

Recycled Old Newsprint Fibers as a Reinforcing Filler in Molded Polyester Composites

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ABSTRACT: Using old newsprint (ONP) fibers as reinforcing filler in polyester (PE) composite has been studied. Using ONP fibers in PE composite resulted in a decrease in modulus of rupture (MOR) and an increase in modulus of elasticity (MOE) and tensile strength as compared with a neat PE composite. Also, water absorption and thickness swelling were increased as a result of using ONP fibers in the composite. Acetylation, steaming, and esterification (using maleic anhydride) of ONP fibers were performed to improve the dimensional stability of the produced composite. Acetylation and steaming of ONP fibers resulted in a decrease in the thickness swelling of the produced composites; MOR, MOE, and tensile strength were also decreased as a result of these treatments. Esterification of ONP fibers using maleic anhydride resulted in a decrease in thickness swelling of the produced composite and, at the same time, an increase in MOR, MOE, and tensile strength. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2018–2023, 2001

Key words: old newsprint; polyester composite; acetylation; steaming; maleic anhydride; esterification

INTRODUCTION

Long bast fibers from plants can be used in place of glass fiber in many different types of liquid composite molding systems such as resin transfer molding, structural reaction injection molding, and sheet molding compounding.¹ All of these techniques include a fibrous mat mixed with liquid resin, which is polymerized to form a reinforced fiber composite. Natural fibers are lower in specific gravity, higher in specific tensile strength, lower in cost, biodegradable, and less energy intensive to process, so they are well suited to these types of technologies.

Natural fiber reinforced composites have a range of mechanical properties that enable their application at the low to medium stress and low

stiffness spectra of materials' use.² The mechanical properties of each specific composite may vary over a large range of values because of the intrinsic variability of the properties of the fibers. However, the incompatibility of the fibers and the polymer matrix and poor resistance to moisture often reduce the potential of natural fibers as fillers and limit their use.

The natural fibers studied as fillers for polyester (PE) composites were jute fiber,^{3–7} pineapple leaf,⁸ sisal,^{9–11} sunhemp,¹² and sponge gourd.¹³ Nabi and Jog¹⁴ reviewed the use of natural fibers in composites, with special reference to the type of fibers, matrix polymers, treatment of fibers, and fiber–matrix interface. Substitution of natural fibers (flax, sisal, hemp, jute) for the hitherto used glass fiber in PE-based automobile parts has been highlighted by Asche.¹⁵

Many researchers have discussed the need to recover and reuse the enormous quantities of old

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newsprint (ONP).¹⁶ Recycling ONP fibers into composites eliminates the necessity of removing ink, dyes, and other additives. ONP fibers have been used in the production of dry-process hardboard,^{17,18} polypropylene and polyethylene,^{19,20} and polyvinyl chloride composites.²¹

The main objective of the present study was to evaluate the mechanical properties and dimensional stability of ONP–PE composites containing a low volume fraction of ONP fibers (10–30%). Different treatments of ONP fibers to improve the dimensional stability of the produced composites were also investigated.

EXPERIMENTAL

ONP Fiberization

ONP was cut into small pieces (2×2 cm), soaked overnight in water, fiberized using a Voith beater (Voith, Inc., Appleton, WI) at 2% consistency. The degree of freeness ($^{\circ}$ SR) of the produced fibers, measured according to the German standard method, was 20. The fibers were squeezed and allowed to air dry; the produced fiber aggregates were run through a mill using a 1-cm mesh screen to de-lump the fibers. The fibers were oven dried at 105°C for 6 h before making composites.

PE

The matrix polymer was a maleic PE resin, Siropol 8340-TP (Saudi Industrial Resins Ltd., Jeddah, Saudi Arabia) containing 40% styrene monomer and 2% calcium naphthenate as catalyst. Two percent (based on the weight of the PE) of methyl ethyl ketone peroxide was used as an initiator.

PE–ONP Composite

Different ratios (10–30%) of oven-dried ONP fibers were mixed with the PE resin, to which the initiator was premixed, and the resulting mixture was pressed in a 30×10 -cm mold under a light pressure of 1 MPa for 40 min to ensure complete curing of the PE resin. The thickness of the produced composites was 0.4–0.5 cm.

