The Effect of Paraffin on Fiber Dispersion and Mechanical Properties of Polyolefin–Sawdust Composites

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ABSTRACT: This article reports on the influence of the paraffin (PAR) on the wood fiber (WF) dispersion in different polyethylene (low-density polyethylene, high-density polyethylene, recycled polyethylene) matrices, as well as on the melt flow behavior and mechanical properties of WF-reinforced polyethylene (PE) composites. In the presence of paraffin, the composites showed improved tensile and flexural strength and modulus, but lower impact strength and elongation at break. The extent of improvement in mechanical properties depends on paraffin content and type of polyethylene; the most effective paraffin was in LDPE-based composites. Paraffin-treated WF showed lower moisture absorption ability in comparison with unmodified wood fiber. The phase segregation process was investigated for PE/PAR blends by DSC method. It was shown that an increase of paraffin concentration in the PE/PAR blend leads to a decrease of PE melting temperature and an increase of paraffin melting temperature; it indicates a net exchange of material from paraffin towards polyethylene. However, generally both components of PE/PAR blends remain immiscible. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 2385–2393, 2004

Key words: polyethylene; wood fiber; composite; mechanical properties; fiber dispersion

INTRODUCTION

The use of natural fibers from renewable resources has considerable interest in the composite field. Wood fiber (WF)–thermoplastic composites especially have received considerable attention from the car, building, and furniture industry, because of their thermoplastic nature, which allows processing of the composites by using traditional processing equipment. Most studies[1–3] have concentrated on wood fiber reinforced thermoplastic composites where nondegradable polyolefins (PO) are used as matrix. However, well-known disadvantages of such materials include hydrophilic character of wood fibers that is responsible for incompatibility and poor fiber dispersion in the polymer matrix. Several techniques ranging from grafting a short-chain molecule onto wood fiber surface to use of adhesion promoters have been used to improve the compatibility of WF and PO.[4–6] One approach that was investigated[7–8] is the use of appropriate additives [stearic acid (SA), sodium silicate, mineral oil] to improve wood fiber dispersion. Dispersing effectiveness of SA depends on the method of its incorporation in composite. The most effective way, as was shown in ref. [7], was WF treatment from solution phase of stearic acid. However, simultaneously with positive influence on WF dispersion, incorporation of SA leads to a decrease of MFI of the composite.[9] It was explained by the interaction of the acid groups of SA with hydroxyl groups of WF, what results in decreasing of the mobility of polymer chains at the interface, and what negatively affects composite flow behavior. Such method of modification also includes an additional step in the preparation of composite.

In the present work, paraffin as dispersing agent was used to reduce agglomeration of wood fibers in the polyolefin matrix. The effect of paraffin concentration on the degree of fiber dispersion, melt flow behavior, mechanical properties of sawdust–PO composites as well as on the water uptake of WF were studied.

EXPERIMENTAL

Materials

Three PO were used as composite matrices, and all were purchased from Solvey Polymers: high-density polyethylene [HDPE; Fortiflex T50–200, melt flow index, 1.58 g/10 min (190°C, 2.16 kg), density 0.953 g/cm³], low-density polyethylene [LDPE; 640 IM, melt flow index, 1.68 g/10 min; density, 0.919 g/cm³]; and recycled polyethylene waste (WPE; melt flow index, 0.95 g/10 min; density, 0.923 g/cm).³ Scrap wood (obtained from local sources) derived sawdust was obtained by grinding hardwood (alder) chips in a high-speed grinder. The wood fiber was collected after it passed through a 60-mesh screen (density, 1.45 g/cm³). Paraffin (TU-6-09-4112-88, Russia) was used

as dispersing agent. Its molecular weight was 262 (ebullioscopy); density was 0.910 g/cm^3, and melt temperatures were 35.8 and 54.7°C. Loading of sawdust in all composites was 30 wt %.

Incorporation of paraffin in composite

Wood fiber was dried in an oven at 105°C for 17 h; after such drying, WF contained 3 wt % moisture.

The following two different methods were tried:

Sawdust treatment in solution phase of paraffin (PAR) was tried, where PAR was dissolved in xylene (the percentage of PAR was 50 wt % by fiber weight). WF was treated for 0.5 h with PAR solution with continuous mechanical stirring. Then, WF were dried in an oven at 105°C for 24 h and stored in an exsiccator for moisture uptake measurements.

