

Study of Polyvinyl Chloride Composites Based on CaCO3 and Alkali Treated Coconut Fibers

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ABSTRACT

The present paper deals with mechanical and morphological study of polyvinyl chloride (PVC) hybrid-composites using CaCO3 as a filler and coconut fibers as a reinforcing material. A series of batches were compounded by using both, alkali-treated and untreated coconut fibers (1%, 3%, 5%, 7.5% to 10%) separately while the CaCO3 content was maintained uniform in all the formulations. The formulation was first dry blended and then compounded on a two-roll mill. The dry blended composition was then compression molded into sheets in the temperature range of 160-180°C. A study was done as per ASTM standards to evaluate tensile properties, impact strength, shore hardness, coefficient of friction, water absorption and using SEM. The mechanical properties keep on increasing till the coir content (treated and untreated) reaches 5% and then starts decreasing beyond 5%. Alkali treated fiber composites have shown superior properties to untreated ones. SEM study supports the fact that the alkali treated fiber reinforced composites are morphologically more uniform than untreated ones resulting in better properties.

Keywords: Polymer Composites, Natural Fiber Reinforcement, Polyvinyl Chloride Composite, Coconut Fibers.

I. INTRODUCTION

The past few decades have seen a great upsurge in research on polymer composites, as these materials can offer enhanced mechanical properties and low cost as compared to virgin polymers. This resurgence of interest is due to the increasing cost of plastics and also because of the environmental aspects of using renewable and biodegradable materials. The advantage of composite materials over conventional materials stems largely from their higher specific strength, stiffness and fatigue characteristics, which enables structural design to be more versatile. Work has been conducted on a wide variety of polymers, including thermoplastics, such as styrenics, polyolefins, etc. and thermosetting materials, such as epoxy resins and phenolics.

A wide research has been carried out on fiber reinforced polymer composites [1-7]. Flax fiber reinforced polyolefins are extensively used today in the automotive industry, but the fiber acts mainly as filler material in non-structural interior panels [8]. Natural fiber composites used for structural purposes do exist, but then usually with synthetic thermoset matrices which, of course, limit the environmental benefits [9]. Natural fibers such as jute, sisal, pineapple, abaca and coir have been studied as a reinforcement and filler in composites [10-12].

The use of inorganic fillers has been practiced for many decades in both elastomeric and plastic materials. It has been reported that simultaneous enhancement of toughness and stiffness can be achieved in polymer/rigid particle system, e.g. PVC/CaCO₃ [13] and HDPE/CaCO₃ [14-15]. To incorporate mineral filler into a polymer, coupling agent is generally used in order to improve the dispersion and bonding of the filler [14-15]. Use of nanoparticulate calcium carbonate to toughen the PVC/CaCO₃ has also been reported.

A strong fiber-matrix interface bond is critical for high mechanical properties of composites. A good interfacial bond is required for effective stress transfer from the matrix to the fiber whereby maximum utilization of the fiber strength in the composite is achieved [16]. There is a limited compatibility between the natural fibers and thermoplastic matrices due to their strong hydrophilic character; which can be improved by surface treatment or chemical modification of the natural fibers. Modification to the fiber also improves resistance to moisture induced degradation of the interface and the composite properties [17]. In addition, factors like processing conditions/techniques have significant influence on the mechanical properties of fiber reinforced composites [18]. Jute has been treated with alkali, for the composite to have good bonding between the fiber and the resin matrix. A process known as mercerization has been commercialized for cotton fibers for superior reactivity with dyes [19]. Several authors have investigated the changes occurring in the fiber properties due to alkali treatment of jute [20-21]. Jute fibers have been treated with NaOH solution of concentration 1%, 8% for 48 h and 2% for 1 h and showed improvements in fiber properties [20, 22]. Similar treatments were attempted on isometric jute varns and reported an improvement of 120% and 150% in the tensile strength and modulus respectively when treated with 25% NaOH solution for 20 min and 60% improvement in the jute/epoxy composite properties reinforced with these treated yarns. The improvements have been attributed to the greater reactivity of the treated fibers with the resin administering superior bonding [23-25]. Coir has also been tested as filler or reinforcement in different composite materials [26, 27].

