

Recycled Milk Pouch and Virgin Low-Density Polyethylene/Linear Low-Density Polyethylene Based Coir Fiber Composites

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ABSTRACT: The viability of the thermomechanical recycling of postconsumer milk pouches [a 50 : 50 low-density polyethylene/linear low-density polyethylene (LDPE–LLDPE) blend] and their use as polymeric matrices for coir-fiber-reinforced composites were investigated. The mechanical, thermal, morphological, and water absorption properties of recycled milk pouch polymer/coir fiber composites with different treated and untreated fiber contents were evaluated and compared with those of virgin LDPE–LLDPE/coir fiber composites. The water absorption of the composites measured at three different temperatures (25, 45, and 75°C) was found to follow Fickian diffusion. The mechanical properties of the composites significantly deteriorated after water absorption. The recycled polymer/coir fiber composites showed inferior mechanical perform-

ances and thermooxidative stability (oxidation induction time and oxidation temperature) in comparison with those observed for virgin polymer/fiber composites. However, a small quantity of a coupling agent (2 wt %) significantly improved all the mechanical, thermal, and moisture-resistance properties of both types of composites. The overall mechanical performances of the composites containing recycled and virgin polymer matrices were correlated by the phase morphology, as observed with scanning electron microscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 775–785, 2007

Key words: composites; fibers; mechanical properties; morphology; polyethylene (PE); recycling; thermal properties

INTRODUCTION

A huge quantity of polyethylene, particularly low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE), is consumed for the flexible packaging of liquid milk in India. It has been reported that around 33,000 metric tons of polyethylene was consumed for the packaging of liquid milk in India in 1995, and this consumption increased to 40,000 metric tons in 1997.^{1,2} In practice, such a packaging trend enhances the volume of polyethylene packaging waste in municipal and domestic garbage after a short service life, causing serious problems in society. Moreover, the huge consumption of polyethylene in the milk packaging sector also reduces petroleum reserves. Therefore, the effort to reduce, recycle, and reuse these postconsumer packaging films has become a challenging task to avoid adverse environmental impact and to restrict the consumption of raw materials.

Natural fibers, such as wood, sisal, jute, hemp, and coir, are now established as reinforcing fibers

used to produce newly developed composite materials with polymers. The natural fibers have several advantages, such as low densities, less abrasiveness, and low costs, over traditional glass and organic fibers (aramid and carbon fibers). These are also ecofriendly because of their biodegradability and renewable characteristics.^{3–5} Many reports are available in the area of wood-fiber-reinforced,^{6–8} jute-fiber-reinforced,^{9–13} sisal-fiber-reinforced,^{14–16} and coir-fiber-reinforced (*Cocos nucifera*)^{17–20} virgin thermoplastic composites. The main drawback of these natural fiber/polymer composites is the inherent incompatibility between hydrophilic fibers and hydrophobic thermoplastic matrices, which calls for improving the fiber–matrix interfacial adhesion through the use of compatibilizers or coupling agents.^{8,21,22}

The degrading nature of natural fiber composites under exposure to environmental conditions such as humidity, sunlight, and microorganisms is one of the most important issues in finding suitable outdoor applications. In fact, several companies now manufacture wood fiber/thermoplastic composites for use as synthetic lumber in applications such as decking and window frames.^{23,24} The poor moisture resistance of natural fibers degrades the mechanical

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performance and dimensional stability of the polymer composites.^{25–28} Recently, Espert et al.²⁹ described the water absorption behavior of cellulosic-fiber-based polypropylene (PP) composites, using ethylene vinyl acetate as a coupling agent. They observed that the water absorption in the composites increased from approximately 2 to approximately 6% when they increased the fiber content from 10 to 30%, and they also observed that the moisture absorption reduced the tensile stress (16–24%) and moduli (21–35%) of the composites. Fraga et al.³⁰ used gravimetric and dielectric measurements to determine the water absorption in glass and jute fiber composites with unsaturated polyester as a matrix. They recorded a maximum water absorption of approximately 8.2% for jute composites (fiber content = 38–40%). Arbelaiz et al.³¹ observed that the equilibrium water uptake of unmodified short flax fiber/PP composites increased from 5.9 (diffusion coefficient = 1.5×10^9 cm²/s) to 13.9% (diffusion coefficient = 17.5×10^9 cm²/s) when they increased the fiber content from 30 to 60%, but the use of maleic anhydride grafted PP as a coupling agent reduced the affinity of the composites to water. The moisture absorption also reduced the tensile strength and tensile moduli of the composites to approximately 15–18 and approximately 20–25% in comparison with those observed for the untreated composites.

Today there is growing importance in producing composite products from recycled plastics. Although most research in this area has been concentrated on the use of homogeneous polymer wastes to produce fiber-reinforced composites, similar investigations with heterogeneous polymer waste have not received much attention. Many authors have studied the effects of the fiber loading and coupling agent on the mechanical properties of homogeneous polyolefin waste/natural fiber composites.^{32–36} They observed that the mechanical performances of the composites decreased with increasing fiber content but significantly improved with the incorporation of a suitable coupling agent. Selke and Wichman³⁷ reported comparative studies of the mechanical performances of recycled high-density polyethylene (HDPE; waste milk bottle)/wood fiber composites and virgin HDPE/wood composites. The recycled HDPE/flax fiber composites showed greater variability in the me-

chanical properties with high fiber contents, whereas fiber contents of 15–20% were optimum to maximize the mechanical properties of the composites.³⁸

In this investigation, we used thermomechanically recycled postconsumer milk pouches made of an LDPE–LLDPE blend as matrix materials in producing coir-fiber-reinforced composites for engineering applications. The mechanical, thermal, morphological, and water absorption properties of the coir-fiber-reinforced recycled polymer composites were compared with those of virgin polymer/fiber composites with or without the use of styrene maleic anhydride (SMA) as a coupling agent. The effects of the fiber content, coupling agent, and kinetics of water absorption at different temperatures for the composites were studied. The changes in the mechanical properties of the composites due to water absorption were also evaluated.

