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Research Article

Fabrication and Biodegradation Studies of Styrene-butadiene Rubber Composites Reinforced with Poly (Methyl Methacrylate) Grafted Coconut Shell Powder

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ABSTRACT

Studies on the use of natural fibers as reinforcing filler into synthetic rubbers have increased recently and opened up new industrial possibilities. Natural fibers have advantages such as the ease of availability, low cost, renewable, and biodegradable nature. However, the main disadvantage of natural fibers in polymer composites is the poor compatibility between fiber and matrix. Therefore, chemical treatments are carried out to modify the fiber surface. Grafting technique is usually used to modify natural fiber. Therefore, poly (methyl methacrylate) (PMMA) is successfully grafted onto coconut shell powder. The graft copolymers were characterized by Fourier transform infrared, X-ray powder diffraction, thermogravimetric analysis, and scanning electron microscopy. The grafted copolymers exhibited low crystallinity and increased thermal stability. Composites were fabricated using the grafted product as reinforcing filler in styrene-butadiene rubber (SBR) matrix. Cure characteristics, thermal transitions, mechanical properties, and the biodegradation behavior of the composites were examined. Glass transition temperature (Tg) of the composites increased with increase in percentage grafting. The filling of the grafted product caused the improved mechanical properties such as tensile strength, tear strength, and hardness. Biodegradation of the composites was more dependent on the presence of lignocellulosic fillers than on SBR matrix.

INTRODUCTION

Synthetic rubbers are an important class of polymers due to its specific applications. In most of these applications, the properties of polymers are modified with fillers, which can improve the properties of the composites and reduce the manufacturing costs while maintaining the quality of the product. Natural fiber-reinforced polymers offer advantages over conventional materials due to its biodegradability, low cost, lower density, greater deformability, high abundance, less abrasiveness to equipment, and eco-friendly nature. Among the agricultural-based fibers, coconut shell (CS) (*Cocos nucifera*) is considered to be one of the significant lignocellulosic materials due to their availability and low production cost.[1,2] Therefore, the utilization of CS as lignocellulosic fillers in polymer composites becomes more favorable due to its high strength and modulus properties.[3,4] The CS powder (CSP) shows some excellent properties compared to mineral fillers (e.g., silica, kaolin, mica, talc, etc.) and should be a suitable material as filler due to its good thermal stability, enhanced mechanical

properties, and diffusion properties[5,6] compared to other natural fillers.

The most serious concern with natural reinforcement material is its incompatibility with the hydrophobic polymer matrix and the tendency to form aggregates during processing. This may cause problems in the material properties and greatly reduce the potential of natural fibers to be used as reinforcement in polymers. For the past few years, there has been a growing interest in the chemical modification of natural fibers to enhance the biocompatibility to broaden its applications. Chemical modification of natural fillers was carried out mainly using alkalization, benzoylation, acetylation, grafting, use of compatibilizers, and coupling agents[7] in addition to other alternatives.

Graft copolymerization is a useful method used to modify the properties of natural polymers. Modifying the properties of natural polymers through graft copolymerization has been reported by Sabaa and Mokhtar[8] and Kaith and Kalia.[9,10] Recently, graft copolymerization of vinyl monomers has been

investigated[11,12] widely and, in particular, the acrylic monomers as a means to modify cellulosic materials. Among the acrylic monomers, methyl methacrylate (MMA) has been widely used for the modification of various organic or inorganic fillers such as cellulose,[13,14] starch,[15] silica, carbon nanotubes,[16] etc. Zhu *et al.*[17] reported that poly (MMA) (PMMA)-modified silica/polyvinyl chloride (PVC) nanocomposite showed improved dispersion of silica nanoparticles in PVC, which enhanced the compatibility between silica and PVC. This endowed compatibility leads to an improvement in mechanical performances of PVC composites reinforced by PMMA-modified cellulose fibers. It is clear that PMMA grafts effectively act as a "chemical bridge" between the reinforcement and matrix through physical entanglements.

The work reported herein focuses on the study of graft polymerization of the MMA onto CSP by radical polymerization method using benzoyl peroxide as initiator. PMMA grafted CSP with variable percentage grafting (%G) was prepared [Figure 1]. The grafted product was used as reinforcing filler in styrene-butadiene rubber (SBR) matrix. The prepared grafted product and composites were characterized by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM). The biodegradation studies of the composites were performed by soil burial method in garden soil. Mechanical properties of the composites were also examined. The deterioration in properties of the composites after biodegradation was investigated by evaluating the mechanical properties of the composites before and after biodegradation testing. The surface morphologies of the degraded material were examined with SEM.