There is a considerable attention in the research community as well as in industry on composite materials where coconut fiber is used as reinforcing filler. Growing attention is nowadays being paid to coconut fiber due to its low cost and availability. This is also due to a range of potential advantages of coconut fibers, such as low specific weight, low cost of production, easy processing, and good thermal and acoustic insulating properties. Over 50% of the coconut fiber produced annually throughout the world is consumed in the countries of origin [28]. Because of its hard-wearing quality, durability and other advantages; it is used for making a wide variety of floor furnishing materials, yarn, rope etc [29]. However, these traditional coir products consume only a small percentage of the potential total world production of coconut husk. Hence, research and development efforts have been underway to find new use areas for coir, including utilization of coir as reinforcement in polymer composites [30-32].

The main objective of the current work is to formulate a series of hybrid composites by varying the coir content in various formulations of PVC/coir/CaCO₃, with and without alkali treatment of coir and to study mechanical and morphological properties of the same.

II. METHODS AND MATERIAL

PVC resin (57 GE R01 suspension grade suitable for injection and compression molding in powder form obtained from Reliance Industries India Ltd.) was used as a polymer matrix. Calcium carbonate (CaCO₃), dioctyl phthalate (DOP), tri basic lead sulphate (TBLS), ethylene vinyl acetate polymer (EVA), low density polyethylene (LDPE), calcium stearate, titanium dioxide (TiO₂) were obtained from various commercial sources and were either used directly or after purification and /or drying as per the standard procedure. Coconut fibers (coir) were obtained from coconut husk and were either treated with alkali or used directly after drying.

Tensile properties were measured using dumb-bell shaped specimens on a tensile testing machine, Model No STS-248, India, according to ASTM D638M-91 procedure at 100% strain rate; the crosshead speed of 50 mm/min was maintained for testing. The values of tensile modulus were also determined at low strains. Optical extensometer was used to measure tensile modulus accurately. Izod impact strength values were evaluated on a Zwick Izod Impact tester (Digital), Model No: S102, Germany, according to ASTM D256 test procedure using notched samples. The average values of the mechanical properties and their standard deviations have been reported. All mechanical tests were performed at room temperature. A JEOL, JSM-6380 Scanning Electron Microscope (SEM) was used to evaluate the dispersion of reinforcing fibers and filler in the polymer matrix. The freshly cut plastic surface was used to take SEM micrograph. Coefficient of friction was determined by using inclined surface coefficient of friction (slide angle) tester as per TAPPI T815 standards.

A. Chemical Treatment of Coconut Fibers

The coconut fibers obtained from coconut husk were cleaned, dried and were cut into approximately 2 cm length. The fibers were soaked in excess of 5% aqueous alkali (NaOH) solution for 4h at room temperature. The treated (soaked) fibers were then removed from alkali solution and washed with distilled water to remove traces of alkali and dried at 60°C for 48 h before use [33].

B. Compounding and Processing

A series of formulations using PVC/CaCO₃/coir were prepared in the present investigation. Table 1 presents the detailed compositions of various batch formulations used in the present work. Compounding of PVC resin was done using various additives and

fillers in sigma mixer rotating at about 1500 rpm. The steps involved initial addition of processing aid and lead stabilizer to the polymer matrix and fillers. This was followed by addition of lubricants and dioctyl phthalate (DOP) after the mixture reached 80-85°C. The mixing

was continued till the temperature reached 110-115°C. The mixture was cooled and previously dried coconut fibers (treated or untreated) were added and mixed uniformly for next 10 min. The mixture was then subjected to a two-roll mill and compounded at 80°C. The uniformly compounded material was then compression molded in the form of sheets in 160 -180°C temperature range using a compression mold having 3.2 mm cavity. The sheets thus obtained were used for mechanical and morphological evaluation purpose.