EXPERIMENTAL

Materials

Postconsumer milk pouches, composed of a 50 : 50 (w/w) LDPE–LLDPE blend, were collected from the municipal dustbin of Ranchi City, India. The collected waste films were contaminated with small amounts of a possible pigment, a stabilizer, a slip agent, and a labeling dye. Table I shows the specifications of the polymers used in the manufacture of milk pouch films (Bihar State Co-Operative Milk Producers Federation, Ltd., Patna, India) used in this investigation. The virgin LDPE (1005FY20) and LLDPE (LL20FS010) used in making the control blend for comparison were obtained from Indian Petrochemical Corp., Ltd. (Vadodara, India). The detergent used for washing was obtained from Nirma India, Ltd. (Ahmedabad, India).

The short coir fibers were collected from the Ministry of Agro & Rural Industries (Assam, India). The physical, chemical, and mechanical properties of the coir fibers are presented in Table II. Sodium hydroxide (NaOH), used for the chemical treatment of the fibers, was obtained from E. Merck India, Ltd. (Mumbai, India). SMA (DYLARK238F20, Nova Chemicals, Thane, India) was used as a coupling agent in this investigation.

TABLE I
Specifications of the Polymers Contained in Waste Milk Pouches

Polymer	Composition (wt %)	Grade	Comonomer	MFI (g/10 min) ^a	Density (g/cm ³)	Tensile strength (MPa) ^b	Elongation (%) ^b
LDPE	50	1005FY20	None	0.4–0.7	0.921–0.923	21.0/19.6	300/500
LLDPE	50	LL20FS010	1-Octene	1.0	0.918–0.920	39.2/29.4	700/800

^a Melt flow index at 190°C with a load of 2.16 kg.

^b Machine direction/transverse direction.

TABLE II
Physical, Chemical, and Mechanical Properties of the Coir Fibers

Fiber	Average diameter (μm)	Average length (mm)	Density (g/cm^3)	Water absorption (%)	Cellulose (%)	Lignin (%)	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation (%)
Coir	40	6.3	1.2–1.3	9–10	43.44	45.84	185	24–26	30

Methods

Pretreatment of the waste milk pouches and blend preparation

Chopping, washing, and drying of the postconsumer milk pouches. The collected waste milk pouches were shredded with a chopping device into small fragments and then washed with a hot aqueous solution of 12% detergent and 5% NaOH at 60°C, and this was followed by repeated washing with cold water. The chopped and cleaned pouch films were subsequently dried in a vacuum oven (0.657 atm) at 50°C for 12 h.

Melt reprocessing of the milk pouch films. The washed and dried milk pouch films were melt-reprocessed (extruded) by a Rheomex 254 single-screw extruder (Goettfert, Germany) fitted with a Haake Rheocord 9000 driving unit (Goettfert, Germany). The processing conditions followed for this extrusion are presented in Table III. The extruded mass was cooled by being passed through water and subsequently pelletized. The recycled material in the pelletized form was dried at 50°C in a vacuum oven (0.657 atm) for 12 h before being subjected to any subsequent steps.

Blending of virgin LDPE and LLDPE. The blend of virgin LDPE and LLDPE (50 : 50 w/w) was prepared with a Rheomex 254 single-screw extruder fitted with a Haake Rheocord 9000 driving unit under the same processing conditions (Table III) as those followed in the aforementioned extrusion process. Similarly, the extruded mass was cooled and pelletized. The pelletized mass was dried in a vacuum oven (0.657 atm) at 50°C for 12 h.

Chemical treatment of the coir fibers

The short coir fibers (~ 6.3 mm) were thoroughly washed with an aqueous detergent solution to remove dirt, were washed with distilled water, and were dried in a vacuum oven at 60°C for 24 h.

Alkali treatment. The washed fibers were immersed in a 5% aqueous NaOH solution for 1 h at 30°C, and this was followed by washing with 0.1N acetic acid and distilled water. The alkali-treated fibers were then dried in a vacuum oven at 60°C for 2 days to obtain mercerized fibers.

Coupling agent treatment. The mercerized coir fibers were immersed in a hot 2% SMA solution (in acetone) at 50°C for 20 min to obtain coupling-agent-coated fibers.

Composite fabrication

Composite mixtures were prepared by the melt mixing of the compatibilized and noncompatibilized coir fibers with recycled milk pouch polymers and virgin LDPE–LLDPE blends in a Haake Rheomix at 130°C with roller blades and a mixing chamber with a 60-cm³ volumetric capacity. The process was carried out for 10 min at an optimum speed of 50–60 rpm, which depended on the quantity of the fibers by weight. Each batch contained various weight percentages of the fibers (10, 20, and 30%). The composite formulations are shown in Table IV.

Each composite mixture was then homogenized in a two-roll mill (150E-400, Collins, Germany) at 130°C and compression-molded with a Delta Malikson 100TY pressman (Mumbai, India) to produce composite sheets (3 ± 0.2 mm thick).

Test specimens were prepared from these sheets according to ASTM Standard D with a counter-cut copy milling machine (6490, Ceast, Italy) with calibrated templates.

