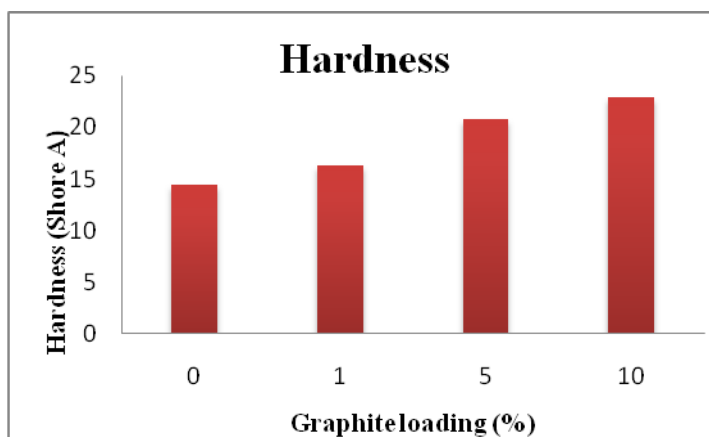


Figure 1: Variation of hardness with graphite loading

As the graphite loading increases hardness increases. It shows that reinforcement phase (graphite) adhere to matrix phase to some degree. Optimum hardness detected at 10% loading. The incorporation of graphite powder improves the hardness of composites drastically. It gives an idea of variation in mechanical properties. As the graphite phase increases in composite the modulus and mechanical properties also increases.

3.2 Effect of cyto toxicity in EVA-Graphite composite

The haemolytic activity of the EVA/graphite composite against normal human erythrocytes was studied. Haemolytic activity of the composite is expressed in percentage hemolysis. Table 3 shows the variation of percentage hemolysis with graphite loading. All the samples exhibited haemolytic effect towards human erythrocytes. However, as the loading of graphite increases, the composites showed dose dependent increase in haemolytic activity as shown in Figure 2. Maximum haemolytic activity is shown in composite contains 500 μ g of graphite.

Table 3: Haemolytic activity of EVA- graphite composite against human erythrocytes, at different graphite loadings.

Graphite loading (μ g/ml)	% of Hemolysis
100	63.75
200	70
300	71.8
400	73
500	78

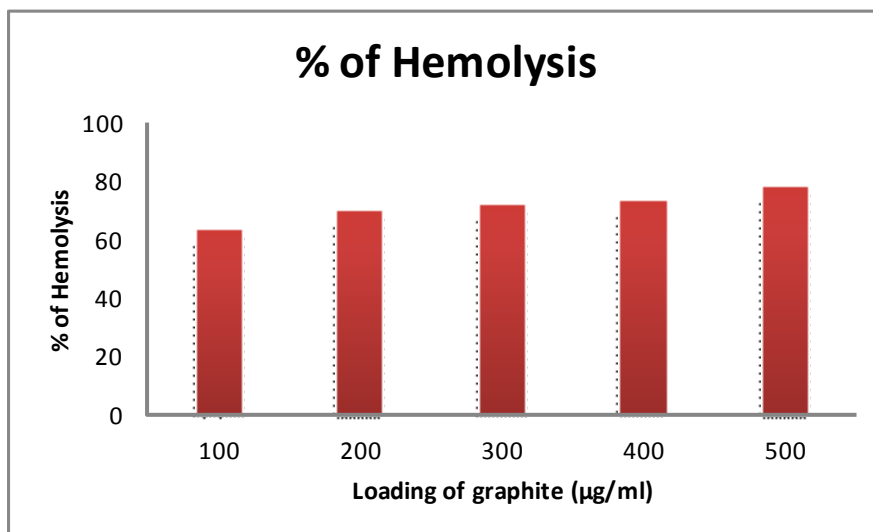


Figure 2: Haemolytic activity of EVA- graphite composite against human erythrocytes. Figure 3 (a) shows the microscopic picture of red blood cells before hemolysis and figure 3(b) shows that after hemolysis of erythrocytes. From the figure we can see the inhibition of platelet aggregation in human blood. It can be seen that haemolytic activity of human erythrocytes can be measured in composites containing even in 100 μg of graphite.

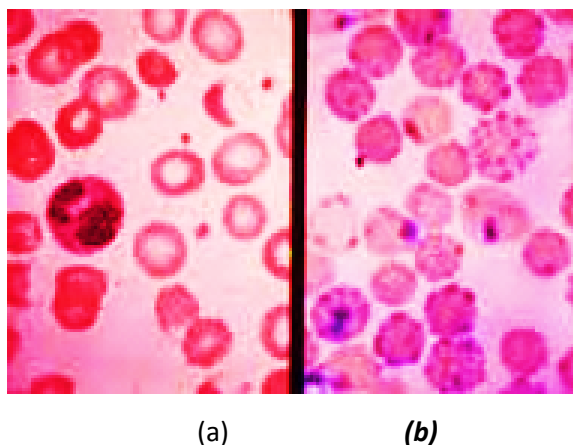


Figure 3 (a) Microscopic picture of human erythrocytes before hemolysis and **(b)** after hemolysis of erythrocytes.

3.3. Electrical Properties

The composites with 5 and 10 percentage of graphite are used for the study of dielectric properties. The instrument HIOKI-3532.50LCR Hi tester model was used and the temperature range was from ambient to 600°C. The recorded data was used to calculate the dielectric constant (ϵ_r) at various temperatures 35, 45, 55, 65, 75, 85 and 95°C for the range of frequency from 50 to 5×10^6 Hz.

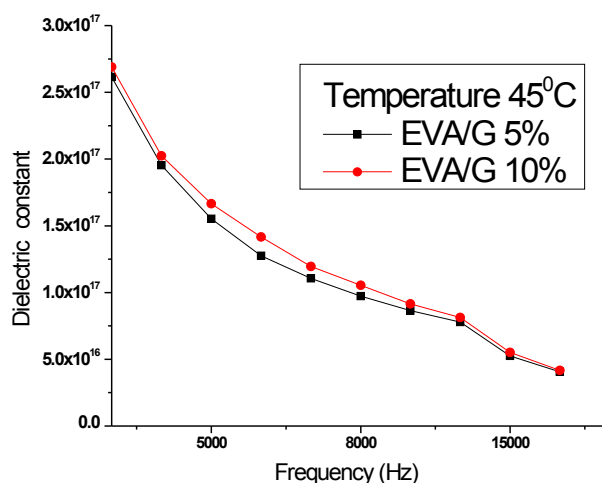


Figure 4: Variation of dielectric constant with frequency for different samples at constant temperature.

Figure 4 shows the variation of dielectric constant of different samples with frequency at constant temperature of 45°C. It can be seen that as the frequency increases dielectric constant decreases. It can also be seen as the graphite loading increases the dielectric constant increases considerably. Sample EVA/G10 has better dielectric constant. Temperature has significant effect in dielectric properties. Figure 5 shows the variation of dielectric constant with frequency at different temperature in sample EVA/Graphite 10 % (EVA/G10). When temperature increases the dielectric constant decreases.

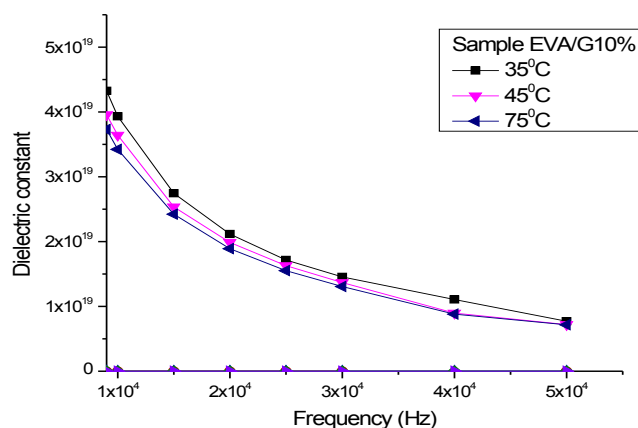


Figure 5: Variation dielectric constant with frequency at different temperature in sample EVA/G10%.

Figure 6 shows the variation of resistivity of different samples with frequency at constant temperature 45°C, it can be seen that as the frequency increases resistivity decreases. It can also be seen as the loading of graphite increases the resistivity decreases.

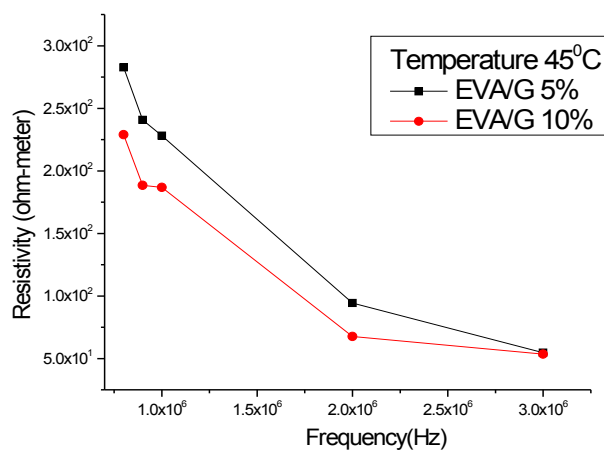


Figure 6: Effect of resistivity with frequency, different samples at constant temperature.

Temperature has significant effect in resistivity. Figure 7 shows the variation of resistivity with frequency at different temperature in sample EVA/Graphite 10 % (EVA/G10). When temperature increases the resistivity decreases.

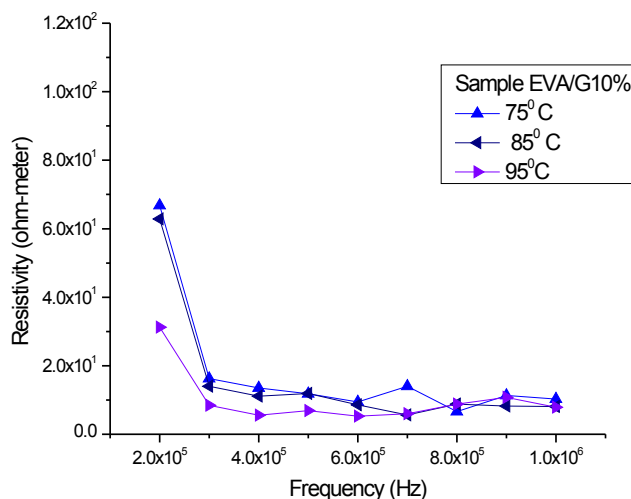


Figure 7: Variation resistivity with frequency at different temperature in sample EVA/G10%.

Figure 8 shows the variation of conductivity of different samples with frequency at constant temperature 45°C. It can be seen that as the frequency increases conductivity increases. It can also be seen that as loading of graphite increases the conductivity increases. And hence EVA/graphite composite can be used as a good conducting polymer composite, maximum conductivity shown in sample containing 10% graphite (EVA/G10%).

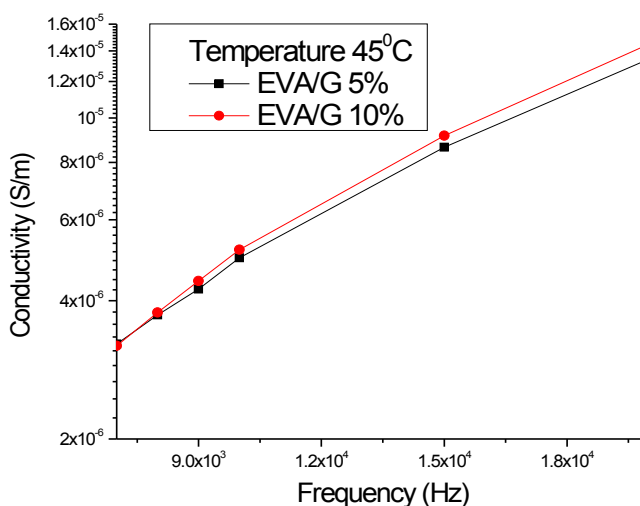


Figure 8: Variation of conductivity with frequency, different samples at constant temperature.