Incorporation of PAR at compounding step of composite was tried, where polymer, WF, and PAR were gradually added to a two-roll mill at 150°C (LDPE and WPE) or 160°C (HDPE) and mixed well for 15 min. Percentage of PAR varied from 0 to 22 wt % by composite weight.

Compression and injection molding

Mixed composites were compression molded for 3 min at 160°C in a laboratory press into 1-mm-thick sheets, which later are cut into standard specimens for tensile measurements. Composites were also injection molded at 200°C into 80-mm-long and 4-mm-thick bars for flexural and impact measurements.

Mechanical testing

A Universal testing machine (UTS-100) was used for tensile and flexural measurements. Tensile measurements were made according to ASTM D 638M. Crosshead speed was 20 mm/min. Flexural measurements were made by three-point bending method according to ASTM D 790M. The specimen was deflected until 5% strain was reached. Crosshead speed was 2 mm/min.

The Charpy impact strength was measured with a Zwick 5102 impact pendulum tester according to ASTM D 256M with notched samples. At least 10 specimens were tested for each set of experiments and the mean values were reported.

Moisture absorption of WF

Pellets (0.55 g) made of compressed (5 MPa) untreated and paraffin-treated WF were conditioned in relative humidity (RH) 99% environment at 20°C. Moisture absorption was determined by weighing the specimens on a balance with a precision 0.0001 g.

WF dispersion degree

A Leitz Laborlux optical microscope was used to determine the WF dispersion in the polymer matrix. Number of WF aggregates in a 1-cm^2 surface area of compression-molded samples was counted at a magnification of ×50.

Melt flow behavior

Melt flow index (MFI) was measured according ASTM D 1238 by using a load of 2.16 kg at 190°C. The capillary diameter was 2.08 mm.

Thermal characteristics

A Mettler TA-4000 differential scanning calorimeter was used to obtain DSC thermograms. Experiments were performed in N$_2$, and heating rate was 10°C/min.

Scanning electron microscopy (SEM)

The morphology of composites was examined by using a JEOL JSM-T200 electron microscope at 25 kV. Fracture surfaces of composites after impact tests were sputter coated with gold before viewing.

RESULTS AND DISCUSSION

In the present study, we used as matrix two virgin polyolefins (HDPE and LDPE) and one waste polyethylene (WPE), which contain mainly LDPE, but also some unknown content of HDPE and low molecular admixture (it was evident from DSC curves, where two melting temperatures, 112 and 121°C, were observed). These polymers differ between themselves by MFI values (see Experimental). High viscosity of wood fiber reinforced thermoplastic composites results in processing difficulties. On the other hand, high viscosity of polymer matrix also leads to poor dispersion of WF. One way of minimizing these effects is to use polymers with high MFI; another was to use lubricants. However, it is generally known that the high melt flow polymers have lower strength and modulus because of the lower molecular weight. Therefore, more often, different dispersing agents are used in WF-reinforced thermoplastic composites. In the present study, we used paraffin as lubricant to facilitate dispersion of WF in the PE matrix and to decrease viscosity of the composites, but modification was done at the compounding step.

Figure 1 shows the number of WF aggregates versus percentage of PAR in the composites based on the three PEs. In the case of unmodified composites, WF tend to form randomly distributed aggregates due to hydrogen bonding between fibers, but their content is different for composites based on different matrices.
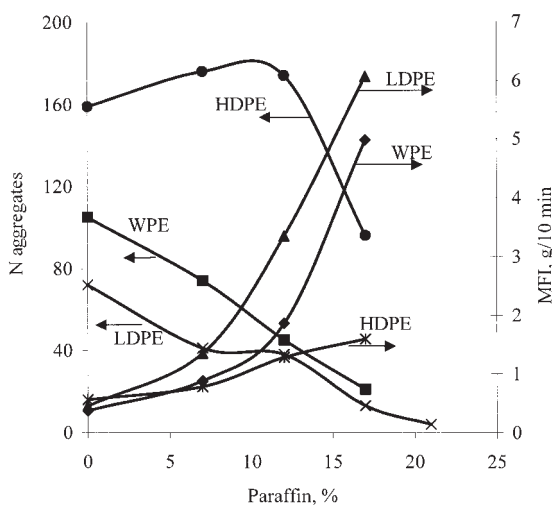
Figure 1 Effect of paraffin content on the number (N) of WF aggregates and melt flow index (MFI) of WF-reinforced composites based on different PE matrices.