Steaming of ONP

ONP fibers were treated with tap water at 170°C for 5 min in a rotating autoclave; the heat-up time was 30 min. The produced fibers were washed

with water, squeezed, left to air dry, and finally passed through a mill using a 1-cm screen to de-lump the fibers. The fibers were oven-dried at 105°C for 6 h before composite making.

Acetylation of ONP

Oven-dried ONP fibers were acetylated using acetic anhydride by the following method.²² Oven-dried fibers (50 g) were placed in a stainless-steel mesh container and the container was dipped into a tank containing acetic anhydride for 1 min at 25°C, removed from the tank, and drained for 3 min. The wetted fibers were put in large, covered, petri dishes and placed in a preheated oven at 120°C for 30 and 120 min. After the reaction, the fibers were washed thoroughly with water, left to air dry, and finally oven dried for 6 h at 105°C, and the increase in weight due to acetylation was calculated [weight percent gain (WPG)]. The WPGs at 120°C for 30 and 120 min were about 8 and 14%, respectively.

Esterification of ONP by Maleic Anhydride (MA)

To 100 g of oven-dried ONP, 75 or 100% (based on the weight of the fibers) of MA were applied to the fibers. MA was first dissolved in the least possible amount of acetone. The mixture was thoroughly mixed and kept in a fume hood to allow acetone evaporation, then placed in a preheated oven for 0.5, 1, or 2 h at 100°C. The excess nonreacted anhydride was removed from the fibers by acetone by Soxhlet extraction, air dried, and oven dried at 105°C for 6 h.

The WPG due to the esterification was calculated. WPG of 12.6 was obtained using 75% of MA at 100°C for 0.5 h, WPGs of 18.6 and 25.7 were obtained using 100% of MA at 100°C for 1 and 2 h, respectively.

Fourier Transform Infrared Analysis

Infrared spectra of ONP, MA-esterified ONP, and acetylated ONP were obtained by using a JASCO FTIR 800 E spectrometer. The samples were measured using the KBr disc technique.

Testing of PE–ONP Composites

Static bending [modulus of rupture (MOR) and modulus of elasticity (MOE)], tensile strength, and water absorption and thickness swelling tests of the produced composites were determined according to ASTM D790-90,²³ ASTM D638-90,²⁴

Table I Effect of the Ratio of ONP on Properties of ONP–PE Composites

	0	10	20	30
MOR (MPa)	31.86 (2.8)	27.93 (2.3)	25.54 (1.7)	21.86 (2.4)
MOE (GPa)	1.024 (0.031)	1.063 (0.035)	1.598 (0.050)	1.218 (0.054)
Tensile strength (MPa)	11.97 (0.81)	13.48 (0.87)	16.55 (1.03)	13.80 (1.06)
Water absorption, % (7-day soaking)	0.74	1.08	2.27	3.58
Thickness swelling, % (7-day soaking)	0.08	1.15	3.51	6.70

Values in parentheses are the standard deviation.

and ASTM D570-81,²⁵ respectively. For testing of flexural properties, a three-point loading system was used, and the span-to-depth ratio was 16:1. All samples were conditioned at 30% relative humidity before mechanical testing. Five specimens of each sample were tested and the results averaged.

RESULTS AND DISCUSSION

Effect of the Ratio of Added ONP Fiber on the Properties of the Produced ONP–PE Composites

Table I shows the properties of ONP–PE composites containing different ratios of ONP fibers. As shown in Table I, adding ONP fibers resulted in a decrease in MOR as compared with neat PE. This decrease was 12.3, 19.8, and 31.4% on addition of 10, 20, and 30% of ONP fibers, respectively. However, MOE and the tensile strength were significantly enhanced on addition of ONP fibers to the PE. Maximum increase in tensile strength and MOE was obtained on addition of 20% of ONP fibers; the percent increase in MOE and tensile strength was 141.5 and 90.4%, respectively. Increasing the ONP more than 20% resulted in a decrease in tensile strength and MOE. With respect to the fracture event of bending tests, the failure mode of neat PE and ONP–PE composites was an abrupt failure, as sketched in Figure 1. The high bulk density and fluffiness of fibers make it difficult to mix evenly more than 20% of the fibers with the PE under the conditions used in this work. As expected, water absorption and thickness swelling were increased as a result of using the ONP fibers; these increased further as the ratio of ONP used was increased.