Temperature has significant effect in conductivity of composites. Figure 9 shows that variation of conductivity with frequency at different temperature in sample EVA/graphite 10% (EVA/G10%). When temperature increases the conductivity increases.

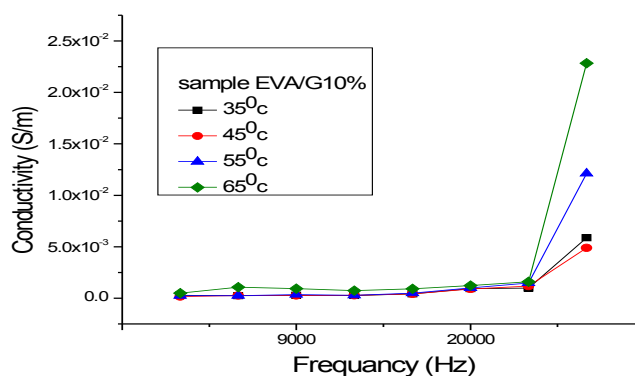


Figure 9: Variation of conductivity with frequency different temperature in sample EVA/G10%.

3.4. Surface Morphology

Figure 10 (a) , (b), (c) and (d) represents optical micrograph of composite containing 0, 1,5 and 10% graphite respectively, the micrograph shown in scale bar 200 μ m.

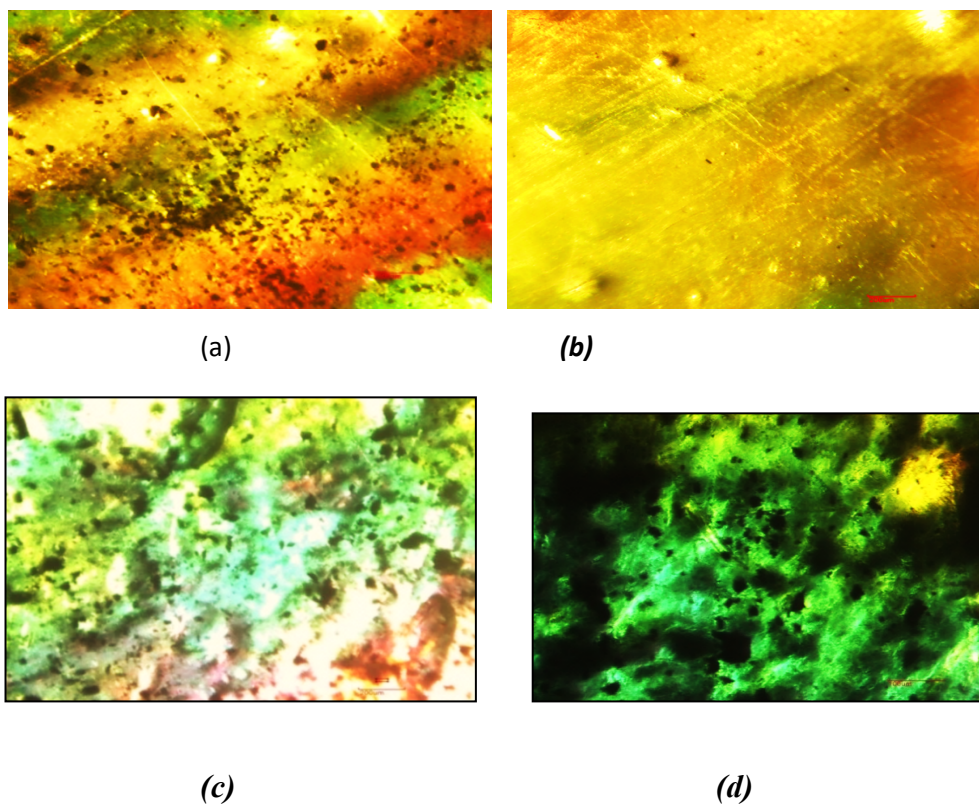


Figure 10: Optical micrograph of EVA/Graphite composite.

4 CONCLUSION

Ethylene vinyl acetate (EVA) is a commonly used copolymer, which offers excellent ozone resistance, weather resistance and mechanical properties. EVA is one of the most widely used polymers for cable insulators and used in many applications including, but not limited to, flexible packaging, thermal-lamination film, hot-melt adhesive, concentrates and photovoltaic cells. Graphite powder can act as a reinforcing

agent in EVA. Mechanical properties of these composites show strong interaction between EVA and graphite powder. The electrical properties such as dielectric strength and conductivity of composite increased with incorporation of graphite in EVA. Study of haemolytic activity against human erythrocytes in EVA/graphite polymer composites showed inhibition of human erythrocytes.

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Synthesis and Characterisation of Hyper Branched Polyesters Based on Trimesic Acid

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ABSTRACT

Hyper branched polyesters (HBPE) are an important class of hyper branched polymers and are extensively studied because of their excellent thermal stability, chemical resistance and mechanical properties. The high functionality combined with low solution viscosity of HBPs led to the application of this material in the development of coating with antimicrobial properties and in nano metal synthesis. The objectives are the synthesis and characterization of HBPE by using a different preparative approach with different monomer system. The present article deals the synthesis of two hyperbranched polyesters based on trimesic acid, by polycondensation polymerization reaction of trimesic acid with triethanol amine and trimesic acid with ethylene glycol. The products HBPEs are characterized using FTIR and ¹H NMR for detailed study of its highly branched structure and composition.

Keywords: *Hyperbranched, polyester, trimesic acid*

1. INTRODUCTION

In polymers, branched polymers have at least one point where a second chain of monomers branches off from the first chain. There are many commercial polymers that are lightly branched. A number of more highly branched polymer architectures also exist. Commonly two general methodologies have been developed for preparing highly branched polymers, single monomer methodology and double monomer methodology. A

broad range of HBPs are prepared by these methods [1-10]. They have unique chemical and physical properties and hence can be used for various applications such as coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science etc.

‘Hyper branched polyesters’ are an important class of hyper branched polymers and they are extensively studied because of their excellent thermal stability, chemical resistance and mechanical properties. These are mainly used for coating application. Hyper branched polyester can be synthesized from easily available and inexpensive raw materials and have impelled many research groups to investigate them in detail. Zhirong Fan et al [11] investigated the synthesis and characterization of $A_2 + B_3$ -type hyperbranched aromatic polyesters with phenolic end groups. Regina Reul et al [12] designed for gene therapy of chronic diseases; HBP-DEAPA 60 is non-toxic biodegradable amine modified hyper branched polyester. Hui Miao et al [13] made fluorinated modification of hyperbranched polyesters used for improving the surface property of UV curing coatings. Peng Liu et al [14] synthesized the hyperbranched aliphatic polyester grafted attapulgite via a melt polycondensation process. Chun-Lei Bao et al [15] Synthesized and described the properties of waterborne hyperbranched aliphatic polyester clear coats. Zhang et al [16] studied about the synthesis, characterization and mechanical properties of polyester-based aliphatic polyurethane elastomers containing hyperbranched polyester segments. Zhao et al [17] investigated the Synthesis and characterization of ZnS/hyperbranched polyester nanocomposite and its optical properties. Flores et al [18] gives the novel epoxy-anhydride thermosets modified with hyperbranched polyester as toughness enhancer.

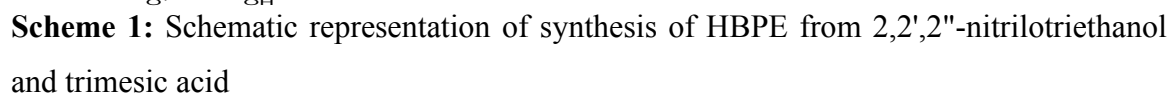
2. EXPERIMENTAL

Triethanolamine (2, 2', 2''- nitrilotriethanol >99%), trimesic acid (1,3,5-tribenzoic acid), ethylene glycol used for the present work were purchased from Sigma Aldrich, India. Dimethyl sulfoxide (DMSO), NMR grade (d_6 - DMSO) and KBr from SD Fine chemicals were reagent grade and used as received. P-Toluene sulfonic acid (p-TSA, >99%) used as catalyst for the reaction was supplied by Rankam Chemicals. HBPE was synthesized by polycondensation of core and chain extender using *p*-TSA as catalyst. The monomers were reacted in a 250 mL four necked flask equipped with N_2 inlet, drying tube and magnetic stirrer. FTIR analyses of samples were carried out using JASCO 400 Infrared spectrometer. Samples were mixed with KBr (sample/KBr ratio, 1/99) to prepare pellets. FTIR spectra were recorded in a spectral range of 450-4000 cm^{-1} with resolution of 2 cm^{-1} , taking four scans for each sample. 1H NMR of samples were recorded on Bruker (400 MHz) NMR spectrometer. For recording 1H NMR spectra, samples were dissolved in deuterated dimethylsulfoxide (DMSO- d_6) and tetramethylsilane (TMS) was used as an internal standard.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of Hyper Branched Polyester (HBPE) based on Trimesic Acid

It is well established that coupling reactions of A_3 monomers in presence of a B_n core molecule can result in significant changes in the properties of the resultant materials. The synthesis was done as a common acid catalysed esterification reaction, with continuous removal of water in order to achieve high molar mass of the final product. Therefore, the synthesis was done as pseudo-one-step procedure. In order to prevent unwanted side reactions (etherification and trans-esterification), a low reaction



temperature was chosen. The obtained HBPE had high solubility in common solvents and relatively low polydispersity.

3.2. Synthesis and Characterisation of HBPE from Trimesic acid and 2,2',2''-Nitrilotriethanol (Triethanol Amine)

HBPE was synthesized by polycondensation. The monomers used were trimesic acid and 2, 2', 2''- nitrilotriethanol (triethanol amine). *P-TSA* was used as acid catalyst. This type of HBPE was prepared by taking 1.33mL (1mol) of 2,2',2''-nitrilotriethanol with 2.10g (1mol) of trimesic acid and with 0.05g p-TSA in a three necked round bottom flask equipped with nitrogen inlet and a drying tube. The flask was placed in a hot oil bath and maintained at 130°C. The mixture was stirred using magnetic stirrer for 3 hour under nitrogen atmosphere. The resulting polyesters were obtained as a brown coloured product. The schematic representation of the reaction is given in the schematic representation scheme 1

The FTIR spectra of monomer and HBPE are given in Figure 1. The FTIR spectrum of 2,2',2''- nitrilotriethanol (triethanol amine) revealed broad absorption band at 3350 cm^{-1} due to the presence of the hydroxy group, the band at 1040 cm^{-1} is assigned to C-N stretching and the band near 2881 cm^{-1} is due to the presence of methylene group. The FTIR spectrum of trimesic acid shows an absorptions band of 3390 cm^{-1} , which is attributed to the absorptions from COOH (carboxylic) group and a band at 1750 cm^{-1} is due to the aromatic C-C bond. The FTIR spectra of HBPE show a sharp band at 1728 cm^{-1} which could be attributed to the absorptions from ester group which indicates the reaction has proceeded. The band at 1097 cm^{-1} is assigned to C-N stretching. The broad band near 3141 cm^{-1} is due to OH group.