Water absorption

The water absorption analysis of the composite samples was carried out according to ASTM Standard D 570-98. Five samples from each batch were immersed in distilled water at different temperatures (25, 45, and 75°C). The samples were removed from the water after certain times (25, 50, 75, 100, 125, 150, 175, and 200 h), weighed in a high-precision balance, and then immersed again in the water. The water content was calculated from the weight difference. After equilibrium water absorption, the composite specimens were removed, dried, and subjected to tensile tests to evaluate the effect of water absorption on the mechanical properties of the composites.

TABLE III
Conditions Used for the Rheomex 254 Single-Screw Extruder

Process	Temperature (°C)				Water bath	Screw speed (rpm)
	Zone 1	Zone 2	Zone 3	Zone 4		
Extrusion	190	200	210	220	30–35	60

TABLE IV
Formulations of Recycled Milk Pouch and Virgin LDPE–LLDPE Blend Based Coir Fiber Composites

Ingredient (parts by weight)	Formulation number													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Virgin LDPE–LLDPE	100	—	90	—	80	—	70	—	90	—	80	—	70	—
Recycled milk pouch	—	100	—	90	—	80	—	70	—	90	—	80	—	70
Coir fiber	—	—	10	10	20	20	30	30	10	10	20	20	30	30
SMA (coupling agent)	—	—	—	—	—	—	—	—	2	2	2	2	2	2

Characterization

Tensile tests

Dumbbell specimens (type I) for tensile tests were prepared according to ASTM D 638. The tensile measurements of the samples were conducted with an Instron 3366 tensile test machine (Grove City, PA) at a crosshead speed of 50 mm/min. The samples were conditioned at 23°C with 50% relative humidity for 40 h before testing.

Differential scanning calorimetry (DSC) analysis

The thermooxidative stability, in terms of the oxidation induction time (OIT) and oxidation temperature (OT), for all polymer matrices and composite samples was evaluated with a TA 10Q-DSC analyzer (New Castle, DE). The OIT was measured according to the E1858 method (static OIT method), in which each sample was initially loaded at the ambient temperature (50°C) and then heated at 10°C/min to the isothermal test temperature (200°C) in a nitrogen atmosphere. The sample was held at this temperature for 5 min. The purge gas was then switched from nitrogen to oxygen at 50 mL/min, and the elapsed time clock was set to zero. The oxidation reaction normally occurred after a certain period. The time to the onset of the oxidation exotherm was measured and reported as OIT in minutes.

The OT was determined by the heating of the sample from 30 to 350°C at a heating rate of 10°C/min in an oxygen atmosphere. The onset and peak temperatures of the oxidation exothermic peak are reported as OTs (°C).

Scanning electron microscopy (SEM) analysis

To study the morphological features of the fiber–matrix interface in the SMA-treated and untreated composites, the tensile test samples were fractured after 15–20 min of freezing in liquid nitrogen. The fractured surfaces were sputtered with gold and analyzed with a JEOL JSM 5000 scanning electron microscope (Peabody, MA).

RESULTS AND DISCUSSION

Water absorption study

Water diffusion in natural fiber/polymer composites was conducted by two possible mechanisms: (1) the direct diffusion of water molecules through the microgaps between polymer chains and (2) the direct diffusion of water molecules through capillary transport into the gaps and flaws at the interfaces between the fiber and matrix.^{27,39} The extent of water diffusion depends on the internal material states, such as debonding at the fiber–matrix interface, matrix cracking, and inherent absorption properties of the constituent materials, and on environmental conditions, such as the temperature. In this study, the amount of water absorption in differently formulated composites was calculated from the weight difference between the samples exposed to water and the dry samples. Figure 1 shows the variation of the water absorption with increasing time for different recycled milk pouch polymer/coir fiber and virgin LDPE–LLDPE blend/coir fiber composites. The water absorption in the composites increased sharply with time up to 50 h, and this was followed by a gradual approach to a saturation point (or equilibrium sorption), beyond which no more water was absorbed till 200 h. Figure 1(a) shows the change in the water uptake with time at different temperatures for a 70/30 recycled polymer/coir fiber composite (formulation 8). The water absorption tendency of the composite significantly increased (~ 30%) with increasing temperature (i.e., from 25 to 75°C). The water uptake (%) of the composites increased also with increasing fiber content, as shown in Figure 1(b), and this was due to the hydrophilic character of the coir fibers. The recycled milk pouch polymer/fiber composites showed a greater tendency to water absorption than the virgin LDPE–LLDPE/fiber composites. This observation could be attributed to the structural irregularity of the recycled polymer as a result of thermooxidative degradation (crosslinking reaction) during recycling,⁴⁰ which created disordered fiber distribution and orientation in the matrix or clumping of fibers during the mixing process, resulting in weak fiber–matrix interfacial bonding.³⁷ A substantial decrease in the water