Formulation	PVC %	Fiber %	CaCO ₃ %	EVA/LDPE	TiO ₂ %	TBLS %	Calcium	DOP %
*				%			Stearate %	
1	29.43	0	50	8.24	1	2.74	1.09	7.5
2	29.43	1	50	8.24	1	2.74	1.09	7.5
3	29.43	3	50	8.24	1	2.74	1.09	7.5
4	29.43	5	50	8.24	1	2.74	1.09	7.5
5	29.43	7.5	50	8.24	1	2.74	1.09	7.5
6	29.43	10	50	8.24	1	2.74	1.09	7.5

* Same formulation (1-6) was repeated for treated and untreated coconut fibers.

III. RESULTS AND DISCUSSIONS

The present work was intended to study the mechanical and morphological behavior of various formulations of PVC filled with CaCO₃ and coir. In the present system of PVC/coir/CaCO₃, the content of other additives viz. CaCO₃, EVA/LDPE, TBLS, DOP, TiO₂ and calcium stearate were kept constant. However, the coir content was varied from zero to 10 % of total formulation, as it was aimed to study the effect of reinforcing material content on composite properties. In the present study EVA/LDPE was used as processing aid, CaCO₃ as inorganic filler while calcium stearate was used as a lubricant. Tri basic lead sulphate (TBLS) was used as a stabilizer and DOP was used to plasticize the system. The role of TiO₂ was as a pigment.

It is known that coir fiber includes 5.25% water soluble compounds, 3.00% pectin and related compounds, 0.25% hemicellulose, 45.84% lignin, 43.44% cellulose and 2.22% In the present work too, alkali treatment of coir fibers ash. Cellulose fibers are generally lignocellulosic consisting of helically wound cellulose microfibrils in an amorphous matrix of lignin and hemicelluloses that run along the length of the fiber. When these fibers are

treated with alkali, loss in weight was observed due to heavy dissolution of lignin and hemicellulose content and the strands became well separated and dispersed into microfibrils. The modulus of the jute fibers was found to be increased when treated. The tenacity at break point also increased while percentage breaking strain was reduced [33]. It was imperative that the fibers became stiff and brittle on account of its high strength and low extensibility. Similar increase in strength of jute fibers on alkali treatment has also been reported [20].

The study on the influence of lignin content on the mechanical behavior of jute found a gradual decrease in both the strength and stiffness of the fiber with lignin removal. The extensibility of the fiber was also found to follow the same trend [33]. Similar experiments, which were carried out on sugarcane fiber provided additional evidence of the significant contribution of lignin to fiber strength.

led to removal of lignin and hemicellulose matrix from the clumps of coconut fiber. The combined effect of alkali treatment and milling (on two roll mill) has led to the formation of separated micro and nanofibers. Similar

kinds of observations have been reported earlier [34]. The SEM study, in the present investigation exhibits separated microfibers in treated coir filled specimens as compared to that of untreated coir filled specimens where the fibers are intact. The coconut fibers were observed in the form of micro and nanofibers having lowest diameter around 50 nm as shown in Figure 5(a) for treated fibers while it was above 300 nm for untreated ones (Figure 5(b)).

A. Mechanical Properties

The present work was divided into two parts for the systematic study of composite materials. First part consisted of six samples where alkali treated coir was used while the other part i.e. part two involved use of untreated coir fibers. The study involved comparison of both, mechanical and morphological properties of treated as well as untreated coconut fiber filled composite materials. Fig. 1 represents tensile strength of the samples from both parts (i.e. treated and untreated coir fiber samples). It is seen that as the percentage of reinforcing filler (treated and untreated both) goes on increasing from 0 to 10 % the tensile strength also increases till filler content reaches 5% and then it starts declining, irrespective of treatment given to the fiber. Similar observations are recorded earlier [35]. However; treated fiber composites have shown higher values of tensile strength and modulus as compared to that of untreated ones for every formulation.

The impact strength of the specimens tested also follow similar trend as that of tensile properties. The impact strength also keeps on increasing till the coir content (treated and untreated) reaches 5% and starts decreasing beyond 5%. When compared, it was observed that the treated fiber composites exhibited higher impact property values as compared to that of untreated fibers for every formulation. This observation was very much similar to the tensile strength study where the similar trend is observed.