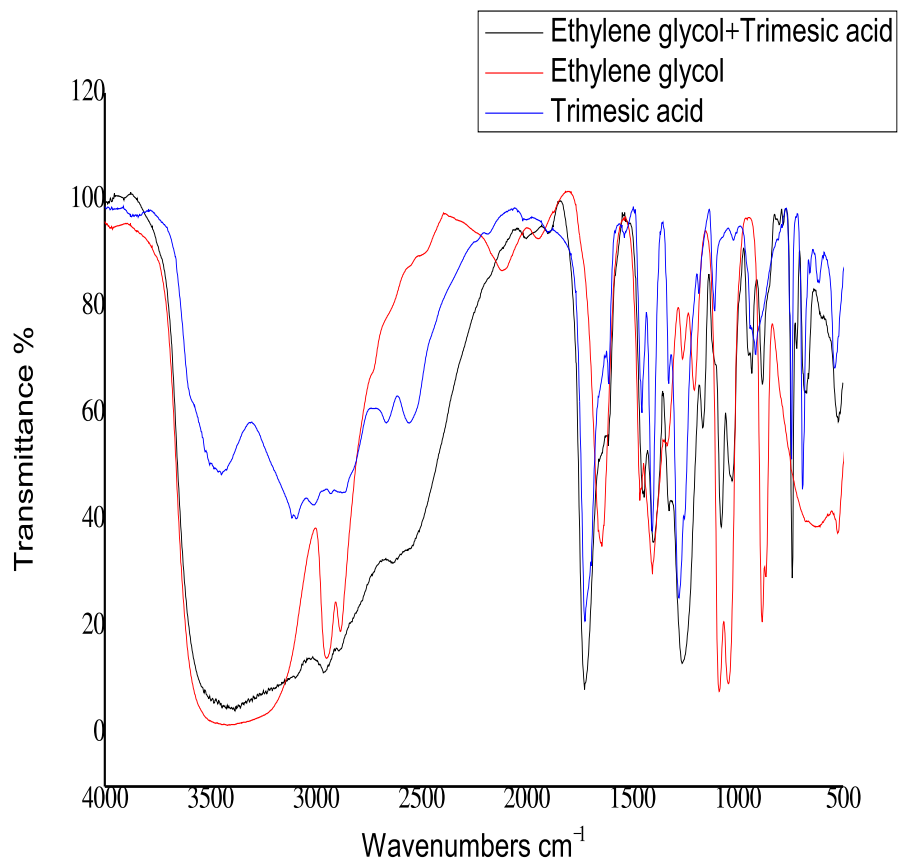


Figure 1: FTIR spectra of monomers and HBPE

^1H NMR data confirmed the chemical composition of the compounds. The ^1H NMR spectra of HBPE is shown in Figure 2. ^1H NMR (400 MHz, DMSO d_6 , δ (ppm): 2.2-3.4 (methylene proton, - CH_2 -); 4-5 ppm (OH proton); 3.2-4 ppm (CH_2OCO). 8-8.8 ppm (Aromatic group)

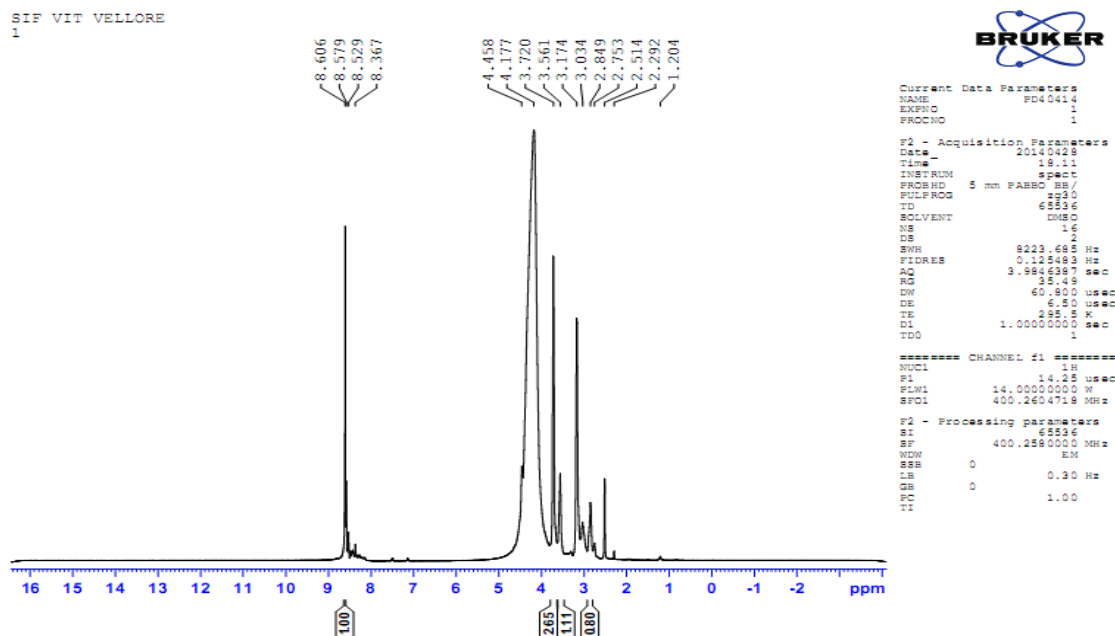
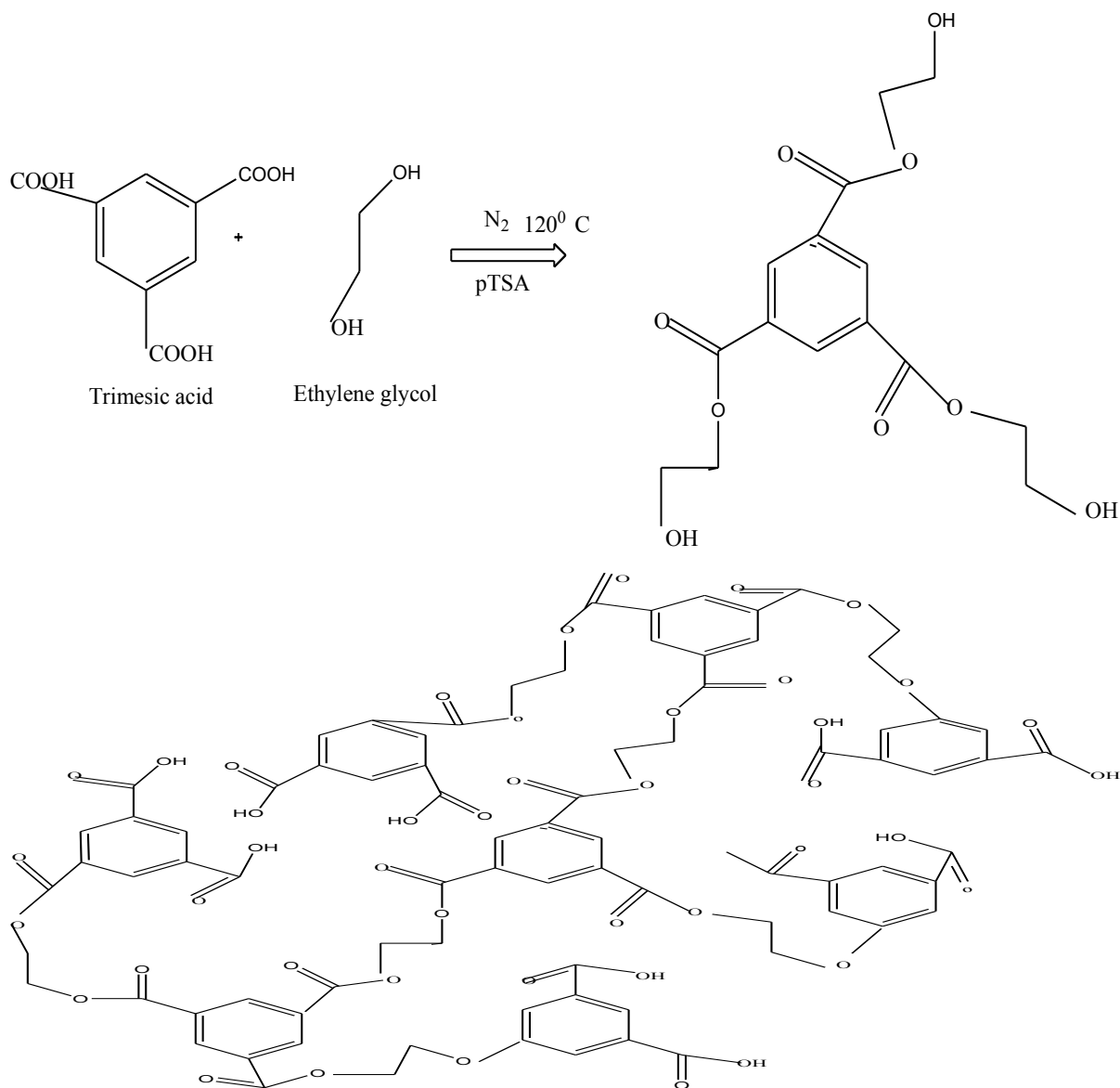


Figure 2: ¹H NMR spectra of HBPE

3.3. Synthesis and characterisation of HBPE from Trimesic acid and Ethylene Glycol

Reaction of trimesic acid monomers in presence of an ethylene glycol is also a coupling reaction of A₃ monomers in presence of a B_n core molecule. This also leads to significant changes in the properties of the resultant materials. It was synthesized by polycondensation method. Here trimesic acid and ethylene glycol were used as monomers with p-TSA as catalyst. Trimesic acid (4.2g, 2mol) and ethylene glycol (1.112ml, 2 mol) and p-TSA (0.05g) were mixed in a 500mL three necked round bottom flask equipped with nitrogen inlet and drying tube. The flask was placed in an oil bath. The reaction was refluxed out at 120°C for 3 hours with stirring on a magnetic stirrer under nitrogen atmosphere. The schematic representation of the reaction is given in Scheme 2.



Scheme 2: Schematic representation of synthesis of HBPE from ethylene glycol and trimesic acid

The FTIR spectra of monomer and HBPE are given in Figure 3. The FTIR spectrum of trimesic acid shows an absorptions band of 3390 cm^{-1} , which is attributed to the

absorptions from COOH (carboxylic) group and a band at 1750 cm^{-1} is due to the aromatic C-C bond. The FTIR spectrum of ethylene glycol shows a broad absorption band at 3500 cm^{-1} due to hydroxyl group and a peak at 2700 cm^{-1} is due to the presence of methylene group. The FTIR spectra of HBPE show a sharp band at 1733 cm^{-1} which could be attributed to the absorptions from ester group which indicates the reaction has proceeded. The band near 3413 cm^{-1} is due to the presence of OH group. Band at 1053 cm^{-1} is assigned to C=C benzene group.

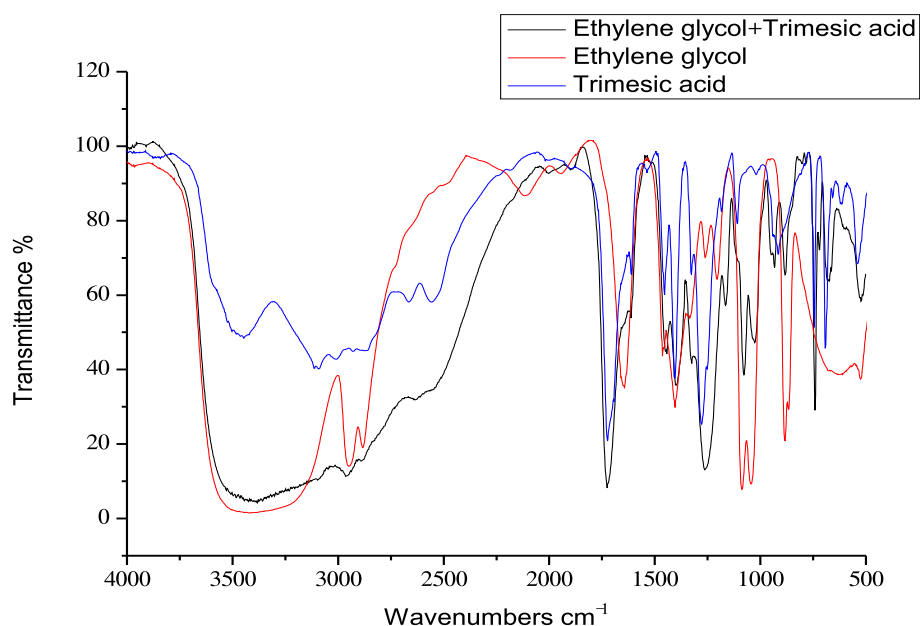


Figure 3: FTIR spectra of monomers and HBPE

4. CONCLUSION

The FTIR studies of HBPE synthesized from trimesic acid and triethanol amine shows a broad absorption band for -OH indicated the presence of large numbers of free hydroxyl groups on the surface of these hyper branched polyesters and a sharp band at 1728 cm^{-1} which could be attributed to the absorptions from ester group which indicates the reaction has proceeded. ^1H NMR data confirmed the chemical composition of the compounds and hence it is also helpful for the structural analysis. The NMR studies of product shows a peak at 3.2-4 ppm which indicate the presence of ester group and it conform the formation of the desired product. It also give the peak for OH proton, methylene proton and proton in aromatic group, which indicate the presence of OH on periphery of HBPE and sustain of aromatic structure in product. Similarly, the FTIR studies of HBPE from trimesic acid and ethylene glycol shows a sharp band at 1733 cm^{-1} which could be attributed to the absorptions from ester group which indicates the reaction has preceded. The band near 3413 cm^{-1} is due to the presence of OH group indicate OH end groups of HBPE. These all confirm the formation of new product of highly branched structure with good coating application and application in nano metal synthesis.