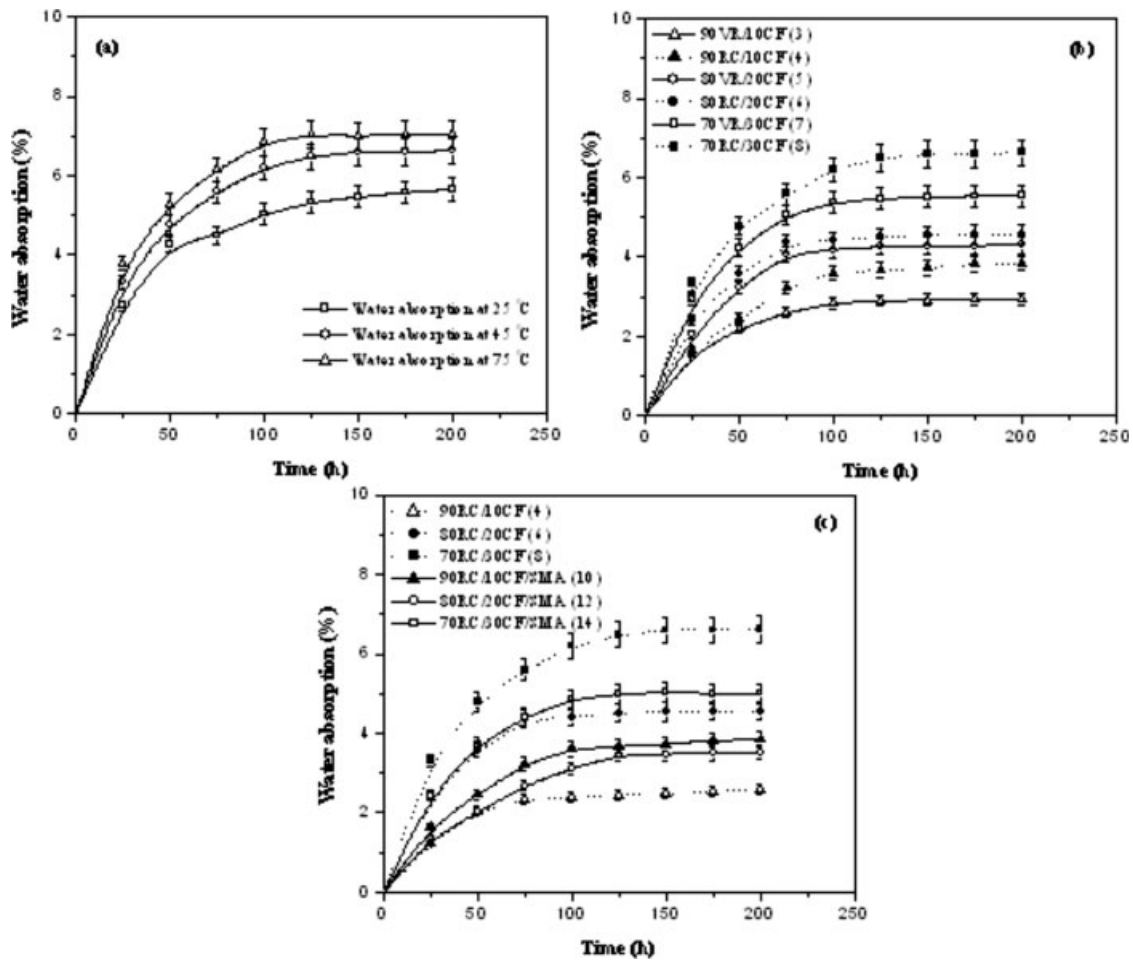


Figure 1 Effect of (a) the temperature (for 70/30 recycled polymer/fiber composites), (b) the fiber content (45°C), and (c) the coupling agent (25°C) on the water absorption in different composites.

absorption was observed for the composites containing SMA (coupling agent)-treated fibers in comparison with the untreated fiber composites [Fig. 1(c)]. This reduction in the water uptake for the compatibilized composites is attributed to an improvement in fiber-matrix interfacial bonding, which reduces water accumulation in the interfacial microgaps or voids and prevents water from entering the fibers.

In general, moisture absorption in natural-fiber-reinforced polymer composites follows Fickian diffusion behavior, in which the rate of the diffusion of the penetrant is much less than that of the polymer segment relaxation. An analysis of the water diffusion behavior and kinetics for the composite samples was performed according to Fick’s theory. The experimental values were fitted to Fick’s equation:

$$\log\left(\frac{M_t}{M_\infty}\right) = \log(k) + n \log(t) \quad (1)$$

where M_t is the water content at time t , M_∞ is the water content at equilibrium, and k and n are constant parameters. For perfect Fickian diffusion,

the value of n is equal to 0.5. For recycled milk pouch/coir fiber composites, the diffusion plots obtained from the fitting of the experimental data to eq. (1) are presented in Figure 2. The values of the constant parameters (n and k) resulting from the experimental data fitting are shown in Table V. The results in Table V indicate that the absorption of water on all the recycled and virgin polymer composites followed the Fickian diffusion mechanism as the values of n were nearly similar for all the composite samples and were close to the value of $n = 0.5$.

In Fick’s model, the diffusion coefficient parameter indicates the ability of a solvent molecule to penetrate a composite structure. For a short period ($M_t/M_\infty \leq 0.5$), the following equation can be used for the determination of the diffusion coefficient (D):⁴¹

$$\frac{M_t}{M_\infty} = \frac{4}{L} \left(\frac{D}{\pi}\right)^{0.5} (t)^{0.5} \quad (2)$$

where L is the thickness of the sample. The diffusion coefficient was evaluated from the slope of the linear part of a plot of M_t/M_∞ versus \sqrt{t} . The values of

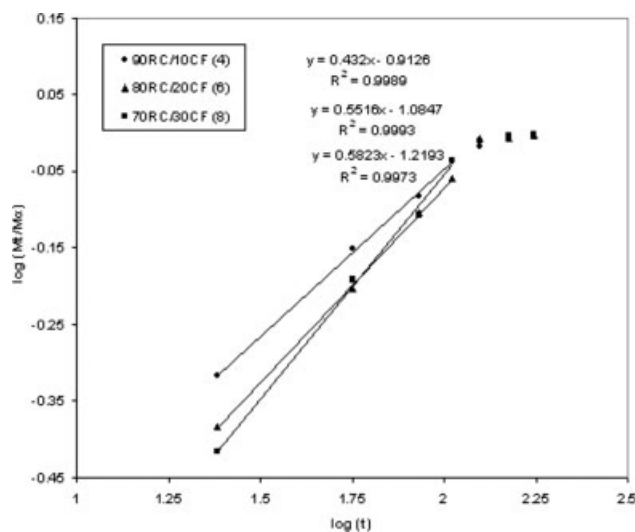


Figure 2 Water diffusion fitting plots for recycled polymer/fiber composites at 25°C.