WF distribution in HDPE/PAR composite is less uniform than that in the LDPE/PAR or WPE/PAR composites. In the case of PAR-modified composites, results indicate a decrease in the number of WF aggregates with an increase in the concentration of PAR for all composites investigated. When the concentration of PAR increased to 15–20 wt %, the number of aggregates decreased to 15, or 10, if LDPE or WPE was used as matrix. At the same loadings of paraffin, HDPE-based composites exhibit a significantly greater number of aggregates (96–40). Further increase in the percentage of PAR did not result in significant reduction in the number of aggregates.

Simultaneously, PAR acts as lubricant and increases MFI of composites (Fig. 1). By plotting the measured MFI of blended components against weight percentage of PAR, we obtained an increase of MFI of LDPE and WPE composites. Importantly, lower MFI values at the same content of PAR was obtained in the case of HDPE-based composites. We can conclude that WF agglomeration is more pronounced in HDPE-based composites because the higher melt viscosity HDPE does not flow well enough to encapsulate the WF. So, uniformity of WF dispersion had been found to be correlate with PE composite MFI.

Fiber surface in unmodified composite is rough. When mixed with polymer, the rough surface would have a relatively strong mechanical interaction with the matrix, resulting in a high viscosity of the composite. Paraffin could act as a lubricant, reducing the friction between the fiber and polymer, leading to lower viscosity.

At a high level of WF dispersion, one might expect an improvement in the strength of the composites. From the other side, introduction of lubricant usually decreases the strength of the polymer. Some balance of these two effects must be achieved to obtain high-performance composites. Therefore, we studied the influence of PAR content (and way of its introduction) on the mechanical strength of our composites. We found that tensile and flexural strength of the composite does not depend on the method of PAR incorporation (from solution phase or in the melt). On the other hand, it is clear that incorporation of the PAR in the melt at compounding step is a more technological way. Therefore, this method of modification was used in further experiments (except DSC and moisture sorption).

Tensile strength, modulus, and elongation of unmodified and paraffin-modified PE–sawdust composites are shown in Figure 2. As can be seen, the presence of PAR significantly affected these parameters, but the influence of PAR depends on the type of matrix. The concentration of PAR in composites varied from 0 to 22% by weight of composite. The increase in σ and E was observed for LDPE- and WPE-based composites until the PAR content reached 12–17 wt %; further increase of PAR content reduced tensile strength and modulus. A possible reason, as was expected, may be that at higher concentrations, PAR plasticizes the matrix, causing a decrease of its mechanical strength. If HDPE was used as composite matrix, increase of PAR content leads to a steady decrease of both tensile strength and modulus. As generally observed, the increase of PAR content reduced elongation of the all composites, as shown in Figure 2.

Similar influence of PAR also was observed on the flexural strength and modulus: values of these parameters went up with increasing content of PAR if LDPE and WPE were used as matrix, but decreased if matrix was HDPE (Table I). However, flexural strength values are significantly higher than corresponding tensile values. As far as in the bending test, one side of specimen is extended, and another is compressed; it probably reflects a higher resistance to compression of the WF-reinforced composites. Homogeneity of the composite, extent of WF distribution, and wetting also needs to be taken into account when interpreting the flexural properties of composite. In addition, PE can penetrate through hollow lumen in WF, depending on the viscosity of the polymer (it probably increases the strength of WF). Balasuria et al.[3] observed such behavior in the case of HDPE (MFI = 7 g/10min)–wood flakes composite. Examination of SEM micrographs of fractured surface of the composite showed that PE penetrates into lumens of WF.