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Development and Characterization of Chitosan incorporated polypropylene composites

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ABSTRACT

The effect of chitosan on the mechanical and thermal properties of polypropylene composites is studied as a function of fiber loadings. The applicability of these materials in packaging field also investigated. It is found that the mechanical properties of these composites are somewhat lower than those of their synthetic counterparts because of the hydrophilic properties of chitosan. Thermogravimetric analysis showed that the addition of chitosan improved the thermal stability of the PP/chitosan composites as compared to that of neat PP. Compared to PP polymer, composite exhibits lower heat flow. The incorporation of chitosan not significantly changed the T_m of the composite.

Keywords: Polypropylene, chitosan, composites

1. INTRODUCTION

Biocomposites are composite materials comprising one or more phase(s) derived from a biological origin. In terms of the reinforcement, this could include plant fibres, regenerated cellulose fibres, etc. Matrices may be polymers, ideally derived from renewable resources such as vegetable oils or starches [1]. Polymer alone could not provide enough strength for structural applications. Reinforcement is needed to provide strength and rigidity. The main reasons for the increasing popularity of bio composites are the availability and consistent quality of a wide range of fibers, and their environmental friendliness. Moreover, new production processes, such as injected molded components, make it possible to use these materials for industrial products.

Abilash et al [2] studied the environmental benefits of eco friendly natural fiber reinforced polymeric composite materials. Faruk et al. [3] reviewed biocomposite reinforced with natural fibers. Chandramohan et al [4] examined the natural fiber reinforced polymer composites for automobile accessories. Singha et al [5] investigated the mechanical properties of natural fibre reinforced polymer composites. Sapuan et al [6] made an experimental study on the material selection for natural fiber reinforced polymer composite using analytical hierarchy process. They are used 29 types of natural fiber composites and proved that kenaf 66%+PP is most suitable material. Sergio et al [7] reviewed thermo gravimetric behavior of natural fibers reinforced polymer composites. TG analysis and the related derivative, DTG, for different polymer composites reinforced with the most common and relevant lignocellulosic fibers are studied. Ramesh et al [8] examined the processing and mechanical property evaluation of banana fiber reinforced polymer composites. Arrakhiza et al [9] studied the mechanical and thermal properties of natural fiber reinforced polymer composites doum-low density polyethylene. The Doum-fibers were compounded in LDPE matrix at various contents and extruded as continuous strands. The mechanical properties of composites were found to be enhanced.

Polypropylene (PP) is a typical commodity plastic and has been widely used in many application fields including packaging films, industrial components and miscellaneous goods, due to its excellence in properties such as stiffness, heat resistance and processability in addition to lightweight material density and also a relatively low price. Polypropylene (PP) has the physical characteristics of a low specific gravity, rigidity, heat resistance and superior workability. Chitosan is a natural carbohydrate biopolymer derived by deacetylation of chitin, a major component of the shells of crustacea such as crab, shrimp, and crawfish. Chitosan is a biodegradable, biocompatible, positively charged polymer. These characteristics make chitosan as a suitable material to be used as a high structural reinforcement in polymer composites. The advantages of composites' are

that they are biodegradable and do not leave residues or result in by-products that are toxic when combusted.

The present article deals with the development of composite materials from polypropylene and chitosan. The effect of chitosan on the mechanical and thermal properties of the resultant composites is studied as a function of filler loadings. The applicability of these materials in packaging field also investigated.

2. EXPERIMENTAL

Table 1 shows the formulations of mixes used in the present work. A, B, C, D and E represent mixes containing polypropylene and chitosan. Mix A is the gum sample. B, C, D and E represent mixes containing 5%, 10%, 15%, and 20%, of chitosan respectively. The composites were prepared by using a extruder.

Table 1: Formulation of PP composites

	A	B	C	D	E
Polypropylene(PP)	1000g	1000g	1000g	1000g	1000g
Chitosan	0g	75g	100g	150g	200g

Tensile properties of different mixes were examined using an Instron Universal Testing Machine at crosshead speed of 500mm/min. The tensile tests were conducted according to the ASTM D 412-06 A test procedures using dumbbell- shaped test pieces. The elongation at break of dumb bells are measured in the INSTRON 4411 using a contact extensometer ISO 5893 specific grade D for type 1 dumb bell. Thermal analysis of the composites were carried out using differential scanning calorimeter(DSC) and thermo gravimetric analyser(TGA).

The heat deflection temperatures (HDT) of the samples were measured by ASTM D648 method using HDT/VSP apparatus. The moisture content analysis was performed using Mettler Toledo HE 53moisture analyser.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of PP-Chitosan Composite

Table 2 shows the mechanical properties of PP-Chitosan composites. It is seen that with increase in filler content in composite mechanical properties decreases. This is due to the non reinforcing nature of chitosan microparticles. Uneven distribution of hydrophilic chitosan particles in hydrophobic matrix also responsible for this reduction.

Table 1 .Mechanical properties of PP-Chitosan composites

Sample	Tensile Strength (Kg/Cm ²)	Elongation (mm)
PPC0	322.75	9.6
PPC5	321.359	7.9
PPC10	288.748	7.7
PPC15	263.78	7.3
PPC20	259.526	6.1

From the table it can be seen that the tensile strength of composites decreased with increasing filler loading because of the poor interfacial bonding between the hydrophilic filler and the hydrophobic matrix polymer. Increase in the filler loading significantly reduced the elongation at break of composites. This observation might be due to the stiffening effect of chitosan and decreased deformability of a rigid interface between chitosan and the PP matrix.

3.2 Moisture content analysis

Table 3 shows the percentage moisture content of the composite. The moisture content of composite increases with increasing filler content.

Table 3: Percentage moisture content of the composite

SYSTEM	% moisture content
PPC0	0
PPC5	0.14
PPC10	0.24
PPC15	0.28
PPC20	0.33

3.3 Thermal Properties

Table 4. shows the heat deflection temperature of the composites.

Table 4: Heat deflection temperature of composite

Sample	HDT (°C)
PPC0	82
PPC5	89
PPC10	94
PPC15	99
PPC20	102

From the table it can be seen that the HDT increases with filler loading. Increase in heat deflection temperature of PP with chitosan is due to the slight variation in modulus. It explains the direct correlation of modulus temperature behaviour. Compared to PP polymer, composite exhibits lower heat flow which might be due to the decreasing of

crystallinity with addition of chitosan. The melting temperature (T_m) and glass transition temperature (T_g) obtained from the DSC studies are summarized in Table 5.

Table 5: T_m and T_g of composites

Sample	T_g ($^{\circ}\text{C}$)	T_m ($^{\circ}\text{C}$)
PPC0	-16	163
PPC5	-15	165
PPC10	-15	164
PPC15	-12	163
PPC20	-12	163

From this table it can be seen that the incorporation of chitosan not significantly changed the T_m compared to PP polymer. The glass transition temperatures (T_g) of the composites increases in the presence of chitosan, a result which signifies that the filler hindered the migration and diffusion of PP molecular chains to the surface of the nucleus in the composites. Thermo gravimetric studies indicates that degradation occurred in two steps. The first range (50–200 $^{\circ}\text{C}$) was associated with the loss of water, and the second range (200–450 $^{\circ}\text{C}$) corresponds to the degradation and deacetylation of chitosan. There was another degradation range (450–600 $^{\circ}\text{C}$), which may be assigned to the degradation of the carbonaceous residue formed during the second step. It also can be seen that PP might undergo a one-step degradation process from 400 to 450 $^{\circ}\text{C}$. This result confirmed that PP has carbon–carbon bonds in the main chain that allow a temperature increase to promote random scission with associated thermal degradation and thermal depolymerization occurring at the weak sites of the chain. The onset temperatures of thermal decomposition and decomposition temperature (T_d) of the composites are shown in Table 6. It can be seen that the composites have better thermal degradation resistance than the neat PP.

Table 6: Thermogravimetric analysis of PP/chitosan composites.

Sample	First decomposition onset Temperature (°C)	Degradation Temperature (°C)
Chitosan	432.62	431
PPC0	434.5	433
PPC5	430.5	435
PPC10	431.42	436
PPC15	432.2	438
PPC20	433.5	436

. The results reveal that 15% loading has highest decomposition temperatures due to the better filler dispersion in the polymer. Above 15% loading result in the poor dispersion of filler and decomposition temperature (Td) decreased.

3. CONCLUSIONS

In the present work, composite materials are prepared in which PP is reinforced with chitosan. From the study of composites, it is found that the mechanical properties of these composites are somewhat lower than those of their synthetic counterparts because of the hydrophilic properties of chitosan. Poor interfacial bonding between the chitosan and the hydrophobic matrix polymer reduces the mechanical properties of the composites. Thermogravimetric analysis showed that the addition of chitosan improved the thermal stability of the PP/chitosan composites as compared to that of neat PP. This is indicated of reinforcement by chitosan in polymer matrix. Compared to PP polymer, composite exhibits lower heat flow which might be due to the decreasing of crystallinity with addition of chitosan. Moisture content of the composite increased with increasing filler content.

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Fabrication of Wood-Plastic Composite by Utilizing Plastic Waste and Saw Dust

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ABSTRACT

Consumption of plastic products has increased dramatically over the past few decades. This trend result in the generation of a vast waste stream that needs to be properly managed to avoid environmental damage. This study designed to transform plastic waste into fabrication of value added products like particle boards. Polyethylene-Saw dust (PE-SD) composites are prepared by melt blending and compression moulding techniques from Recycled Polyethylene (PE) and saw dust (SD). The mechanical properties and contact angle analysis of PE-SD composites were investigated. The results showed that the addition of SD increased the tensile strength, elastic modulus of the PE-SD composites, and strain at break was decreased as per SD concentration. Contact angle measurements revealed that presence of SD increased the hydrophilic nature of the composites by reduced its contact angle. Plastic waste can be reduced though the fabrication of value added product such as Wood-Plastic Composite (WPC) from the sawdust and recycled Polyethylene.

Key words: *Recycling of plastic, Plastic Pollution, Wood-Plastic composites, Saw dust-PE Composite*

1. INTRODUCTION

As a result of the increase in the consumption of plastics, the wastes generated from their production, transportation and consumption create various environmental problems. The problem of waste plastic management can be solved if economic, political, technological, energetic, material and environmental dimensions are all considered [1]. Since plastics are generally high calorific value products ranging approximately from 18000 to 38000 kcal/kg, utilization for their energy alone or for related chemical production may be an alternative option [2]. Some polymers such as; polystyrene and poly (methyl methacrylate) undergo to produce monomers and other mono-aromatics besides other hydrocarbons [3, 4]. However, polyethylene and polypropylene having 0 and 2% monomer yield should not be used for monomer production processes. These kind of polymers undergo pyrolysis process to produce valuable hydrocarbons [5]. Recycling processes for waste plastics are classified into two categories: mechanical and feedstock recycling. The former covers a range of physical methods aimed at converting the polymeric residue into plastic pellets or directly into secondary plastic materials [6, 7].