the diffusion coefficient for all the formulated composites at different temperatures (25, 45, and 75°C) are given in Table VI. The values of the water diffusion coefficient increased with increasing fiber content in the composites because the hydrophilic nature of the coir fibers caused higher water diffusion inside the composites containing higher fiber contents. The increase in the temperature also led to enhanced values of the water diffusion coefficients for all composite samples (Table VI). The recycled polymer composites exhibited higher values of the diffusion coefficient than the virgin polymer composites because of poor interfacial bonding between recycled polymer and fibers. However, the addition of a coupling agent (SMA) significantly reduced the values of the water diffusion coefficient of the composites (Table VI), and this was attributed to a lower

rate of diffusion arising from better fiber–matrix adhesion in the SMA-treated composites. The decrease in the rate of diffusion in the SMA-treated composites was due to the lower number of microgaps in the fiber–matrix interfacial region; moreover, the coupling agent blocked more hydrophilic groups such as hydroxyl groups on the fiber surfaces. The hydroxyl groups of the fiber interacted with the anhydride rings of SMA, thereby forming an ester linkage.

Mechanical properties

The variation of the mechanical properties as a function of the fiber loading for each recycled and virgin polymer/coir fiber composite is shown in Figure 3. The mechanical properties of the virgin LDPE–LLDPE/fiber composites were superior to those of the recycled milk pouch/fiber composites. The reason is related to the prehistory of the thermomechanical degradation of the recycled polymer during recycling operations. As shown in Figure 3(a,b), both the tensile strength and tensile moduli of the composites increased with increasing fiber loading. This was attributed to the reinforcing effect imparted by the fibers, which allowed a uniform stress distribution from the polymer matrix to the dispersed fiber phase. The SMA-treated composites showed better tensile properties than the untreated composites (Fig. 3), and this indicates that efficient fiber–matrix interfacial bonding developed with the addition of SMA. As demonstrated in Figure 3(c), the elongation at break (%) of the polymer matrices sharply decreased with fiber reinforcement, and this indicated a decrease in the ductility of the polymer matrix with the incorporation of fibers. The toughness of the recycled composites was inferior to that of the virgin composites, whereas the SMA-treated

TABLE V
Values of Diffusion Parameters n and k Obtained from Fitting Plots

Sample formulation	Temperature (°C)					
	25		45		75	
	n	k (h ²)	n	k (h ²)	n	k (h ²)
90VR/10CF (3)	0.4154	0.0570	0.4817	0.1050	0.5093	0.0990
90RC/10CF (4)	0.4320	0.0603	0.5033	0.1070	0.5198	0.1026
80VR/20CF (5)	0.5064	0.0822	0.5765	0.0746	0.5998	0.0668
80RC/20CF (6)	0.5516	0.0881	0.5769	0.1067	0.6094	0.0660
70VR/30CF (7)	0.5658	0.1126	0.6024	0.1201	0.6259	0.1030
70RC/30CF (8)	0.5823	0.1222	0.6259	0.1238	0.6408	0.1120
90VR/10CF/SMA (9)	0.4077	0.0522	0.4568	0.1207	0.5043	0.0515
90RC/10CF/SMA (10)	0.4287	0.0700	0.4689	0.1238	0.5145	0.0508
80VR/20CF/SMA (11)	0.5019	0.0714	0.5060	0.0798	0.5987	0.0790
80RC/20CF/SMA (12)	0.5359	0.0814	0.5765	0.0799	0.6062	0.0668
70VR/30CF/SMA (13)	0.5530	0.1100	0.5775	0.0653	0.6133	0.1077
70RC/30CF/SMA (14)	0.5610	0.0995	0.6013	0.0751	0.6210	0.0986

RC, recycled plastic; CF, coir fiber; VR, virgin polymer.

TABLE VI
Diffusion Coefficients for the Composites Formulated at Different Temperatures

Sample formulation	Diffusion coefficient $\times 10^{13}$ (m ² /s)		
	25°C	45°C	75°C
90VR/10CF (3)	5.059	7.179	9.504
90RC/10CF (4)	5.255	7.271	9.652
80VR/20CF (5)	5.586	7.272	9.960
80RC/20CF (6)	5.599	7.308	10.290
70VR/30CF (7)	6.253	7.555	10.312
70RC/30CF (8)	6.449	7.683	10.814
90VR/10CF/SMA (9)	4.115	5.267	7.512
90RC/10CF/SMA (10)	4.212	5.334	7.709
80VR/20CF/SMA (11)	4.229	5.406	7.996
80RC/20CF/SMA (12)	4.364	5.852	8.262
70VR/30CF/SMA (13)	4.855	6.354	8.935
70RC/30CF/SMA (14)	4.924	6.453	9.033

RC, recycled plastic; CF, coir fiber; VR, virgin polymer.

composites exhibited higher toughness than untreated composites, as shown in Figure 3(d).

The mechanical properties of the composites were significantly affected by water absorption, as

presented in Figure 4. All the tensile properties (strength, moduli, and toughness) of the composites deteriorated after water uptake. Moreover, for the recycled polymer composites, the tensile strength and tensile moduli decreased by approximately 35–40 and 11–30%, respectively, as a result of the water absorption treatment, depending on the fiber loading. The reason is the change in the structure and properties of the fibers, matrix, and interfaces from the effect of water molecules that penetrated the composites. The water absorption also caused the weakening of the fiber–matrix interfacial adhesion, as reflected in the mechanical properties of the composites.