Effect of Steaming and Acetylation Pretreatments of ONP Fibers on the Properties of PE–ONP Composites

Hsu et al.²⁶ reported that simple steam pretreatment of wood fibers caused partial hydrolysis of

hemicellulose in hardwoods and softwoods, which markedly increased the compressibility of wood fibers. This, in turn, significantly reduced the buildup of internal stresses in the composites during hot pressing. Youngquist et al.²⁷ found that steam and acetylation pretreatments of wood fibers decreased water absorption and thickness swelling of hardboard. Rowell²⁸ reported that wood flakes, strand, and fibers can be chemically modified using an acetylation process, and that, when these materials are converted into panel products, they possess greatly improved dimensional stability properties and reduced biodegradation by decay. Also, Nada and Hassan¹⁸ found that acetylation of ONP fibers resulted in a decrease in water absorption and thickness swelling of bagasse-ONP low-density boards but a decrease in MOE, MOR, and tensile strength occurred. In the present study, steaming and acetylation pretreatments of ONP fibers were performed with the aim to improve the dimensional stability of the produced PE–ONP composite. Figure 2 shows the infrared (IR) spectra of ONP and acetylated ONP fibers. A significant increase in

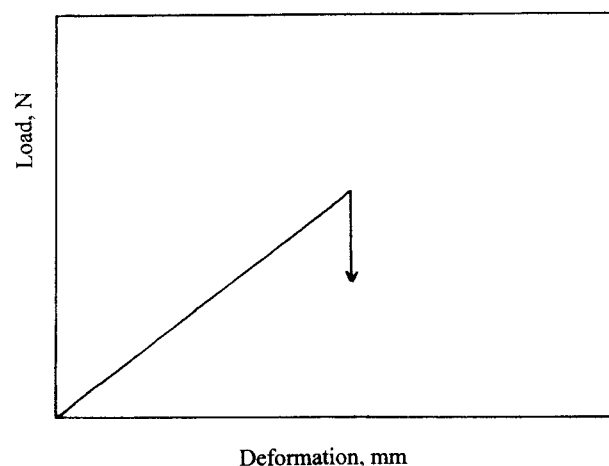


Figure 1 Schematic of the load versus deformation curve displaying the failure mode observed for the different ONP–PE composites in bending tests.

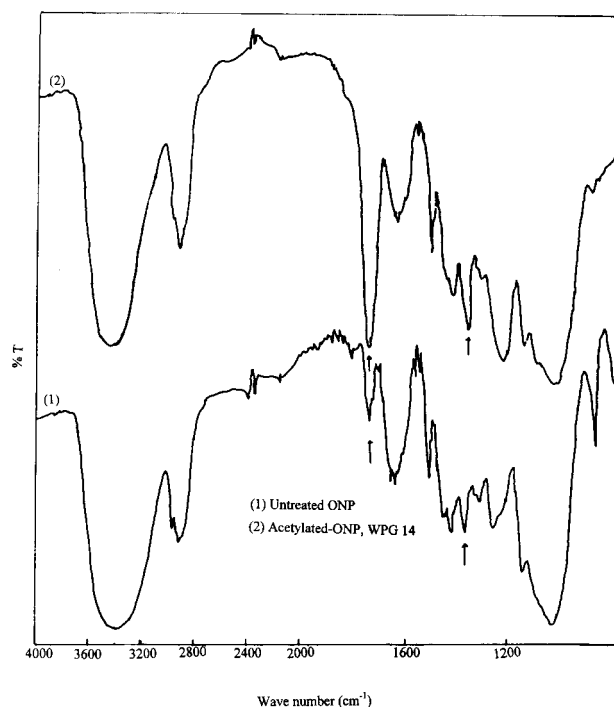


Figure 2 IR spectra of untreated and acetylated ONP.

the intensity of 1735 cm^{-1} and 1375 cm^{-1} bands, which are due to stretching vibration of C=O group and bending vibration of CH_3 group, respectively, took place as a result of the acetylation. Table II shows the effect of steaming and acetylation of ONP fibers on the properties of ONP-PE composites containing 20% ONP fibers. As shown in Table II, both pretreatments resulted in a remarkable decrease in thickness swelling of the composites as compared with the untreated ONP-PE composite. Steaming pretreatment was much more effective than acetylation in reducing the thickness swelling. Contrary to the general trend in composites made from a high percentage

of lignocellulosic fibers, water absorption did not decrease after acetylation. Introduction of the acetyl groups onto the cell wall components reduced further swelling because of water absorption, but the amount of water absorbed was slightly higher than that of the untreated ONP-PE composite. Steaming did not significantly affect MOR or MOE of the composites but resulted in a considerable decrease in tensile strength whereas acetylation resulted in a considerable decrease in MOR, MOE, and tensile strength.