The use of conventional wood-based panels, such as particleboard and medium density fibreboard (MDF), is quite limited for exterior and moist applications, due to the strong tendency of such materials to absorb water. By contrast, wood plastic composites (WPCs) show a considerably reduced affinity towards water, compared to conventional wood based panels, what is caused by their relatively high thermoplastic content. WPCs represent a growing class of materials used by the residential construction industry and the furniture industry. Further expansion into the residential construction industry and development of applications for the furniture industry require an understanding of the fire resistance of flat-pressed WPCs. Wood is typically impregnated with solutions of FRs, commonly salts, such as mono ammonium phosphate (MAP) and diammonium phosphate (DAP), ammonium sulfate, zinc chloride, sodium tetraborate, boric acid, and guanylurea

phosphate [8-11]. Polyolefin (LDPE, HDPE, PP) are a major type of thermoplastic used throughout the world in such applications as bags, toys, containers, pipes (LDPE), housewares, industrial wrappings and film, gas pipes (HDPE), film, battery cases, automotive parts, electrical components (PP). Addition polymers (like polyethylene) in contrast to condensation polymers (i.e. poly (ethylene terephthalate) (PET)) cannot be easily recycled by simple chemical methods [12, 13]. Disposing of waste plastics in to the landfill is becoming undesirable due to legislation pressures (waste to landfill must be reduced by 35% over the period from 1995 to 2020), rising costs and the poor biodegradability of commonly used polymers. The approaches that have been proposed for recycling of waste polymers include [14, 15], *Primary recycling* referring to the “in-plant” recycling of the scrap material of controlled history. *Mechanical recycling*, where the polymer is separated from its associated contaminants and it is reprocessed by melt extrusion. *Chemical recycling* leading in total depolymerisation to the monomers, or partial degradation to other secondary valuable materials. The recycling of model and waste products based on LDPE, HDPE and PP was examined using two different methods: the traditional method of dissolution/re-precipitation and the more challenging technique of pyrolysis. The first belongs to the mechanical recycling techniques while the second to the chemical/feedstock recycling. During the first technique, the polymer can be separated and recycled using a solvent/non-solvent system. For this purpose, different solvents/non-solvents were examined at different weight percent amounts and temperatures using either model polymers as raw material or commercial waste products (packaging film, bags, pipes, food-retail products). This technique has been widely used by Papaspyrides *et al.* [16-18] and other researchers [19].

Saw dust, a waste from wood processing industries, also creates environmental hazard unless reprocessed for different applications like particle board, pulp. The recycled PET and saw dust can be used to produce wood plastics by flat-press method which might a

good value added products from waste and would help to minimize the waste. This technology possesses some advantages like higher productivity with relatively lower pressure requirement and as a consequence naturally given wood structure lefts undestroyed. Thus, the density of WPCs reduces considerably and increase the moisture resistance properties compared to the conventional wood based composites.

This study investigated the technical evaluation of fabrication of wood plastic composite by utilising plastic waste and saw dust from different mixing ratios of saw dust (SD) with waste polyethylene (PE).

2. EXPERIMENTAL

2.1 Materials

Sawdust was obtained from the local saw mills in Kerala, India. Sawdust was screened to remove the impurities. It was then dried in an oven at $103 \pm 2^\circ\text{C}$ for 24 hours for a moisture content of 2%. Clean consumer PE products wastes were collected locally and grind in a grinder for getting the recycled PE powder. The PE powder was sieved by 60 mesh size sieve to remove the oversized particles. The PE powder was then dried in an oven at $103 \pm 2^\circ\text{C}$ for 24 hours for a moisture content of 3% or less. Sodium Hydroxide pellets were of analytical grade obtained from Nice Chemicals, India.

2.2 Pre- treatment of saw dust (NaOH treatment)

The saw dust is first subjected to mild chemical delignification process using 5% of NaOH solution using an autoclave at 125°C for 1 hour. Pressure was released suddenly and the process is repeated 3 times. Then washed well with water and then dried in an oven at $103 \pm 2^\circ\text{C}$ for 24 hours for removing the moisture content

2.3 Preparation of saw dust – PE composite

Composite of PE and SD at various composition were prepared by the melt mixing techniques. The melt mixing of PE and SD in different formulation is performed in Brabender twin –screw computer (GmbH & Co.KG, Duisberg, Germany) at temperature of 160 °C for 9 minutes at a screw speed of 90 rpm. The different composition is used for the PE and SD blends are 100-0, 90-10, 80-20, and 70-30. PE-SD composite panels were manufactured using these extruded pellets by compression moulding process. The samples were compression moulded at 160°C for 3 minutes, in a specially designed mould, so that the mould with the sample inside could be cooled and keeping the sample under pressure.

2.4 Characterization techniques

2.4.1 Mechanical Analysis

The static tensile properties (i.e. modulus, strength and toughness) of PE-SD composites were measured at room temperature (25°C) and atmospheric conditions (relative humidity of $50 \pm 5\%$) using Tinos Olsen Universal Testing Machine (Model #5985) equipped with a 10kN load cell. The tests were carried at a crosshead speed of 10 mm per min. Five identical specimens were tested for each formulation.

2.4.2 Contact Angle Measurements

Contact angle measurements of the PE-SD composites were conducted in a SEO Phoenix-10 by using double distilled water. Measurements were carried out on samples of dimension $2 \times 2 \times 0.2 \text{ cm}^3$ at room temperature. The volume of the sessile drop was maintained as 5 μl in all cases using a micro syringe. For accuracy, measurements were repeated 5 times on different pieces of the same sample. Along with contact angle, work of adhesion, wetting energy and surface energy were calculated.

Work of Adhesion is the work required to separate the solid and liquid phases, or the negative free energy associated with the adhesion of solid and liquid phases. Used to express the strength of the interaction between the two phases. It is given by the Young-Dupree equation as:

$$WA = (1 + \cos\theta) \gamma_L \dots\dots\dots (1)$$

Where γ_L is the surface tension of the liquid used for the contact angle measurement.

The Interfacial Free Energy :(γ_{sl}) can be calculated using the Duper's equation given below,

$$\gamma_{sl} = \gamma_s + \gamma_L - WA \dots\dots\dots (2)$$

Where γ_s is the total solid surface free energy. Spreading coefficient (Sc) is a measurement of the ability of one liquid to spontaneously spread across another. The work done in spreading one liquid over a unit area of another.

$$Sc = \gamma_s - \gamma_{sl} - \gamma_L \dots\dots\dots (3)$$

3. RESULT AND DISCUSSION

3.1 Mechanical analysis

All mechanical testing results are summarized in Table 1. The tensile strength and elastic modulus of PE- SD composites increased with SD content upto 20% and it decline its properties at 30% SD content (Figure 1 and 2). The tensile strength increased from 11.8 to 15 MPa with 20 wt% of SD. This variation might be due to the interaction between the NaOH treated sawdust and PE. Elongation-at-break shows a decreasing nature as the increase in SD content (Figure 3). The difference in polarity and molecular weight, decrease the interaction between the SD and PE and leads to formation SD aggregates in the composites. As the load is applied to the composite, the lack of

interfacial adhesion between the PE and SD will limit the load transfer process. These aggregates can lead to failure at lower stresses and modulus. Also may be due to the formation of cavities in the composite, due to the weak interactions.

Table 1. Mechanical testing results of PE-SD composites

Sample Name	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
100 PE	11.81	11.85	661
90 PE 10 SD	12.94	15.1	760
80 PE 20 SD	14.99	12.98	853
70PE 30 SD	12.84	10.41	757

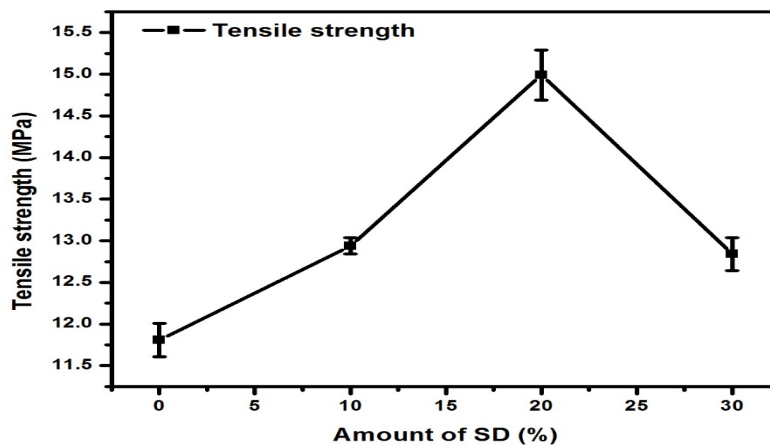


Figure 1: Tensile strength of PE-SD composites

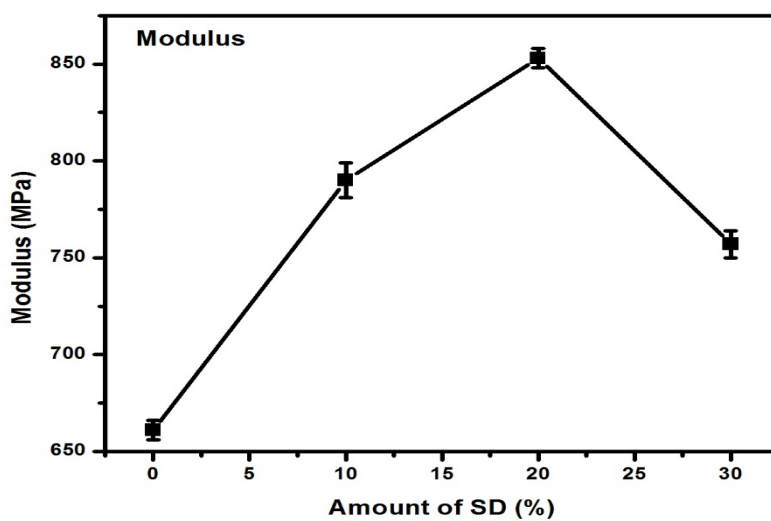


Figure 2: Tensile modulus of PE and PE-SD composites

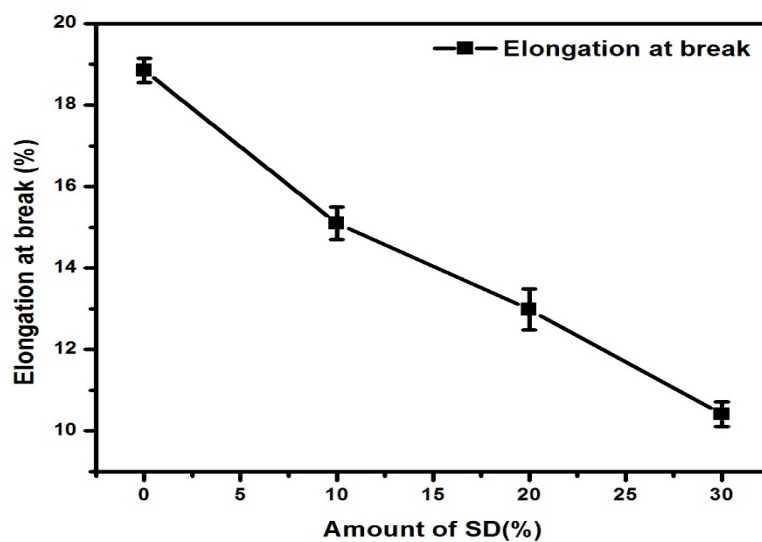


Figure 3: Elongation at break of PE-TSD and PE-ASD composites

3.2. Contact angle analysis

The wetting behaviour of the composite with respect to water is analysed, which focuses on the effect of the filler concentration on wetting characteristics such as work of adhesion, total surface free energy, interfacial free energy, spreading coefficient. PE shows a wetting behaviour by the addition of TSD and the decrease in contact angle value is in perfect correlation with increase in filler concentration. The hydrophilic nature of the composite is found to increase with the addition of SD. Figure 4 presents the representative figures of contact angle measurements of PE and PE- SD composite with water. The increase in hydrophilicity is very well understood from the images. All parameters of contact angle studies are summarized in Table 2. The nature of solvents affects the contact angle measurements. PE-SD composite shows decrease in contact angles with increase in SD concentration. By the addition of SD, polymer surface becomes more polar, *i.e.* hydrophilic and the contact angle decreases accordingly. With water, the contact angle of PE (73°) decreases to 40.7° for PE-15 TSD composite, *i.e.* it becomes a wetting surface.