Morphological investigation

The difference in the mechanical performances of SMA-treated and untreated composites could be corroborated by morphological evidence. SEM photomicrographs of cryogenically fractured surfaces of SMA-treated and untreated 80/20 recycled milk pouch/coir fiber composites (formulations 6 and 12)

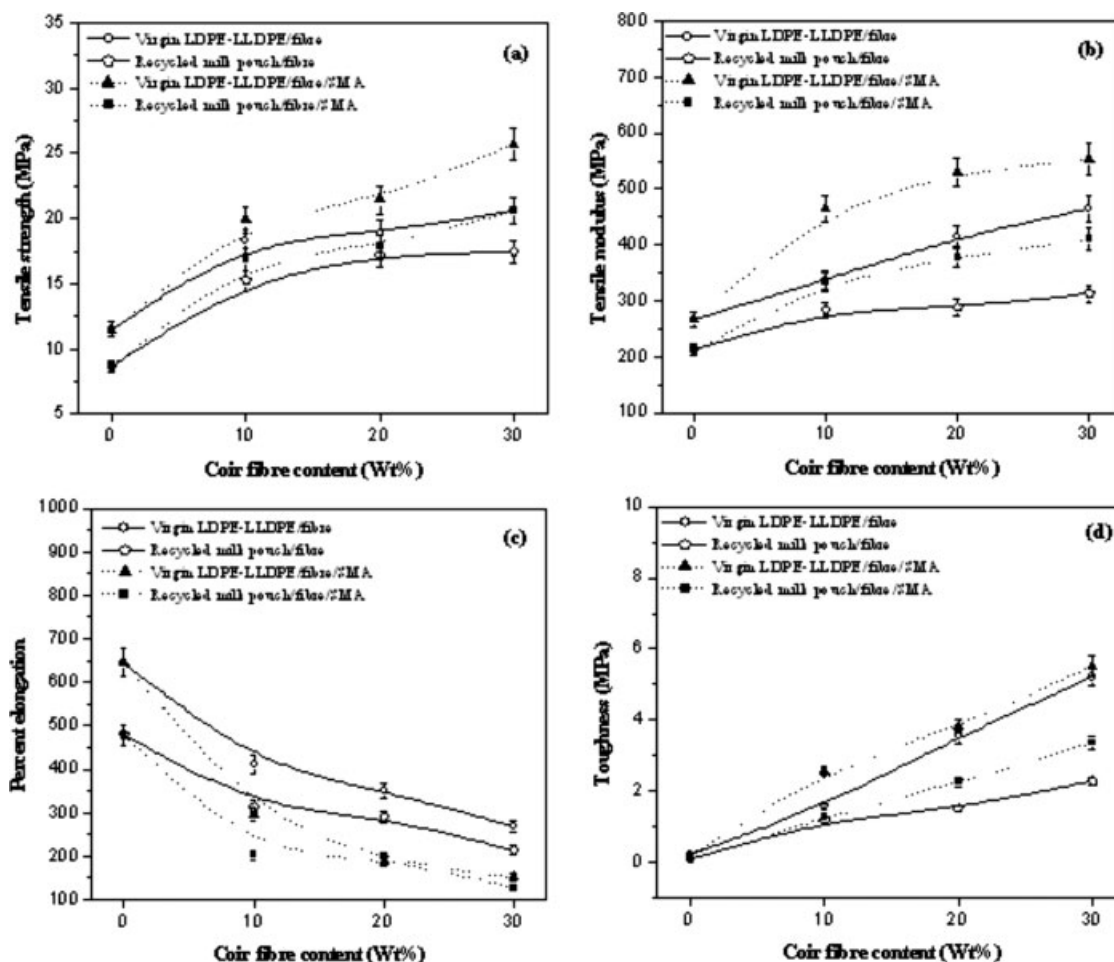


Figure 3 Mechanical properties of differently formulated recycled and virgin LDPE-LLDPE blend based coir fiber composites.