HDPE-based composites have the lowest MFI, and paraffin has little influence on it. Oppositely, incorporation of PAR in LDPE- and WPE-based composites importantly increase their MFI (Fig. 1). Everyone can imagine that if the viscosity of PE is low, it flows well around the WF, improves its distribution, and as a result, increases the strength values of the composite.
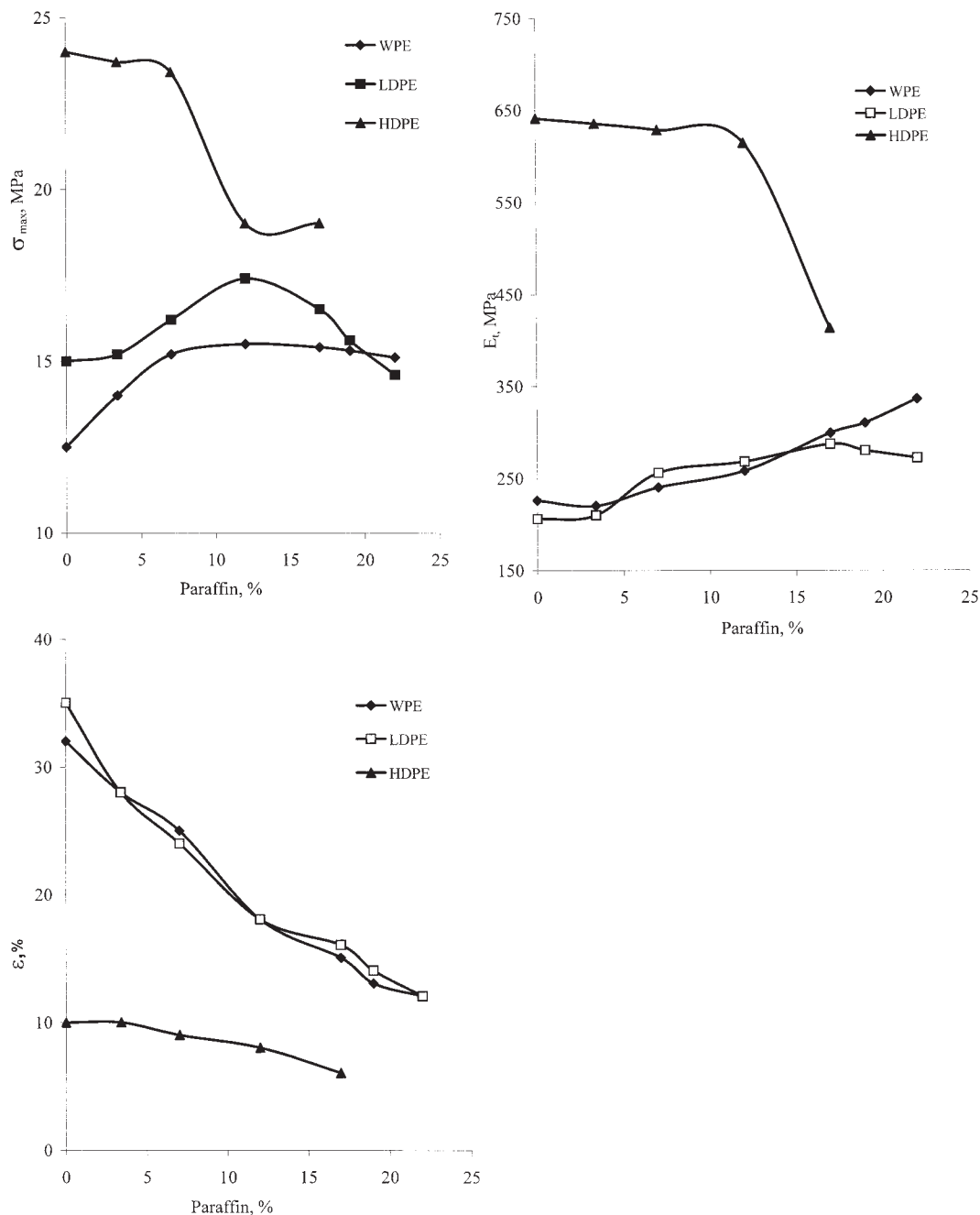
Figure 2 Effect of paraffin on (a) tensile strength (σ_{max}); (b) tensile modulus (E); and (c) elongation at break (ϵ) of the WF-reinforced composites.

Because the fiber loading and matrix remain the same regardless of composite system, it is expected that all observed differences in composite tensile and flexural properties must be attributed to paraffin content.