Figure 1. Tensile Strength versus % coconut fiber



Figure 2. Impact Strength versus % coconut fiber The above observations i.e. higher tensile and impact properties for treated fibers as compared to that of untreated ones and decline in properties after certain percentage (i.e. 5% in the present study) of reinforcing fibers can be interpreted based on following observations.

The improvement in mechanical properties of treated coir fibers can primarily be attributed to the superior bonding between the coir fibers and polymer matrix. This is because when coir is treated with alkali there is dissolution of hemicelluloses layer surrounding the fibers that leads to improved impregnation of fibers in polymer matrix and hence improved mechanical properties.

Another theory to support the improved mechanical properties of treated fiber composites can be explained as, when fibers are treated with alkali, the fiber strands become well separated and get dispersed due to dissolution of hemicelluloses and lignin to from micro and nanofibers. It is well established fact that lignin provides strength and stiffness to the microfibers in natural materials. The incorporation of these micro and nanofibers into PVC matrix in the present study is associated with replacement of lignin (due to alkali treatment) with polymer matrix. That is the micro and nanofibrils are embedded in PVC matrix instead of lignin as observed in natural polymers. The PVC matrix, in absence of lignin, provides strength and stiffness to the composite material. In addition the treated fibers as such show improved properties due to increased crystallinity, tenacity and modulus than raw fibers. This explains for the increased mechanical properties of the treated fiber reinforced composite material.

There is initial decrease in values of mechanical properties in case of untreated fiber composites where as treated fiber composites show improvement in values. At low fiber volume fraction, a drastic decrease in tensile strength is usually observed. This has been explained with dilution of the matrix and introduction of flaws at the fiber ends where high stress concentrations occur, causing the bond between fiber and matrix to break. At high fiber volume fraction, the matrix is sufficiently restrained and the stress is more evenly distributed. This results in the reinforcement effect outweighing the dilution effect. As the volume fraction of fibers is increased to a higher level, the tensile properties gradually improve to give strength higher than that of the matrix. At very high fiber volume fraction, the strength again decreases due to insufficient matrix material. The decline in properties can also be due to a lack of fiber dispersion owing to the wide differences in polarity and also the strong intermolecular hydrogen bonding between the fibers at higher concentration. This lack of fiber dispersion can result in clumping and agglomeration of cellulosic fibers which will act as stress concentration points to initiate cracks during loading. This effect contributes to inferior mechanical properties at higher concentration of fibers.

The reinforcement caused by fibers in the thermoplastic matrix is governed by the parameters like fiber dispersion, fiber-matrix adhesion, fiber aspect ratio, fiber orientation, and fiber volume fraction.

Good dispersion is the one where fibers are separated from each other (i.e. there are no clumps and agglomerates), and each fiber is surrounded by the matrix (polymer). After alkali treatment the fibers get separated while the untreated fibers are in the form of clumps. These fiber-rich areas (i.e., clumps) lead to an inhomogeneous mixture and are susceptible to microcracking. Microcracks contribute to inferior mechanical properties of composites. Moreover the untreated, raw fibers have 'natural' matrix that is loosely held on the surface of the fiber. This loosely held matrix acts as a stress concentration point and lead to failure. This is indeed the case in the present work. That is, comparative study of treated and untreated fibers revealed the fact that the treated ones exhibit better properties as compared to that of untreated ones which is clearly seen in Figure 1 and 2.

B. Coefficient of Friction

The property, coefficient of friction, exhibited irregular trend in the present study irrespective of the treatment given to the fibers. The irregularity in the trend can be attributed to the uneven appearance of coir fibers on the surface which can be seen visually on the compression molded



Figure 3. Coefficient of friction versus % coconut fiber

specimen. Though the filler is abrasive in nature, unevenness of appearance of fibers on the surface of the compression molded sheet might have lead to inconsistent contact with the friction surface, leading to irregular trend in as seen in Fig. 3. However, as a gross effect of filler content on coefficient of friction, the study suggests that there is a positive bias on the improvement of coefficient of friction.