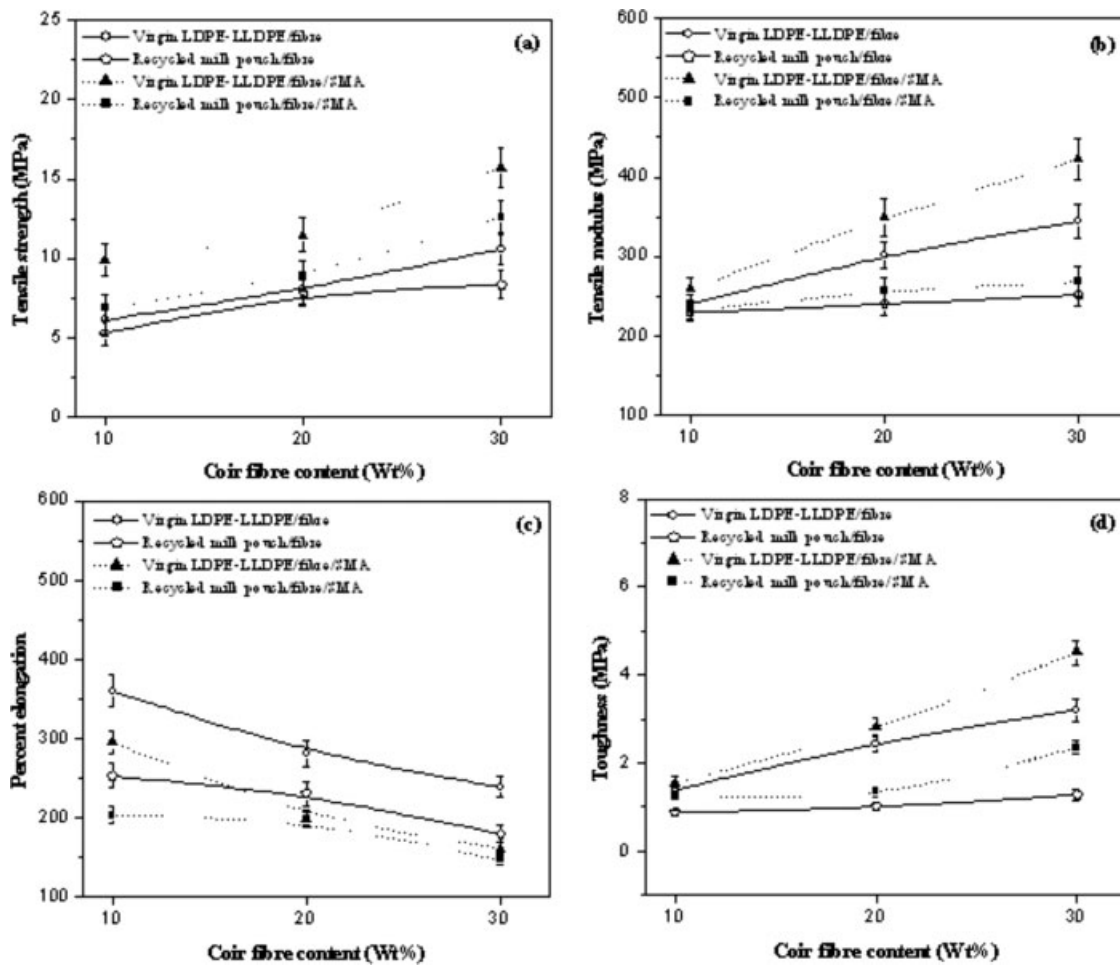


Figure 4 Effect of the water treatment on the mechanical properties of differently formulated recycled and virgin LDPE-LLDPE blend based coir fiber composites.

are displayed in Figure 5. The photomicrographs clearly indicate a significant difference in the interfacial features of the treated and untreated composites. In the case of the untreated composites, the fibers

appeared to be free from the polymer matrix, and a large number of holes or voids resulting from fiber pullout were observed [Fig. 5(a)]. This indicates poor interfacial adhesion and dispersion between the

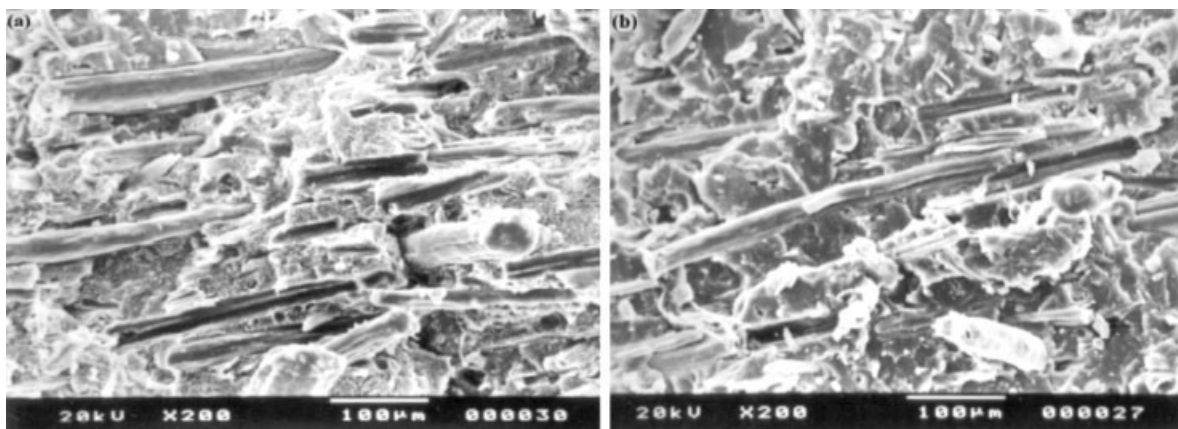


Figure 5 SEM microphotographs of fracture surfaces of (a) untreated and (b) SMA-treated 80RC/20CF (6 and 12) blends.

fibers and the polymer matrix. On the other hand, for SMA-treated composites, a significant reduction in fiber pullout and barely any gaps between the fibers and matrix were noticed [Fig. 5(b)]. Hence, the SEM photomicrographs confirmed that the incorporation of a coupling agent effectively developed strong interfacial bonding between the fibers and matrix in the treated composites, and this was reflected in their mechanical performances.

Thermal properties

The properties of polymers, particularly recycled polymers, deteriorate through thermal aging during processing, and decomposition caused by atmospheric oxygen is a primary reason. Polymers with high thermal stability are always challenging criteria for every industry for the enhancement of the durability of products. OIT analysis provides a useful tool for quality-control purposes or the life assessment of materials. The thermooxidative stability of the polymer matrices and their differently formulated composites was assessed by the measurement of the OIT and the dynamic determination of the oxidation stability (OT measurement) in DSC analysis. The OIT is an important parameter for the thermal characterization of materials. Figure 6 shows the thermogram obtained from the OIT measurements of the recycled milk pouch polymer and its coir fiber composites. In the thermogram, two melting peaks (~ 107 and $\sim 122^\circ\text{C}$) for the two polymer components in the matrix, LDPE and LLDPE, can be found. The theoretical crystalline melting temperature for LDPE is approximately 108 , and that for LLDPE is approximately 124°C . This observation indicates that