EXPERIMENTAL

Materials and methods

SBR-1502 with 75% butadiene content having molecular weight Mn. 176.000 g/mol was purchased from synthetic and chemicals limited, Bareilly, Uttar Pradesh, India. CSP was purchased from Sip India Exports, Erode, Tamil Nadu, India. The powder was dried in hot air oven at 60°C and sieved to get up to 90 micron size. MMA monomer (Sigma Aldrich) and toluene (Merck) were purified by vacuum distillation to remove inhibitors. Benzoyl peroxide initiator (Sigma-Aldrich), ethanol (Merck), and other materials such as sulfur, stearic acid, zinc oxide, N-cyclohexyl-2-benzothiazylsulphenamide, and 2,2,4-trimethyl-1,2-dihydroquinoline were of analytical grade and used without further purification.

Graft copolymerization

The dried CSP [Table 1] was treated with 10% NaOH for 5 h with continuous stirring using a mechanical stirrer and was kept for 24 h. Washed with distilled water until it became neutral. The resulting alkalized CSP (ACSP) after the removal of lignin was filtered and was dried in vacuum at 70°C for 24 h. Graft polymerization of MMA onto ACSP was carried out by radical polymerization method.[17] The required amount of MMA monomer was solubilized in toluene in a 250 ml RB flask in nitrogen atmosphere. To this homogenized solution, ACSP and benzoyl peroxide were added and the mixture stirred at 85°C for 90 min. The product was precipitated in ethanol, then washed with water, filtered, and dried under vacuum for 48 h
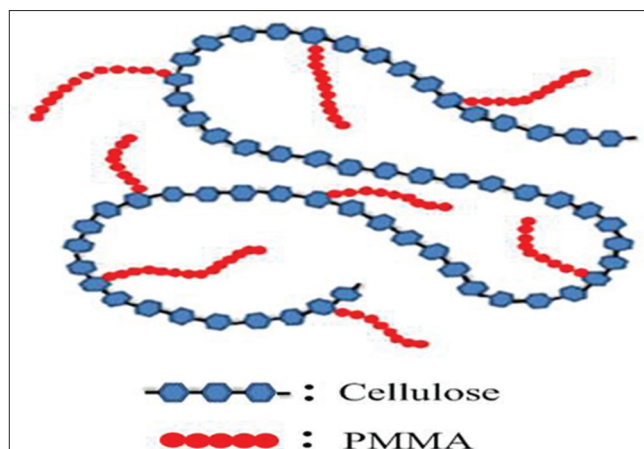

Figure 1: Diagrammatic representation of poly (methyl methacrylate)-g-coconut shell powder

at 60°C. Percentage grafting (%G) was determined using the following Eq. 1.

$$\% \text{ Grafting } (\%G) = \frac{(W1 - W0)}{W0} \times 100 \qquad (1)$$

Where, W_0 and W_1 denote, respectively, the weight of original ACSP and the weight of the PMMA grafted ACSP (PMMA-*g*-ACSP).

Preparation of the composite

The composites were prepared using the mixing formulation given in Table 2. Compounding was done in accordance with ASTM D15–627, using a two roll mixing mill at 27°C. Water cooling was done to ensure that the mill roll temperature was not too high to avoid the cross-linking during mixing.

Characterization

Infrared (IR) spectral analysis

The IR spectra of the CS cellulose and the graft copolymers were recorded in the range of 400–4000 cm^{-1} using KBr pellets with JASCO (Model 4100) Fourier transform spectrometer at room temperature.

X-ray diffraction analysis

X-ray powder diffraction (XRD) spectra of CSP, ACSP, and PMMA-*g*-ACSP) samples were recorded with Bruker AXS D X-ray diffractometer using CuKα radiation (λ=1.5406 A°) running at an accelerating voltage of 30 kV. The diffractogram was recorded in terms of 2θ in the range of 5–90°. The crystallinities of the samples were calculated by Xc (%) = (Fc/Fc+Fa) × 100; where, Fc and Fa are the areas of the crystalline and non-crystalline regions, respectively.

TGA and DSC

TG was performed using SDT Q600 V20.9 Build 20. The sample was heated at a rate of 10°C/min in nitrogen atmosphere. The weight of material was measured continuously, as a function of increasing temperature for a given heating rate, up to end temperature under nitrogen purging. DSC experiments were carried out with a Mettler Toledo DSC 822e instrument

fitted with a liquid nitrogen cooling system. The samples were placed in hermetically closed pans in the DSC cell. The heating rate and temperature range were 10°C min^{-1} from −90°C to 30°C, respectively, in nitrogen atmosphere.