Effect of Esterification of ONP with MA on the Properties of ONP-PE Composites

In a previous study,²⁹ it was found that residual ink and other residues present in recycled ONP fibers did not significantly affect its extent of esterification using MA. The esterified ONP fibers were used in this study with the aim to crosslink the esterified fibers to the matrix polymer to improve the mechanical properties and dimensional stability of the produced composites. As shown in the previous section, although acetylation and steaming improve the dimensional stability of the produced composites, the MOE, MOR, and tensile strength were decreased or did not significantly improve. Figure 3 shows the IR spectra of the esterified fibers having different levels of WPGs. The intensity of the absorption peak at 1725 cm^{-1} was significantly increased because of the carbonyl group of the introduced carboxylic groups. The peak at 1640 cm^{-1} appeared in the spectra of esterified ONP because of the double bond of the introduced propenoic acid side chain.

Table III shows the properties of the esterified ONP-PE composites containing 20% of the esterified ONP fibers. As shown in Table III, at WPG 13, a slight increase in MOR and tensile strength

Table II Effect of Acetylation and Steaming Pretreatments on the Properties of ONP-PE Composites

	PE	Untreated ONP-PE	Steamed ONP-PE	Acetylated ONP-PE (WPG 8)	Acetylated ONP-PE (WPG 14)
MOR (MPa)	31.86 (2.8)	25.54 (1.7)	25.2 (2.0)	22.21 (1.8)	23.37 (2.1)
MOE (GPa)	1.024 (0.031)	1.598 (0.050)	1.477 (0.058)	1.407 (0.049)	1.354 (0.067)
Tensile strength (MPa)	11.97 (0.81)	16.55 (1.03)	13.42 (1.06)	14.8 (1.02)	14.69 (0.84)
Water absorption, % (7-day soaking)	0.74	2.27	3.2	3.22	3.14
Thickness swelling, % (7-day soaking)	0.08	3.51	0.4	2.08	0.74

Values in parentheses are the standard deviation.

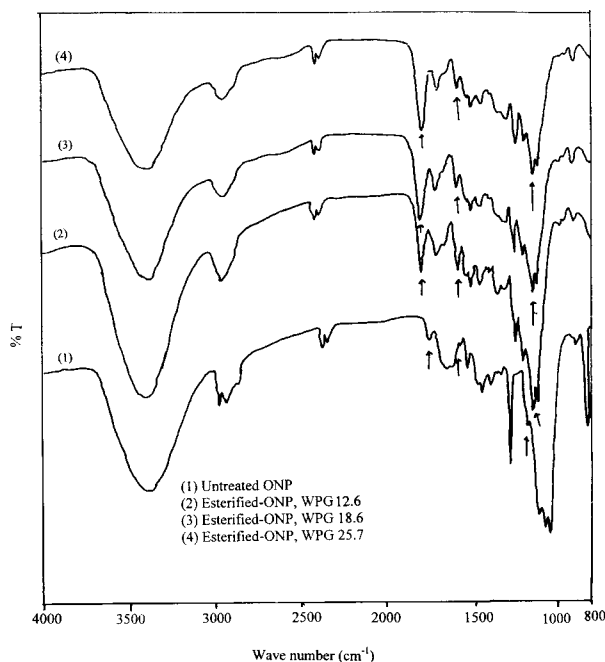


Figure 3 IR spectra of untreated and esterified ONP.