The results obtained and interpreted above are confirmed by an investigation of the fracture surfaces of the LDPE–WF composites. SEM micrographs of their fracture surfaces are shown in Figure 3. The morphology of the LDPE–WF composite demonstrates that interfacial adhesion between matrix and WF is poor, and large WF aggregates are observed. For paraffin containing LDPE–WF composite, no WF aggregates

TABLE I
Effect of the Paraffin on Flexural and Impact Strength of the WF Reinforced Composites

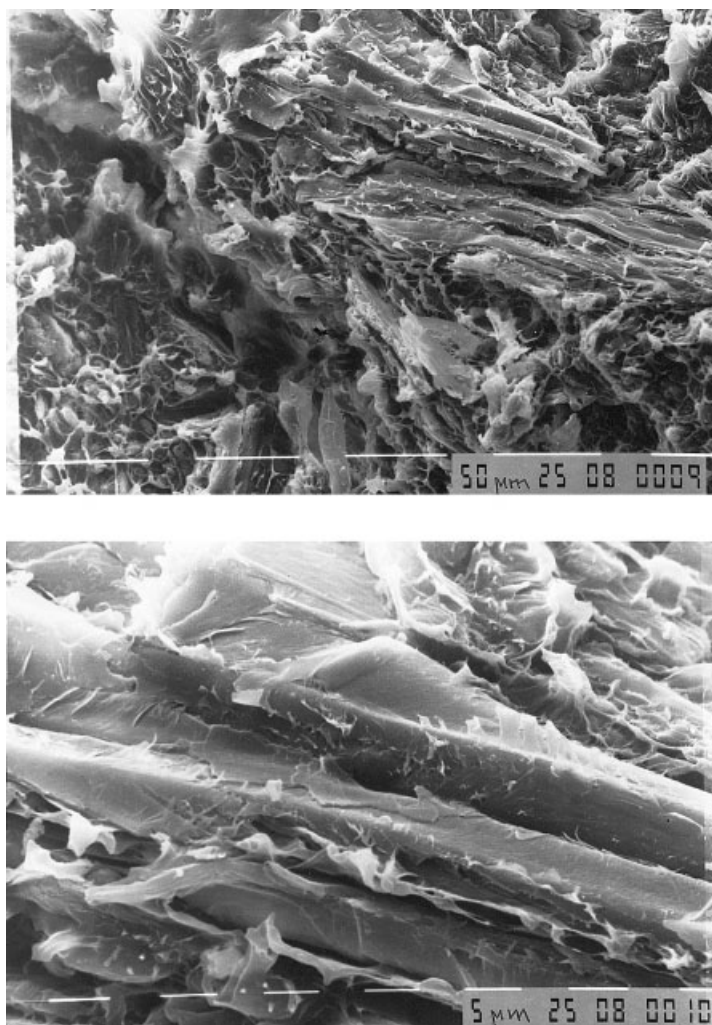|	Paraffin content (%)	σ_{fl} (MPa)	E_{fl} (MPa)	σ_{imp} (J/m²)
WPE + 30% WF	0	13.6	450	9.5
	12	14.4	465	6.3
	17	16.9	563	4.3
LDPE + 30% WF	0	14.6	477	7.1
	12	15.2	493	4.7
HDPE + 30% WF	0	32.3	1535	4.4
	7	28.6	1386	4.3
	12	26.0	1142	4.0

Figure 3 Scanning electron micrographs of the fracture surface of the composite: LDPE/WF (paraffin, 12 wt %); (a) scale bar, 50 μm; (b) scale bar, 5 μm.

can be detected, and it is difficult to differentiate WF from the matrix [Fig. 3(a)] on this size scale. The wood fibers are more easily visualized at higher magnification [Fig. 3(b)]. The surface appearance also implies great ductility of polymer matrix.

Impact strength of composites, as shown in Table I, decreases steadily, while increasing the loading of PAR. Impact strength depends largely on polymer matrix ductility (i.e., the resistance to crack propagation). Incorporation of PAR leads to a decrease of ϵ (matrix become more brittle), and consequently, to a decrease of impact strength. There are two mechanisms by which the WF can reduce the impact strength, as follows: (1) WF tend to reduce ϵ to break and so reduce area under the stress–strain curve; (2) stress concentration may occur at regions around WF ends, areas of poor adhesion, and regions where WF contact one another.