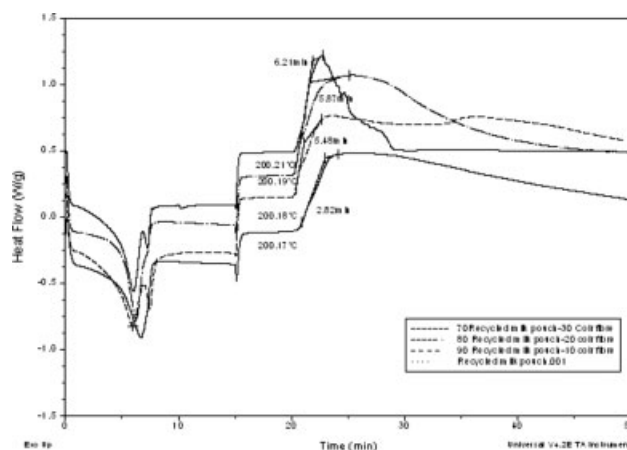


Figure 6 DSC thermogram obtained during OIT measurements of composite samples.

the crystalline phases of both LDPE and LLDPE in the blend matrix remain separated because LDPE and LLDPE are practically immiscible in the crystalline phase.⁴² The results of the OIT measurements for all the formulated samples are presented in Table VII. The OIT of the recycled polymer was lower than that of the virgin LDPE–LLDPE blend, indicating the poor oxidative stability of the recycled polymer. However, the oxidative stability (OIT value) of the polymer matrix was significantly increased by fiber reinforcement, and this was due to the heat deflection property of the fibers. As observed in Table VII, the OIT of the composite was shifted toward a higher value with increasing fiber content. The oxidative stability (e.g., OIT value) was higher for the composites made with SMA-treated fibers versus the

TABLE VII
Data Obtained from DSC Measurements for the Formulated Composites and Polymer Matrices

Sample formulation	OIT measurements			OT measurements	
	T_m ($^\circ\text{C}$) ^a	χ_{cr} (%) ^b	OIT (min)	Onset OT ($^\circ\text{C}$)	Peak OT ($^\circ\text{C}$)
VR (1)	107, 124	38.3	3.98	190.4	208
RC (2)	108, 121	35.5	2.42	183.7	184
90VR/10CF (3)	107, 124	31.9	5.75	192.6	210
90RC/10CF (4)	108, 123	29.7	5.48	191.5	189
80VR/20CF (5)	107, 124	29.1	6.04	195.0	211
80RC/20CF (6)	108, 123	26.6	5.87	193.3	192
70VR/30CF (7)	107, 123	26.1	6.59	200.6	212
70RC/30CF (8)	108, 122	25.3	6.21	197.6	193
90VR/10CF/SMA (9)	107, 122	33.1	6.28	194.9	215
90RC/10CF/SMA (10)	108, 121	31.5	6.12	192.7	192
80VR/20CF/SMA (11)	107, 121	31.0	7.78	197.2	216
80RC/20CF/SMA (12)	108, 121	30.0	7.15	196.4	196
70VR/30CF/SMA (13)	107, 122	27.9	8.59	207.4	218
70RC/30CF/SMA (14)	109, 118	26.9	8.07	201.8	202

^a Crystalline melting temperature.

^b Crystallinity.

RC, recycled plastic; CF, coir fiber; VR, virgin polymer.

untreated composites (Table VII). Table VII shows that both the onset and peak OTs of the composites increased with increasing fiber content. However, the OT was recorded to be higher for the SMA-treated composites than the untreated composites, and this indicated that the oxidative stability of the composites could be enhanced by the addition of SMA as a coupling agent.

The degree of crystallinity for each polymer matrix and formulated composite was evaluated from OIT measurements. The crystallinity (χ_{cr}) was determined with eq. (3):

$$\chi_{cr}(\%) = 100 \times \frac{\Delta H_f}{\Delta H_f^0} \quad (3)$$

where ΔH_f^0 and ΔH_f are the heat of fusion of the 100% crystalline polymer (290 J/g for polyethylene⁴³) and the measured heat of fusion, respectively. The crystallinity of the polymer matrix decreased with the incorporation of short coir fibers, as shown in Table VII. The lowering of the polymer crystallinity could be attributed to the reduction in the structural regularity and close packing ability of the polymer chains in the presence of the fibers. However, the onset OTs of the SMA-treated composites were higher than those of the untreated composites (Table VII), and this indicated that SMA as a coupling agent could ensure the high thermooxidative stability of the composites.

CONCLUSIONS

The thermomechanical recycling of postconsumer milk pouches (an LDPE–LLDPE blend) and their suitable utilization as polymer matrices in the development of short coir fiber composites could constitute an attractive approach to solving a municipal waste disposal problem. A comparative study on the water absorption, mechanical, and thermal properties of recycled and virgin LDPE–LLDPE blend based coir fiber composites was carried out in this investigation. The composites containing recycled plastics with coir fibers offered comparable properties and lower costs with respect to competitive materials, especially those based on synthetic fibers. However, the properties of the recycled polymer composites were somewhat inferior to those of virgin polymer composites, but the addition of 2% SMA as a coupling agent significantly improved the properties of the composites. The water diffusion in the composites followed the kinetics of Fickian diffusion. The kinetic parameters were influenced by the temperature, fiber content, type of matrix, and coupling agent. The mechanical properties of the composites were significantly affected by water absorption. The

improvement in the interfacial morphology of the composites by the incorporation of SMA as a coupling agent was well observed in SEM studies. The excellent thermooxidative stability of the SMA-treated recycled polymer/coir fiber composites could allow postconsumer milk pouches to be further processed to produce composite products.

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