C. Shore Hardness

Figure 4. represents a comparison of shore A hardness for all specimens. No definite trend was observed for the untreated samples. The polymer where highest (10%) untreated filler was used exhibited highest value of hardness. However, in case of treated fibers, the observation is in line with the earlier observations made for tensile and impact properties. That is, after initial increase of hardness at 1% filler, it retains the hardness till 5% addition, from where it starts decreasing. Though there is no definite trend, the unfilled polymer (0% filler) shows lower shore A hardness as compared to that of filled polymers, irrespective of chemical treatment given to the fibers in general.



Figure 4. Shore hardness versus % coconut fiber

D. Water Absorption

Preliminary experiments have shown that the composites with alkali treated fibers shows less water absorption in comparison to the untreated fiber composites, though water absorption increases with increasing percentage of fibers. Similar observations have been made in an earlier work where the study was conducted on effect of alkali treatment on water absorption of abaca fibers [35].

E. Scanning Electron Microscopy

Morphological behavior of the composite was studied by scanning electron microscopy (SEM). Fig. 5 a, b,









Figure 5. SEM of (a) alkali treated 10%, (b) untreated 10%,(c) alkali treated 5% and (d) untreated 5% coconut fibers

c, d represent scanning electron micrographs of the composite materials of alkali treated 10%, untreated 10%, alkali treated 5% and untreated 5% coir fibers respectively. The observations made by SEM supports the mechanical behavior observed in the present study as mentioned above. It was seen that, in general, there was improvement in mechanical properties of the reinforced composite samples. Moreover, alkali treated fibers lead to improved properties than that of untreated ones. When compared, Fig. 5a-d, it is clearly seen that the coir fibers in untreated samples (Fig. 5: b,d) are in clusters

where as the treated ones (Fig. 5: a,c) show finely separated fibers (microfibrils). In addition the SEM observation also supports the behavior that above 5% coir fibers the mechanical properties start deteriorating. As it is clearly seen that when the fiber loading is 5% (Fig. 5: c, d) the fibers can scarcely be seen in SEM indicating it is well impregnated in polymer matrix where as 10% loading samples (Fig. 5: a, b) in polymer show abundance of fibers. Also the higher fraction of fibers in polymer led to non uniform distribution of fibers in polymer matrix leading to voids whereas at lower loading percentage the fiber-polymer matrix compatibility is quite uniform with less voids as seen in SEM. The presence of voids in polymer composite leads to stress concentration points leading to failure of composites as observed in the present study whereas the samples with fiber loading till 5% have shown increase in mechanical properties.

TABLE 2: COMPARISON OF PROPERTIES OF TREATED AND UNTREATED COCONUT FIBER FILLED COMPOSITE MATERIAL

Property	Sample	0 %	1 %	3 %	5 %	7.5 %	10 %
Tensile strength (Mpa)	Treated	18	22	24	27	21.68	13.54
	Untreated	18	12.81	19.34	21.45	19.31	11.14
Impact strength	Treated	5.3	7.43	7.48	7.95	5.5	4.7
(Kg cm/cm)	Untreated	5.3	4.68	6.10	6.7	4.8	4.5
Shore hardness	Treated	95.33	97.33	97.33	97.33	96.66	96.66
ASTM D 1706-61	Untreated	95.33	96.83	95.83	95.83	96.83	97.66
Coefficient of friction	Treated	0.2004	0.2156	0.1943	0.2229	0.2376	0.2216
	Untreated	0.2004	0.1763	0.2125	0.2555	0.1793	0.2370
Water absorption %	Treated	0	0.007	0.016	0.026	0.063	0.094
	Untreated	0	0.031	0.032	0.034	0.065	0.099

IV. CONCLUSION

The present study revealed that both alkali treated and untreated coir fiber based composite have shown improvement in mechanical properties. The mechanical properties keep on increasing till the coir content (treated and untreated) reaches 5% and starts decreasing beyond 5%. Amongst the both, alkali treated fiber based composites have shown superior properties to untreated ones. This is attributed to superior bonding, microfibril formation in alkali treated coir fibers (due to alkali treatment and milling) and uniform impregnation of these coir micro fibrils in polymer matrix. SEM study supports the fact that the alkali treated fiber reinforced composites are morphologically more uniform to untreated ones.

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VI. REFERENCES

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