Curing and mechanical testing of composites

Optimum cure time (t_{90}) for each compound was determined using Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D 2084–93, operating at 160°C. The compounds were vulcanized in a hydraulic press to optimum cure time. Stress-strain behavior was studied by Universal Testing Machine INSTRON-3365 (Series IX Automated Materials Testing System 1.38, model-441, Instron Corporation, United States). Tensile strength and tear strength of the composites were studied according to ASTM D 412–1998. Shore A Durometer was used to measure the hardness of the composites according to ASTM D 2240–2004.

Biodegradation analysis by soil burial test

Samples having 1.75 mm thickness and 6 mm for the measurement of tensile strength and hardness, respectively, were cut from vulcanized rubber sheets, weighed, and buried in soil for 3–6 months. After 3/6 months, the samples were removed from the soil, washed with distilled water, and dried at room temperature. The degradation was assessed and evaluated by measuring the weight loss, tensile strength, and hardness before and after soil burial. Evaluation of soil buried samples was also carried out using SEM.

SEM

The surface morphology was studied using JEOL Model JSM-6390LV SEM, with magnification of ×500 and ×1500.

Table 1: Chemical composition of CSP

Composition	Weight (%)
Cellulose	34
Hemicellulose	21
Lignin	27
Starch	0
Protein	2
Fat	5

CS: Coconut shell, CSP: Coconut shell powder

Table 2: Mixing formulation of composites

Ingredient	Phr
SBR	100
Zinc oxide	5
Stearic acid	2
TDQ	1
Processing oil	1/20th of filler
PMMA-g-ACSP	10
CBS	1.8
Sulfur	2.4

SBR: Styrene-butadiene rubber, TDQ: 2,2,4-Trimethyl-1,2-dihydroquinoline, CBS: N-cyclohexyl-2-benzothiazylsulphenamide, PMMA: Poly (methyl methacrylate), ACSP: Alkalized coconut shell powder

The SEM micrograph was taken at a voltage of 20 kV.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectrum of the CSP showed an absorption frequency at 3407.6 cm^{-1} which is due to –OH stretching [Figure 2]. The peak at 2920.6 cm^{-1} is due to C–H stretching and the absorption bands at 1436.1 and 1155.7 cm^{-1} are attributed to C–C and C–O stretching, respectively. Compared with the spectra of CSP, the PMMS-*g*-CSP graft copolymers showed strong absorption frequencies at 1451.1 cm^{-1} and 1153.4 cm^{-1}. There is a new characteristic band at 1731.2 cm^{-1} attributed to the stretching vibration of carbonyl group.[18] The intensity of this band increases with increase in percentage of grafting. This effect could be due to the amount of PMMA on the graft copolymers, which proved that MMA monomer is grafted successfully onto ACSP.

XRD studies

The calculated crystallinity index (CI%) was found 42.19% for unmodified CSP, whereas it was 52.06% for ACSP. The higher CI of ACSP than CSP was due to the removal of residual lignin. XRD pattern [Figure 3] shows that the alkalized CSP peaks are more intense than virgin CSP.[19] That is, the chemical treatments are able to remove part of the amorphous materials such as hemicellulose, lignin, and other non-cellulosic materials. Compared to the diffraction patterns of ACSP, the diffraction
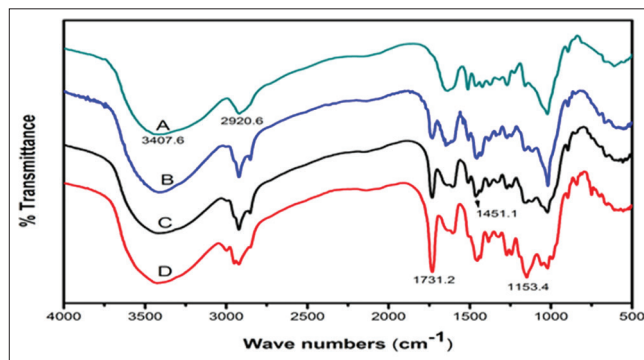
Figure 2: Fourier-transform infrared spectra of (A) alkalized coconut shell powder (ACSP), (B) poly (methyl methacrylate) (PMMA)-*g*-ACSP (11.82 %G), (C) PMMA-g-ACSP (24.55 %G), (D) PMMA-g-ACSP (40.22 %G)
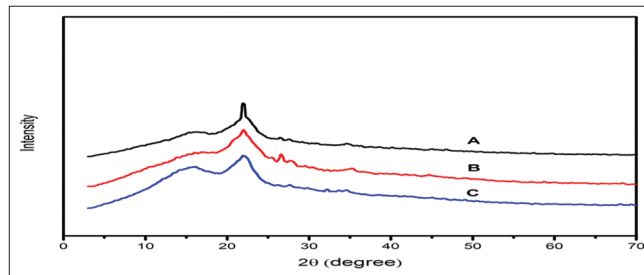
Figure 3: X-ray powder diffraction pattern of (A) alkalized coconut shell powder (ACSP), (B) Coconut shell powder, (C) poly (methyl methacrylate) (PMMA)-g-ACSP (40.22 %G)