Table 2. Wetting properties of PE-TSD composite on water system

Sample Name	Contact angle (°C)	Work of adhesion $W_A=(1 + \cos\theta)\gamma_l$ mJ/m ²	Wetting energy $\gamma_{sl}=\gamma_s + \gamma_l - W_A$ mJ/m ²	Spreading coefficient $Sc = \gamma_s - \gamma_{sl} - \gamma_l$ mJ/m ²
100 PE	73.02	94.04	21.24	51.56
90 PE 10 TSD	51.71	117.91	45.11	27.69
80 PE 20 TSD	45.68	123.13	50.33	22.47
70 PE30 TSD	40.70	127.99	55.19	17.61

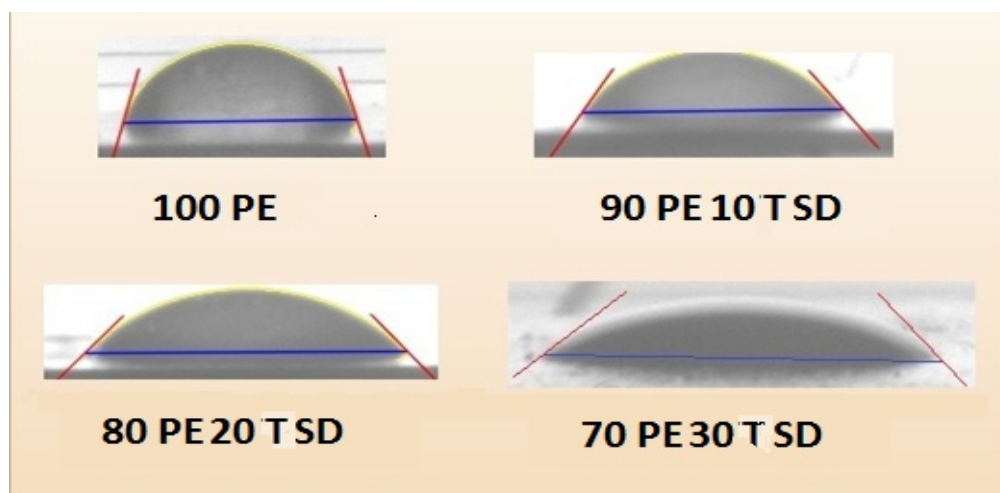


Figure 4: Contact Angle Measurements of PE-SD composites

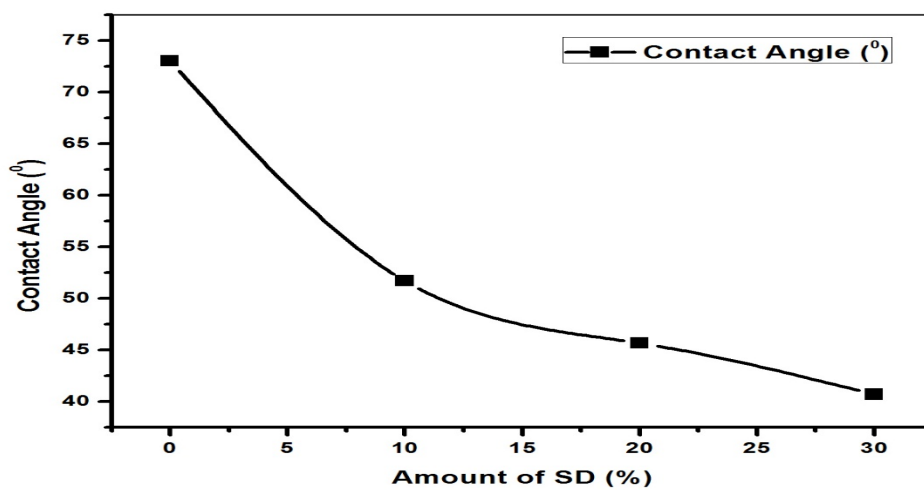


Figure 5: Contact angle curve of PE-SD composites

Surface free energy characteristics of PE-SD composite are given in table 2. The total surface free energy is showing an increasing trend with SD concentration. According to the principle of wetting process, if the solid-vapour interfacial energy is low, the tendency for spreading to eliminate the interface will be less. In that case the system exhibits more hydrophilic nature. Lowering the free energy of the system, the polymer chain must preferentially interact with the SD surface, where wettability plays a dominant role in successfully achieving the desired structure. Surface energy is the energy associated with the interface between two phases. The solid surface is rich in hydrocarbon molecule. The forces that hold between hydrocarbons together are much weaker than the force that acts between water molecules and consequently water on a hydrocarbon surface remain in non-wetting foam. Composite with SD, however, shows significantly decreased contact angles, indicating that the hydrophilic nature of the composites was significantly enhanced, i.e., the surface free energy of the nanoparticle was reduced and by which it affects the total surface energy of the entire composite system. The spreading coefficient (Sc) indicates that a liquid will spontaneously wet and spread on the solid surface if the value is positive whereas, a negative value of (Sc) implies the lack of spontaneous wetting. This means the existence of a finite contact angle. Wetting characteristics of water increases upon filler addition. The polar-polar interactions across the interface is a measure of wetting. The work of adhesion, (WA) which is the work required to separate the composite surface and the liquid drop, increases with filler concentration. Work of adhesion shows an increasing tendency as the interfacial bonding is decreased. It is clear from the table that, SD addition increases the polar behaviour of the surface and by which it shows an increasing tendency of work of adhesion towards polar solvents. Generally work of adhesion can be correlated to the filler matrix interaction.

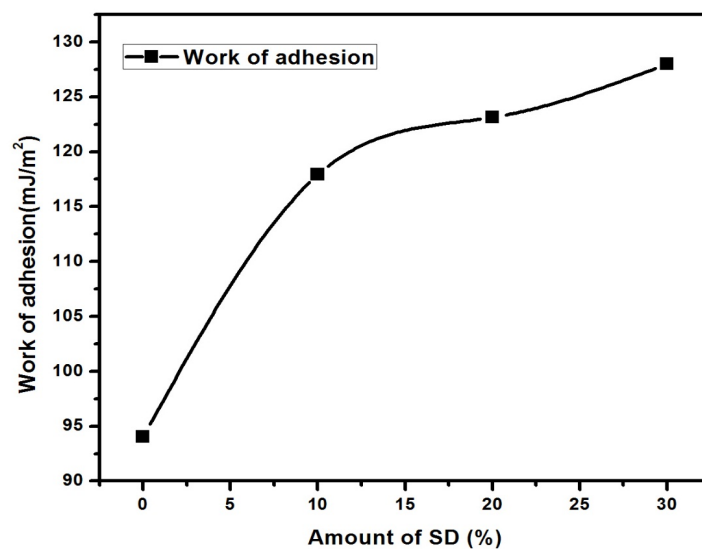


Figure 6: Work of adhesion curve of PE and SD composite

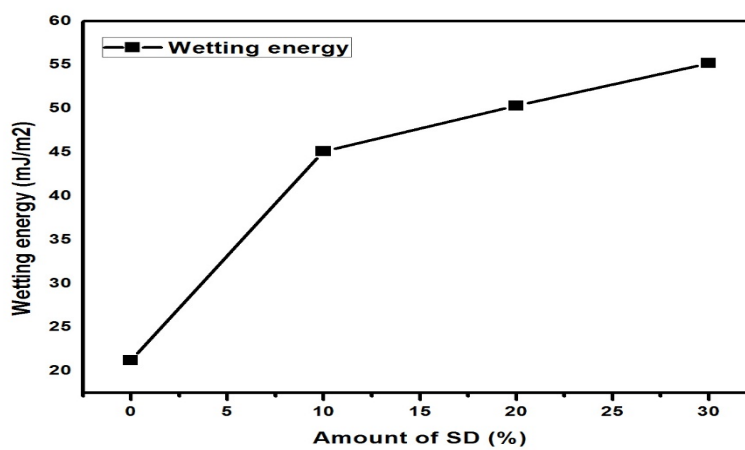


Figure 7: Wetting energy of PE and SD composites

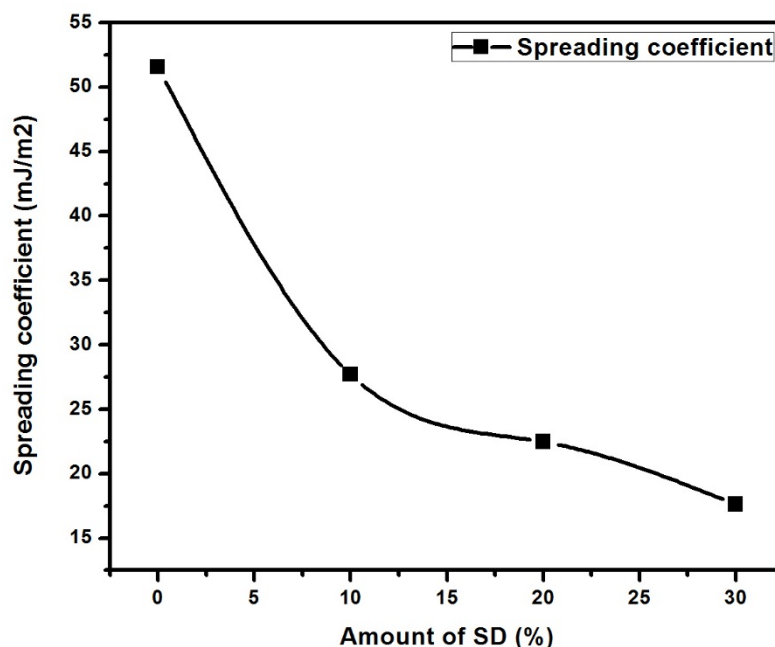


Figure 8: Spreading coefficient curve of PE and SD composite

4. CONCLUSIONS

This study investigated the technical evaluation of Fabrication of wood plastic composite by utilising plastic waste and saw dust from different mixing ratios of SD with waste Polyethylene. On the basis of mechanical properties, it appears that fabrication of PE-SD composites with using a brabender twin-screw compounder and compression-moulding machine process is technically feasible for various structural purposes. The addition of SD increased the tensile strength, elastic modulus of the PE- SD composites, and strain at break was decreased as per SD concentration. Contact angle measurements revealed that presence of SD increased the hydrophilic nature of the composites by reduced its contact angle. Reduction of plastic waste production through the Wood Plastic Composite

fabrication from the sawdust and PE is technically feasible, it would be better to mix additives like coupling agents to enhance interaction between SD and PE by reducing the melting temperature of PE, and thus, could ensure the adequate physical and mechanical properties of composites.

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Encapsulation and Controlled Release Studies on Polyethylene Glycol

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ABSTRACT

The present study aimed at developing a host – guest assembling by encapsulations of common small organic moieties in the cavities of selected host system. A primary criterion for the inclusion of guest within host's cavity is their size. The cavities of some molecules are large enough to accommodate simple organic compounds, in the form of ions or gases. The guest encapsulation in reversible system is occur spontaneously, when the host – guest complex is thermodynamically stable. The aim of the polymer encapsulation mostly is to improve the interactions between the hydrophilic inorganic particles and hydrophobic matrix. The efficiency which can be related to the amount of polymer formed on the surface and Stability of the encapsulated product. This study investigated the synthesis of benzil encapsulated Polyethylene glycol (PEG), and studied the controlled release of benzil, from the host-guest complex. IR Spectrum shows characteristic peaks due to benzil in benzil encapsulated PEG indicates the encapsulation. The rate of release of benzil from the host guest assembly was studied at different time intervals by UV- Visible Spectrometry. This studies shows that the release of encapsulated benzil is time dependent and linear. Silver nanoparticles are synthesized by simple reduction method and are effectively encapsulated into benzil encapsulated PEG. It could effectively release from the host complex and studied using UV- visible Spectrometry. When silver nanoparticle incorporated in PEG, the absorption peak shift from 400 to 406 nm due to the encapsulation of materials in biocompatible PEG.