occurred and the thickness swelling was slightly decreased as compared with untreated ONP–PE composites. At WPG 18.6, there was a further increase in MOR of the produced composites. At high WPG (25.7), there was a significant increase in tensile strength, MOR, and MOE; MOR of this sample was close to that of the neat PE composite. The increases in MOR, MOE, and tensile strength may be due to crosslinking of the esterified fibers to the polymer matrix. Water absorption increased but thickness swelling decreased as the WPG of the esterified fibers increased. As in the case of the acetylated ONP fibers, the introduction of the propenoyl side chain due to esterification reduced any further swelling because of wa-

ter absorption. Water absorption and thickness swelling of the esterified ONP–PE composites were higher than those of acetylated ONP–PE composites. This may be because acetylation results in loss in hemicelluloses by the action of acetic acid byproduct, which may reduce water absorption, and the lower hydrophilicity of the acetyl group ($-\text{CO}-\text{CH}_3$) than the propenoic acid ($-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$) side chain resulting from acetylation or esterification, respectively. Comparing thickness swelling and water absorption results of steamed, acetylated, and esterified ONP–PE composites shows that steaming was the most effective treatment in improving the dimensional stability of the produced composites. Esterification of the fibers by MA was the most effective treatment in improving the dimensional stability and, at the same time, the tested mechanical properties of the produced composites, as compared with the untreated ONP–PE composite.

Effect of ONP Fibers on the Curing of PE

Figure 4 shows the time–temperature curve of the exothermic reaction due to crosslinking of the PE with styrene for the different ONP–PE composites. The temperature was followed as a function of time by immersing a thermocouple in the center of the resin and fiber mixture in a glass test tube; the system was thermally isolated using glass wool. As shown in Figure 4, none of the ONP fibers (nontreated, acetylated, steamed, and esterified) affected the curing behavior of the PE. In other words, the residual ink and other additives in recycled ONP and treatment of the ONP fibers did not affect the resin time–temperature curve. The peak temperature of the exothermic reaction of both PE and ONP–PE composites was reached after 35–37 min. The peak temperatures were

Table III Effect of Esterification of ONP Fibers Using Maleic Anhydride on the Properties of the Produced ONP–PE Composites

	PE	Untreated ONP–PE	Esterified ONP–PE (WPG 12.6)	Esterified ONP–PE (WPG 18.6)	Esterified ONP–PE (WPG 25.7)
MOR (MPa)	31.86 (2.8)	25.54 (1.7)	25.91 (1.8)	27.25 (1.6)	30.94 (2.03)
MOE (GPa)	1.024 (0.031)	1.598 (0.050)	1.614 (0.048)	1.448 (0.051)	1.901 (0.036)
Tensile strength (MPa)	11.97 (0.81)	16.55 (1.03)	16.76 (0.47)	16.7 (0.45)	17.99 (0.72)
Water absorption, % (7-day soaking)	0.74	2.27	4.10	4.43	4.8
Thickness swelling, % (7-day soaking)	0.08	3.51	3.01	2.1	1.4

Values in parentheses are the standard deviation.

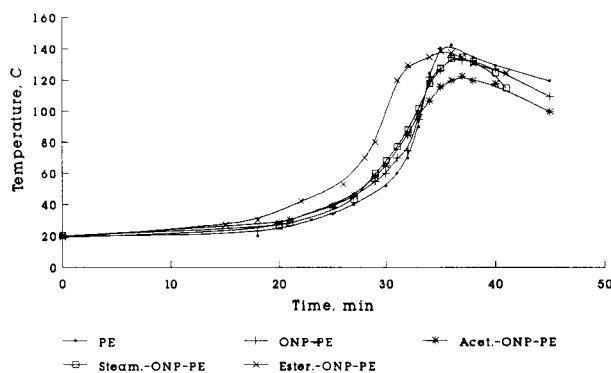


Figure 4 Time-temperature curve of curing of the PE resin for the different ONP-PE composites.

143, 135, 123, 139, and 135°C for PE, untreated ONP-PE, acetylated ONP-PE, esterified ONP-PE, and steamed ONP-PE composites, respectively.

CONCLUSIONS

ONP fibers can be used as reinforcing filler in PE composites. Steaming, acetylation, or esterification of the fibers before composite production could improve the dimensional stability of the produced composites. Esterification of ONP fibers by MA was the most effective treatment to improve the dimensional stability and, at the same time, the bending and tensile strengths of the produced composites among the other treatments (acetylation and steaming).

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