patterns of the grafted cellulose show a decrease in intensity and a broadening of peak at around $2\theta=21.2\circ$. The crystallinity was found to decrease in the PMMA grafted ACSP (11.82% grafting, Xc =0.3681; 40.22% grafting, Xc = 0.3853), as compared to ACSP (Xc = 0.5206). It may be explained by the fact that the randomness of the amorphous phase in the graft copolymers was increased by the grafting with PMMA, which gives rise to a perturbation of long-ranged spacing between the chains.[20,21]

TGA

The TGA and DTG are measured to assess the thermal stability of both untreated and PMMA grafted ACSP, and the results are summarized in Table 3. The initial weight loss of the fiber occurs <100°C due to evaporation of water [Figure 4]. From the DTG curve, CSP that decomposed in two stages, the decomposition peak at temperature around 250°C is due to the decomposition of hemicelluloses, and the second, decomposition peak at temperature 350–400°C[22] is due to the decomposition of cellulose and lignin. The initial

Table 3: Thermal decomposition data of ACSP, the graft copolymers of 11.82%G and 40.22%G

Sample	Ti (°C)	$T_{50\%}$ (°C)	T_{max} (°C)
ACSP	238	324	348
PMMA-g-ACSP (11.82%G)	247	338	364
PMMA-g-ACSP (40.22%G)	253	342	368

ACSP: Alkalized coconut shell powder, PMMA: Poly (methyl methacrylate)

decomposition temperature of PMMA was around 400°C, so the grafting of PMMA onto CSP enhances the initial decomposition temperature of the grafted product with respect to the percentage of grafting. It can be seen that 50% weight loss temperature and maximum decomposition temperature of PMMA-g-ACSP (11.82 %G) and PMMA-g-ACSP (40.22 %G) were higher than those of ACSP. The possible reason may be that the stereostructure of PMMA-g-ACSP is more in compact than that of ACSP and the carbonization is less.[23]

DSC

To study the transition phenomena of the cured composites, DSC measurements were carried out. Each sample was scanned as the temperature was raised from −90 to room temperature at a heating rate of 10°C/min. Figure 5 shows the DSC thermograms of SBR composites. T*g* value of grafted ACSP/SBR composites is higher than that of vulcanized neat SBR. Furthermore, the T*g* value increases with the increase in percentage grafting. This may be due to the restriction in chain mobility and flexibility due to the presence of grafted PMMA on the ACSP chain, and the molecular mobilization of the rubber matrix in composites was restricted.[24]

Cure characteristics and mechanical properties

The cure characteristics of the prepared composites were studied. It was observed that [Table 4] both cure time and
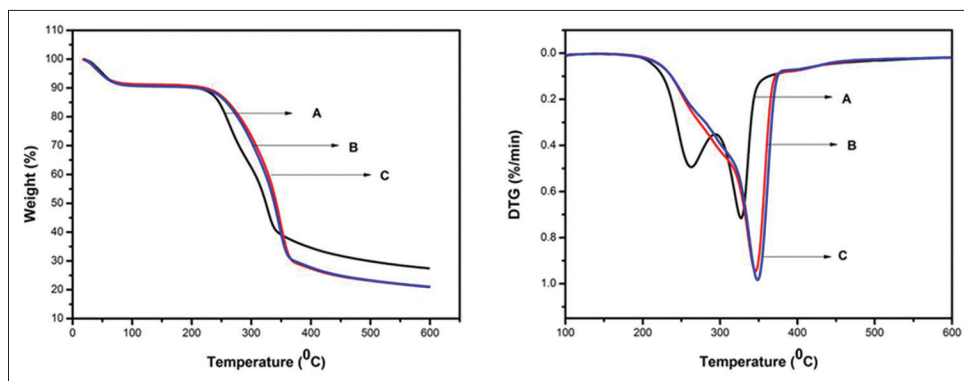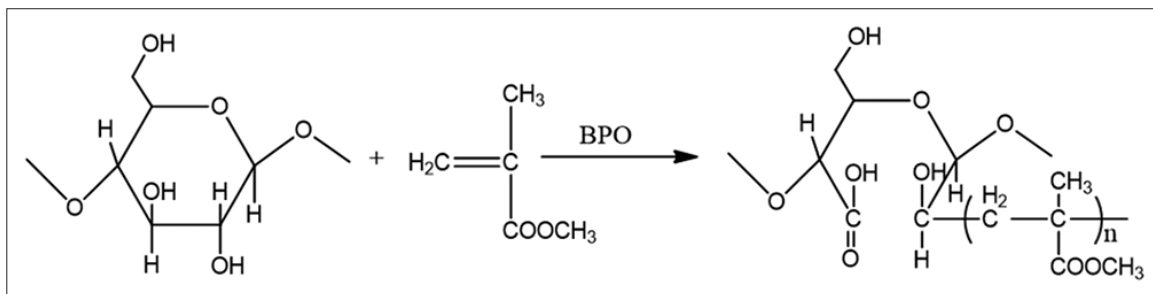