Key words: *Encapsulation, Silver nanoparticle, Polyethylene glycol, Benzil*

1. INTRODUCTION

The design and synthesis of molecules that are capable of spontaneously associating into large, well-defined assemblies (super molecules) joined by non-covalent intermolecular interactions remain one of the foremost challenges in supra molecular chemistry [1]. These two approaches of supra molecular synthesis exploit the specificity and directionality of these relatively weak non covalent interactions, either hydrogen or coordination bonds, over strong covalent bonds. The study of the supra molecular structure–function correlations will then orientate the rational design and synthesis of self-assembled supra molecular functional materials. They display interesting physicochemical properties that could be exploited in supra molecular recognition and catalysis [2-5] and supra molecular photo, electro, and magneto chemistry [6-8]. Self-assembly based on molecules has emerged as an attractive approach for the fabrication of these new materials, and considerable effort has been directed toward supra molecular networks assembled by covalent and hydrogen bonds or other molecular interactions [9-13]. Nanoparticle encapsulation and functionalization are therefore essential for obtaining the required selectivity, sensitivity and stability. Metallic Nano particulate inks have received considerable attention in recent years for their use in printing applications, such as microelectrodes, light emitting diodes (LEDs), organic transistors, reconfigurable antennas, radio frequency identification tags (RFIDs), bio-circuits and many more [14-17].

PEG is also known as polyethylene oxide (PEO) or polyoxyethylene (POE) depending on its molecular weight. PEG is a polyether compound with many applications from industrial manufacturing to medicine. PEG refer to oligomers and Polymers with molecular mass below 20,000 g/mol, PEO, polymer with a molecular mass above 20,000 g/mol, POE, a polymer of any molecular mass. Different forms of PEG are also available

depending on the initiator used for the polymerization process the most common initiator is a non-functional methyl ether PEG, or methoxy poly (ethylene glycol) abbreviated MPEG. PEG is soluble in water, methanol, benzene & dichloromethane & is insoluble in diethyl ether and hexane. Methoxy polyethylene glycol is used in numerous applications such as surfactants, in cosmetics, in ointments etc.

Silver and gold nanoparticles are widely used in conductive inks due to their high conductivity, thermal stability, and chemical inertness [18-20]. Silver metal nanoparticles have attracted a great deal of attention due to their potential applications in several fields, such as catalysis [21, 22] photonics [23, 24] electronics [25] and sensing [26-27]. For these applications, precise control over the size, shape and composition of the particles are crucial issues [28].

Encapsulation is the phenomenon of inclusion of molecules (guest) within others (host). The host molecule forms stable complexes with one or more guest molecule through some non-covalent interactions. For the non-covalent forces to operate effectively the receptor must provide a cavity that matches the size and shape of the guest and the binding sites in host –guest molecule must be properly aligned to maintain complementarity between different subunits. This is the basis for most synthetic work in the field of molecular encapsulation. The present study is aimed in developing a host – guest assembling by encapsulations common small organic moieties in the cavities of selected host system. A primary criterion for the inclusion of guest within host's cavity is their size. The cavities of some molecules are large enough to accommodate simple organic compounds, in organic ions or gases. The guest encapsulation in reversible system occur spontaneously upon the condition of the appropriate guest molecule, provided that the host – guest complex is thermodynamically stable. The aim of the

polymer encapsulation mostly is to improve the interactions between the hydrophilic inorganic particles and hydrophobic matrix.

This study investigated the synthesis of benzil encapsulated Polyethylene glycol (PEG), and studied the controlled release of benzil, from the host-guest complex using UV- visible spectrometry. Silver nanoparticles were synthesized by simple and versatile reduction method. These silver nano particle were encapsulated to a benzil encapsulated PEG and it is characterized by UV-Visible spectrometry.

2. EXPERIMENTAL

2.1 Materials

Polyethylene glycol was purchased from Merck (Germany). The solvents used were of analytical grade obtained from Sigma Aldrich, India.

2.2 Preparation of benzil encapsulated PEG

1: 2 ratio of benzil in methanol and PEG in cold water are mixed. The mixture is stirred thoroughly for one hour on a magnetic stirrer. Filtered, washed and dried.

2.3 Synthesis of Silver nano particles

1:1 ratio of 0.005M NaBH_4 and 0.002M sodium dodecyl sulphate are mixed and kept for about half an hour. To this solution equal volume of 0.001 M AgNO_3 is added drop by drop. The solution is kept for stirring on a magnetic stirrer for one hour.

2.4 Encapsulation of silver nano particle into benzil encapsulated PEG

15ml of synthesized silver nano particle solution is mixed with 0.2 g of benzil encapsulated PEG. It is then stirred for half an hour on a magnetic stirrer. It is then filtered washed and dried.

2.5 Characterizations

UV- Visible spectra were recorded on T 90+ UV-Visible spectrometer and IR spectral analysis were done by ABB BOMEM IR spectrometer.

2.5.1 Kinetic studies of benzil release

0.2 g of the encapsulated complex was weighed accurately, it is dissolved in 25ml of methanol. Stirred for one hour on a magnetic stirrer and the solution is diluted to 1:20 and the amount of benzil released is studied by UV-Visible spectrometry. Calibration curve was drawn using – 0.05% solution of benzil. In order to conduct kinetic studies 0.2 g of the benzil encapsulated PEG is accurately weighed out into a 25ml methanol and stirred on a magnetic stirrer for about 120 minutes. Amount of benzil released is determined at different time intervals 10, 20, 30, 40, 50, 60 up to 120 minutes using UV – Visible spectrometry.

2.5.2 Release Experiments of silver nano particular

0.1 g of the silver and benzil encapsulated PEG is dissolved in 15ml of hexane, stirred well and analyzed using UV – Visible spectrometry.

3. RESULTS AND DISCUSSION

3.1 IR Analysis of benzil encapsulated PEG

IR spectral studies of the benzil encapsulated PEG was carried out by using ABB BOMEM IR spectrometer. Figure 1 shows the IR Spectrum of benzil and benzil encapsulated PEG. The spectrum of benzil encapsulated PEG shows the characteristic peaks benzil due to C=O, C=C and C-H Stretching. The peak at 1659cm^{-1} corresponds to C=O stretching, peak at 3315cm^{-1} due to O-H stretching and peak at 2921cm^{-1} is corresponds to aromatic C-H stretching. It supported the encapsulation of benzyl in PEG.

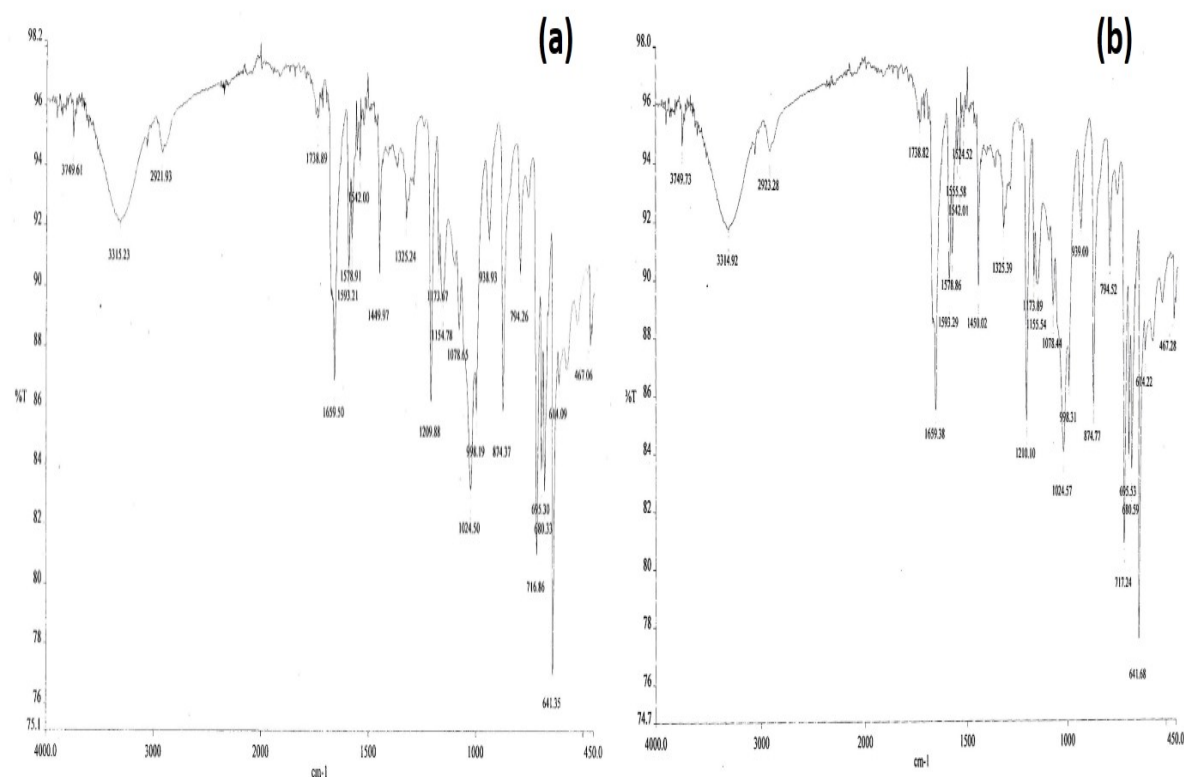


Figure 1. IR Spectrum of (a) neat benzil and (b) benzil encapsulated in PEG.

3.2 UV-Visible Analysis of benzil and benzil encapsulated PEG

Figure 2 shows the UV-Visible spectrum of neat benzil and benzil encapsulated in PEG. Benzil give rise to an absorption band in the UV – visible region at 206 nm corresponding to the $n \rightarrow \pi^*$ transition of carbonyl function and the peak at 258 nm is due to the extensive conjugation present in it (Figure 2 a). Figure 2 b shows the UV-Visible spectrum of benzil encapsulated in PEG, it also show the peak at 260 and 214 nm corresponds to $n \rightarrow \pi^*$ transition of carbonyl function groups and extensive conjugation

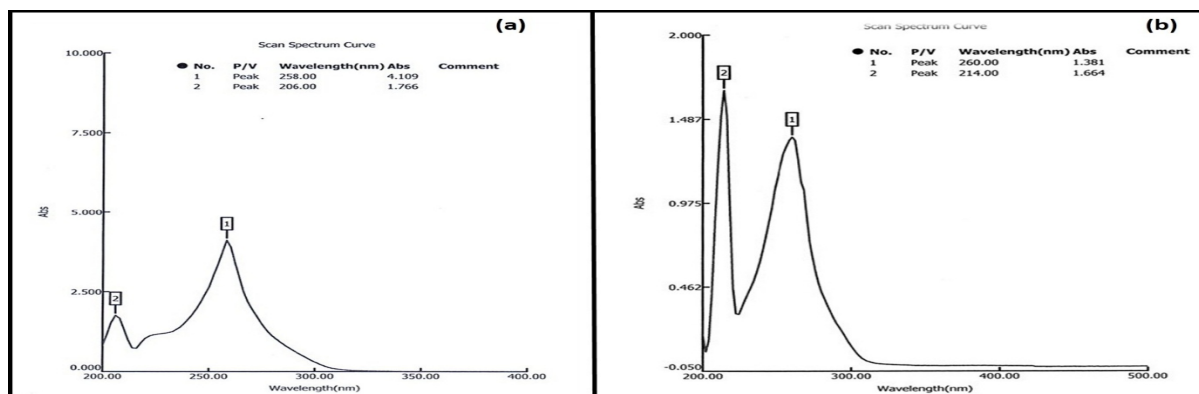


Figure 2. UV-Vis Spectrum of (a) benzil and (b) benzil encapsulated PEG.