Figure 4: Thermogravimetric analysis, DTG curves of (A) alkalized coconut shell powder (ACSP), (B) poly (methyl methacrylate) (PMMA)-g-ACSP (11.82 %G), (C) PMMA-g-ACSP (40.22 %G)

Scheme 1: Synthetic procedure of grafting of poly (methyl methacrylate) onto cellulose.[18]

scorch time are lesser for the grafted ACSP reinforced SBR composites. This indicates the enhanced interaction between the filler and the matrix. Maximum torque is a measure of stiffness and crosslink density of the composites. Higher the maximum torque, higher is the crosslink density. Scorch time is a measure of scorch safety. Scorch safety increases with increase in scorch time. It is clear that the tensile strength and tear strength of the composites [Figure 6] were improved by the addition of grafted filler into the polymer matrix. The stronger rubber-filler interaction would increase the effective transfer of stress from the matrix to filler particles and thereby enhance the tensile strength.[25] Alkali treatment reduced both hemicellulose and lignin contents, resulting in an increase in the cellulose content of the fiber. The higher cellulose content after alkali modification[26] and the PMMA grafting is believed to be responsible for the increased mechanical properties of the composites. Furthermore, the hydrophobic nature of PMMA chains effectively prevents the gathering as well as the agglomeration of filler particles and improves compatibility with the SBR matrix. The results reveal that the hardness of the composites increases consistently with increasing percentage grafting. The more reinforcing filler would result in harder vulcanizates.

SEM studies

Morphological studies of ACSP and grafted PMMS-g-ACSP were performed by SEM. As shown in Figure 7, smooth and clean surface of ACSP were observed in the micrograph of original cellulose. The change in surface morphology after grafting with PMMA was clearly revealed by the SEM image as grafting affected the surface of ACSP[18] The surface roughness resulted from deposition of PMMA, which formed during graft copolymerization with MMA. This rough surface facilitates mechanical interlocking due to the exposure of PMMA chains to the SBR matrix, thereby enhancing the filler–matrix adhesion. From the SEM images of the vulcanizate, it is clear that the compatibility of the grafted filler increases with the percentage of filler loading.

Table 4: Cure characteristics of vulcanized composites

Samples	Maximum torque (Nm)	Scorch time (min)	Cure time (min)
SBR	10.13	5.13	12.44
PMMA-g-ACSP/SBR (11.82%G)	11.90	3.28	10.23
PMMA-g-ACSP/SBR (17.64%G)	10.94	3.51	9.38
PMMA-g-ACSP/SBR (24.55%G)	10.78	3.56	9.36
PMMA-g-ACSP/SBR (31.68%G)	10.77	4.05	9.31
PMMA-g-ACSP/SBR (40.22%G)	10.39	4.21	9.23

SBR: Styrene-butadiene rubber, PMMA: Poly (methyl methacrylate), ACSP: Alkalized coconut shell powder
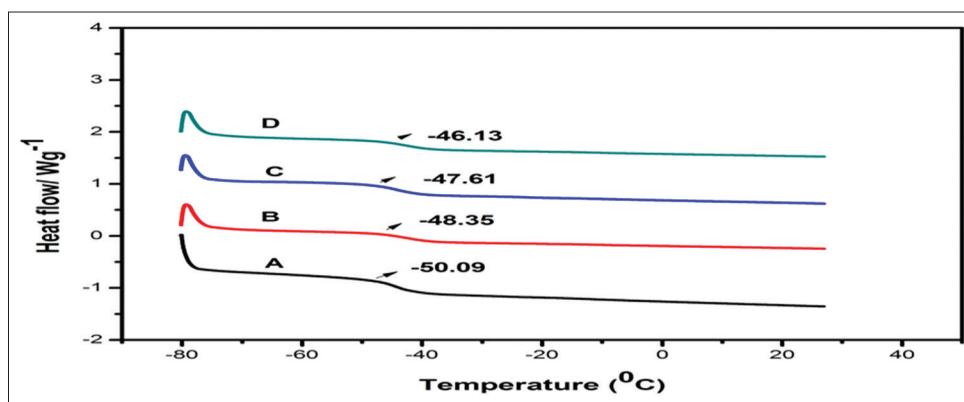

Figure 5: Differential scanning calorimetry curves of (A) styrene-butadiene rubber (SBR), (B) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP)/SBR (11.82 %G), (C) PMMA-g-ACSP/SBR (24.55 %G), (D) PMMA-g-ACSP/SBR (40.22 %G)
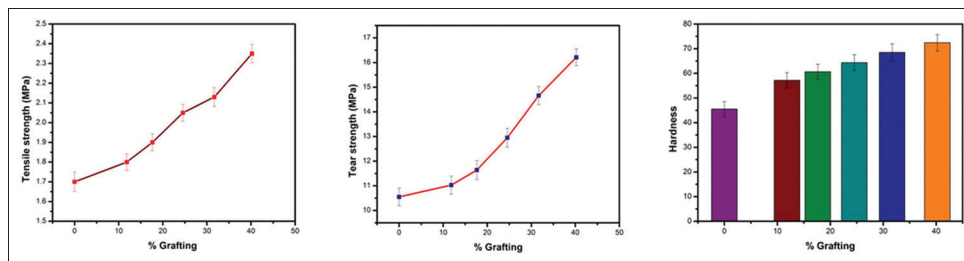

Figure 6: Effect of %G on the tensile strength, tear strength, and hardness of styrene-butadiene rubber vulcanizates

Biodegradation of PMMA-g-ACSP/SBR composites

In the biodegradation study of the composites, tensile and hardness specimens were exposed to garden soil for a period of 3 and 6 months. Weight of samples, tensile strength, hardness, and surface morphology were compared before and after soil burial. The lignocellulosic filler in a polymer matrix is attacked by microorganisms when it is in contact with the soil or water. The microbes digest the cellulose and leaving behind a porous structure with high interfacial area. With the depletion off the cellulose, the polymer matrix begins to degrade essentially by microbial attack, which slowly reduces the weight of the polymer matrix until the entire material gets digested.[27]

Weight loss of the samples as a function of biodegradation time obtained from soil burial test is shown in Figure 8. It is clear from the graph that as the percentage grafting increases the weight loss decreases. The soil microorganisms could consume the cellulose component of filler, lead to the breakage of interaction between the filler and the matrix. This might have caused vulnerable centers in the polymer matrix and facilitated the degradation. It is also evident that the extent of biodegradation is directly proportional to the number of days.[28] The soil buried composites for 6 months showed better weight loss than for 3 months exposure. Grafting of PMMA into lignocellulosic filler results in increased hydrophobicity of the filler, leading to proper wetting between matrix and filler, and consequently, a stronger interface is formed which is resistant to decay by microbes.

Figure 9 exhibits the loss in tensile strength and hardness of the composites. Again composites exposed to soil for 6 months exhibited better loss in mechanical properties than for 3 months exposure. Among the composites studied, minimum loss in tensile strength and hardness was found by comparatively highly grafted filler added composites. That is, chemical modification plays a major role in the deterioration of mechanical properties. PMMA grafting helps to improve the interaction between the filler and matrix. This might be the reason for better resistance of composites toward microbial attack.

SEM images of degraded composite surfaces

Figure 10 shows the SEM images of composites with different percentage grafting of PMMA after 3 months of soil burial. The microbial action on the surface of composites and the degradation of the composites are visible in the figure. The surface roughness after microbial attack was observed in all cases[29] [Figure 10 a-d]. This is due to the enhanced interaction between modified filler and the matrix[30] helped to increase the rate of biodegradation in a uniform rapid way. For the composites buried in the soil for 3 months, there were only little differences visible between the samples. This is due to the presence of non-biodegradable PMMA in the cellulose structure prevents the biodegradation process. Comparatively, the composites with minimum percentage grafting (h) of PMMA showed better biodegradation.