The benzil encapsulated on PEG is dissolved in methanol and UV – visible spectrum is collected after different time interval (10, 20, 30, 40 min etc.) and the amount of benzil released is determined. Figure 3 (a) shows the UV-visible spectrum of benzil encapsulated on PEG at different time interval and figure 3(b) shows the calibration curve. Weight of benzil released from encapsulated PEG at different time intervals are determined from the calibration curve given below.

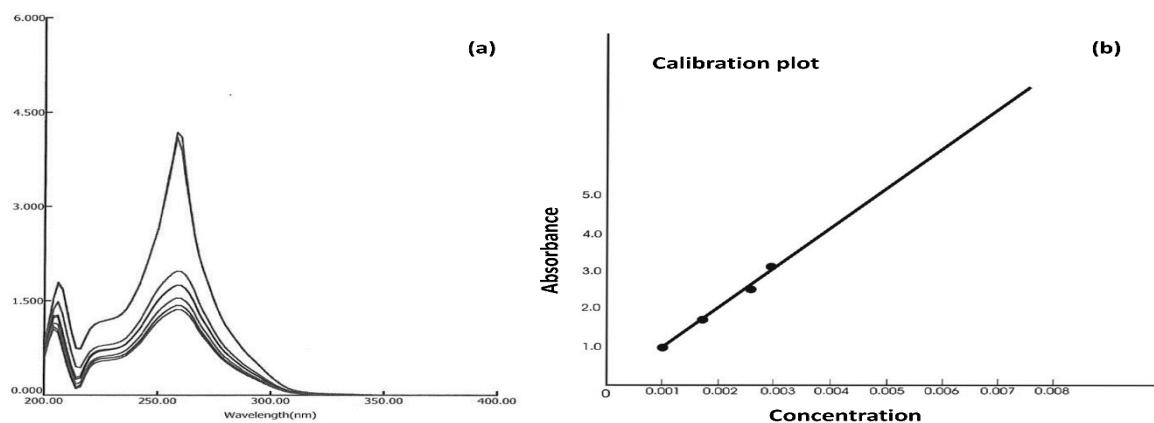


Figure 3. (a) UV-visible spectrum of benzil encapsulated on PEG at different time interval 3(b) calibration plot

Weight of benzil released from benzil encapsulated PEG at different time intervals are shown in The Table 2. Figure 4 shows a plot of benzil released against time is given. From the kinetic studies we see that as the time increases the amount of benzil released increases steadily and it becomes constant after 60 minutes.

Table 1. Weight of benzil released from benzil encapsulated PEG at different time intervals

Time (Min)	Absorbance	Concentration (M)
10	1.382	0.0195
20	1.423	0.0202
30	1.501	0.0217
40	1.761	0.0262
50	2.310	0.033
60	4.423	0.0637
90	4.423	0.0637
120	4.423	0.0637

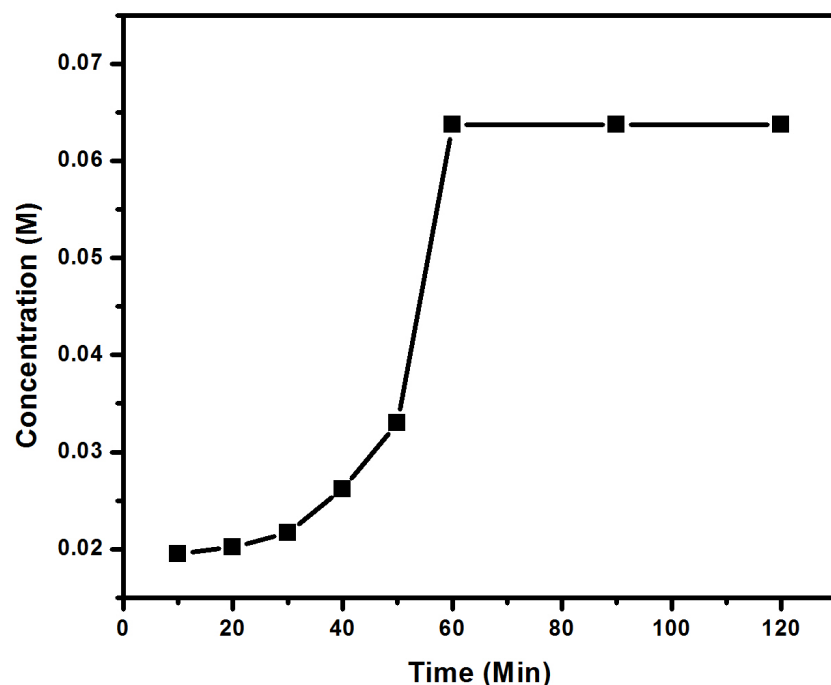


Figure 4: A plot of concentration of benzil released against time

3.3. UV-Visible Analysis of Silver nano particles

Silver nano particles are prepared by the reduction of AgNO_3 with NaBH_4 in presence of SDS. The product is characterized using UV- Visible Spectrometry. The spectrum shows a peak at 406 nm. Silver nano particle are extra ordinarily efficient at absorbing and scattering light. This strong interaction between Ag nano particle light occurs because of the conduction electron on the metal surface undergo a collective oscillation when excited by light at specific wavelength known as surface Plasmon resonance (SPR). Strong scattering cross section allow 100 nm nano particles to be easily visualized with a conventional microscope. 60 nm Ag nanoparticle appear as blue point, this bright blue

color is due to as SPR that is peaked at a 450 nm wave length. In Ag nano particle SPR peak can be tuned from 400 nm (violet) to 530 nm (green light) by changing particle size refractive index. Physical state of the nano particle can be obtained from spectral data. As the diameter increases, the peak Plasmon resonance shifts to longer wave lengths and broadens. At diameter greater than 80 nm, a second peak become visible at a shorter wave length than the primary peak it is due to quadruple resonance. UV- visible spectra provide a mechanism to monitor how the nano particles change over time. When silver nano particle aggregate, the SPR become different. Thus the presence of Ag. nano particle its extinction by the addition of NaCl can be obtained from the following spectra. Figure 5 shows the UV – Visible spectrum of silver nanoparticle. As the diameter of the silver nanoparticle increases SPR shifts to longer wavelength and broadens.

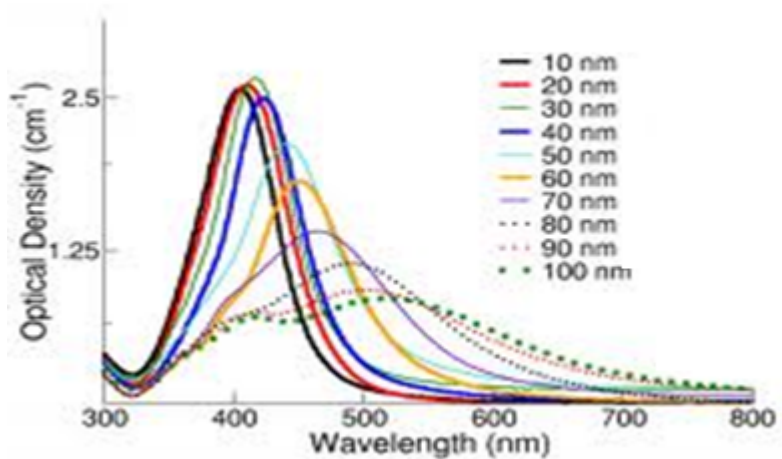


Figure 5: UV – Visible spectrum of silver nanoparticle

3.4 UV-Visible Analysis of Silver nano particle encapsulated in benzyl encapsulated PEG

Figure 6 (a) shows the UV-Visible Spectrum of Silver nano particle encapsulated in benzyl encapsulated PEG. The silver nano particles are effectively encapsulated they are characterized by releasing experiment to which it is dissolved in n hexane the UV- visible spectrum is taken. The peak at 392 shows the presence of Ag nano particle , which has a different size then in free state. Figure 6 (b) shows the UV-Visible Spectrum after the realease of silver nanoparticles.

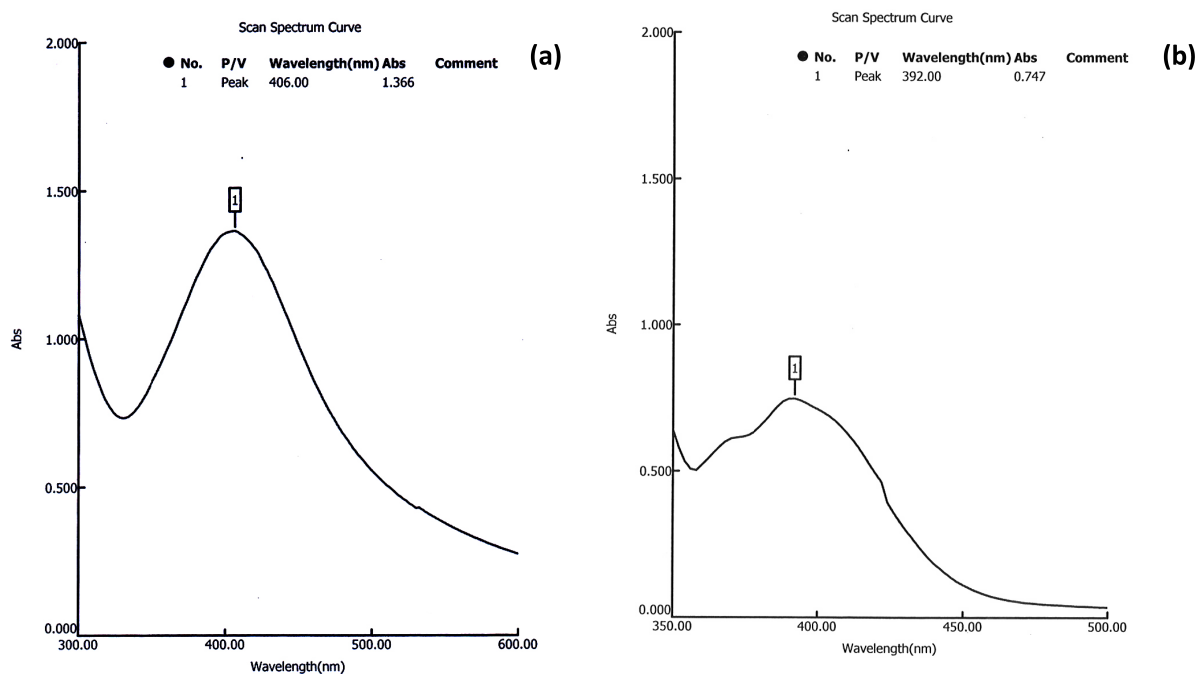


Figure 6: (a) UV-Visible Spectrum of Silver nano particle encapsulated in benzyl encapsulated PEG (b) After the realease of silver nanoparticles

4. CONCLUSIONS

The benzil encapsulated PEG is prepared. The host system form well defined cavity of appropriate size, so that benzil is successfully encapsulated. IR Spectrum shows characteristic peaks due to benzil in benzil encapsulated PEG. The rate of release of benzil from the host guest assembly was studied at different time intervals by UV-Visible Spectrometry. This studies shows that the release of encapsulated benzil is time dependent and linear. Silver nanoparticles are synthesized by simple reduction method and are effectively encapsulated into benzil encapsulated PEG. It could effectively release from the host complex and studied using UV- visible Spectrometry. UV- visible Spectrum of silver nanoparticle exhibited a well-defined absorption peak at 400 nm. When incorporated in PEG it shift to 406 nm encapsulation of materials in biocompatible PEG is a topic of interest in large number of Scientific and industrial areas. The area of encapsulation and controlled release is most developed in drug delivering system. By this studies we could offer an effective host system for the delivery of benzil and silver nano particles.

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