Figure 11 shows the SEM images of composites after 6 months of soil burial. Comparing with the previous case, the
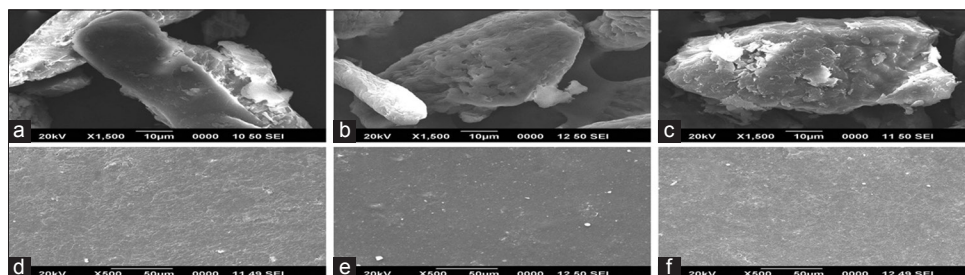

Figure 7: Scanning electron microscopy images of (a) coconut shell powder, (b) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP) (11.82 %G), (c) PMMA-g-ACSP (40.22 %G), (d) PMMA-g-ACSP/styrene-butadiene rubber (SBR) (11.82 %G), (e) PMMA-g-ACSP/SBR (24.55 %G), (f) PMMA-g-ACSP/SBR (40.22 %G)
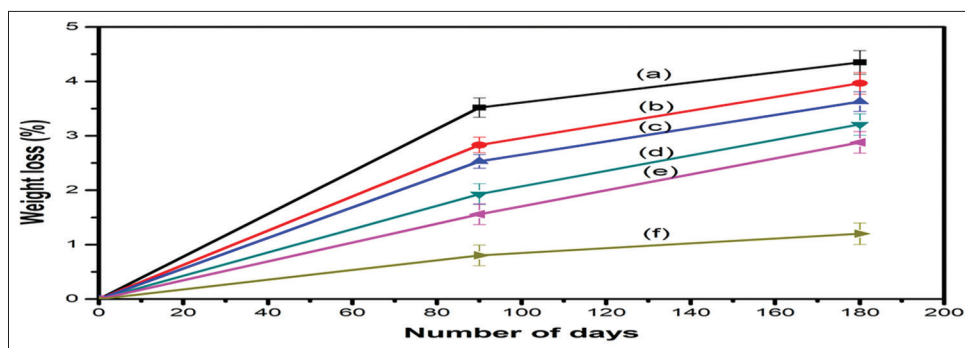

Figure 8: Weight loss of composites (a) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP) (11.82 %G), (b) PMMA-g-ACSP (17.64 %G), (c) PMMA-g-ACSP/styrene-butadiene rubber (SBR) (24.55 %G), (d) PMMA-g-ACSP/SBR (31.68 %G), (e) PMMA-g-ACSP/SBR (40.22 %G), (f) SBR
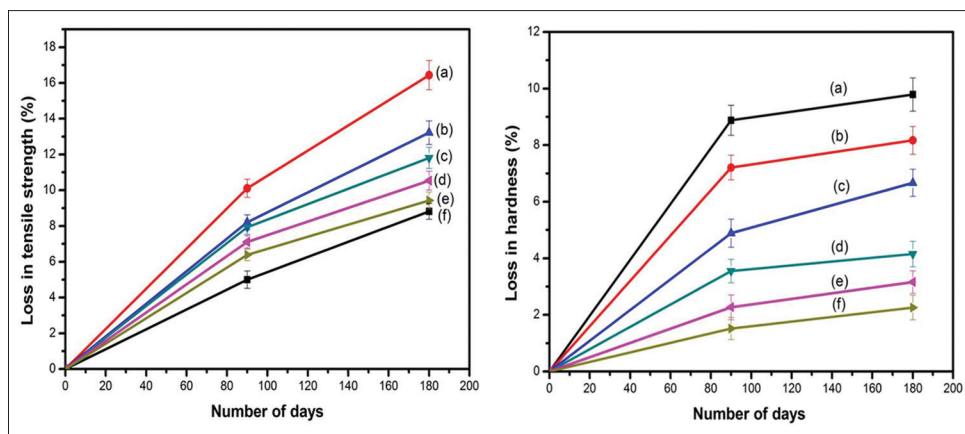
Figure 9: Loss in tensile strength and hardness of composites (a) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP) (11.82 %G), (b) PMMA-g-ACSP (17.64 %G), (c) PMMA-g-ACSP/styrene-butadiene rubber (SBR) (24.55 %G), (d) PMMA-g-ACSP/SBR (31.68 %G), (e) PMMA-g-ACSP/SBR (40.22 %G), (f) SBR
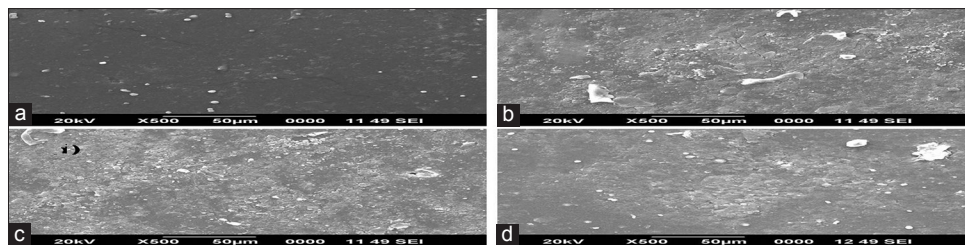

Figure 10: Scanning electron microscopy surface of composites exposed to soil for 3 months (a) styrene-butadiene rubber (SBR), (b) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP) (11.82 %G), (c) PMMA-g-ACSP/SBR (24.55 %G), (d) PMMA-g-ACSP/SBR (40.22 %G)

Figure 11: Scanning electron microscopy images of composites exposed to soil for 6 months (a) styrene-butadiene rubber (SBR), (b) poly (methyl methacrylate) (PMMA)-g-alkalized coconut shell powder (ACSP) (11.82 %G), (c) PMMA-g-ACSP/SBR (24.55 %G), (d) PMMA-g-ACSP/SBR (40.22 %G)
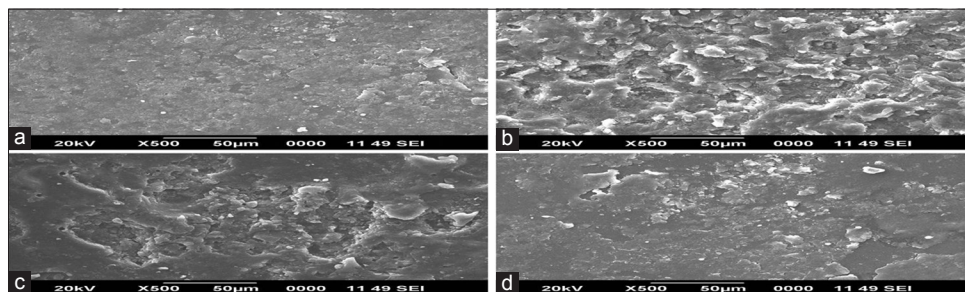
formation of cracks is more intense for composite with minimum percentage grafting of PMMA. The surface morphology studies add testimony to the results obtained from tensile, weight loss, and hardness studies after biodegradation tests.

CONCLUSION

The graft polymerization of MMA onto CSP has been successfully conducted. The graft copolymer was characterized by FTIR, XRD, and SEM which elucidated the change in structure in comparison with CSP. From the X-ray diffraction analysis, the crystallinity of the graft copolymers decreased with increase in grafting. Thermal studies revealed that the thermal stability of grafted product is higher than that of the neat CSP. Mechanical properties such as hardness, tensile

strength, and tear strength show an increasing trend with increase in percentage grafting of the filler. The results were in agreement with the SEM images. It is also concluded from the above discussion that the grafted product can be used as a reinforcing filler in SBR matrix. The biodegradation behavior of prepared composites was studied in soil burial environment for 3/6 months. The degradation of the composites was found to be dependent on chemical modification. The weight loss, tensile strength, and hardness decrease after soil burial testing due to the possible microbial attack or biodegradation of the composites. The decrease in mechanical properties was significant with percentage grafting of PMMA on the filler surface. The composite containing filler with 40.22 %G was found to be less prone to biodegradation due to better filler/matrix adhesion. Surface morphology studies were performed

using SEM to monitor the extent of degradation after 3 and 6 months of soil burial. The studies revealed that percentage grafting of PMMA onto the filler particles seriously affects the biodegradation process. The extent of biodegradation by microbial attack follows the order in composites as PMMA-*g*-ACSP/SBR (11.82 %G) > PMMA-*g*-ACSP/SBR (17.64 %G) > PMMA-*g*-ACSP/SBR (24.55 %G) > PMMA-*g*-ACSP/SBR (31.68 %G) > PMMA-*g*-ACSP/SBR (40.22 %G) > SBR.

ACKNOWLEDGMENT

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