The balance of impact toughness/rigidity of composite presented by Charpy notched impact strength/flexural modulus must be achieved. Different at-

tempts[10–11] were made to improve the brittleness of WF–thermoplastic composites: the use of different impact modifiers such as ethylene vinyl acetate, polyisobutylene, and ethylene–propylene thermoplastic elastomers.

The loss in impact strength of our composites was attributed mainly to the decrease of elongation of modified composites as a result of the addition of higher modulus component (PAR). An increase of Young's modulus with an increase in paraffin content was observed (Table II), indicating that the modulus of PAR is higher than the modulus of PE. A similar effect was observed by Luyt and Kruppa[12] for LL-DPE/wax blends. It can be associated with a higher degree of crystallinity of PAR ($\Delta H = 187.5$ J/g) in comparison with LDPE ($\Delta H = 108.4$ J/g), WPE ($\Delta H = 121.4$ J/g), or HDPE ($\Delta H = 174.4$ J/g).

Also, chain mobility of paraffin located at the interface is important. In the case of PAR, its ability in preventing catastrophic crack growth in high speed test is limited. It was expected, as far as paraffin-

TABLE II
Effect of the Paraffin on Mechanical Properties of the Polyethylene

Polymer	Paraffin content (%)	σ_y (MPa)	σ_{max} (MPa)	σ_{break} (MPa)	ε (%)	E_t (MPa)	σ_{fl} (MPa)	E_{fl} (MPa)
WPE	0	8.3	13.4	10.0	755	121	8.7	163
	16	10.0	13.2	10.5	723	128	9.8	225
	26	9.7	10.6	7.6	637	147	10.9	243
LDPE	0	8.7	15.2	15.0	739	70	8.3	175
	16	9.1	12.3	12.2	744	137	9.0	214
HDPE	0	24.1	—	28.1	1285	305	17.0	593
	16	20.3	—	17.0	970	281	12.4	379

treated WF interface was not bonded to polymer and does not exist in good interfacial adhesion.

As far as PAR improved mechanical properties of WF–polyethylene composites, the next set of experiments was related to the investigation of PAR influence on mechanical properties, melt flow behavior, and melting characteristics of polymer matrix (Table II, Fig. 4).

Only a few articles[12–13] described the properties of polyethylene/paraffin wax blends. Luyt and Kruppa[12] investigated LLDPE and LDPE/paraffin wax blends, which contained 2–40 wt % wax. They found that the wax content has no influence on the melting point of LLDPE, but slightly decreases T_m of LDPE. Increase of Young's modulus and decrease of elongation at break were also observed with an increase of wax content in blend.

Hlavata et al.[13] investigated the influence of three types of lubricants (Ca stearate, stearic acid, and paraffin) on the structure and toughness of model LDPE/PP and commingled polyolefin waste blends. They found that paraffin is most effective in model blends, probably due to its partial miscibility with LDPE.
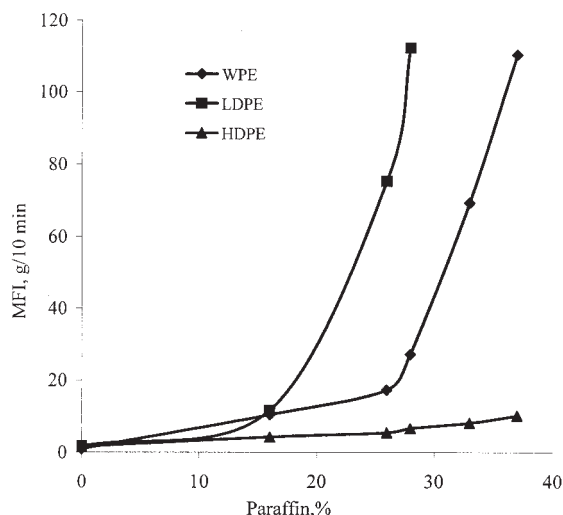
An increase of σ_t, σ_{fl}, and E of LDPE and WPE with an increase in PAR content was observed in our experiments, indicating that the modulus of the PAR is higher than the modulus of LDPE and WPE. It is possibly associated with a higher degree of crystallinity of paraffin. On the other hand, an increase in PAR content caused a decrease in elongation of all polyethylenes, because PAR is harder than PE. As was expected, strength parameters of HDPE decreased with an increase of PAR content.

The viscosity of blends that consist of components that are miscible behave according to the additivity
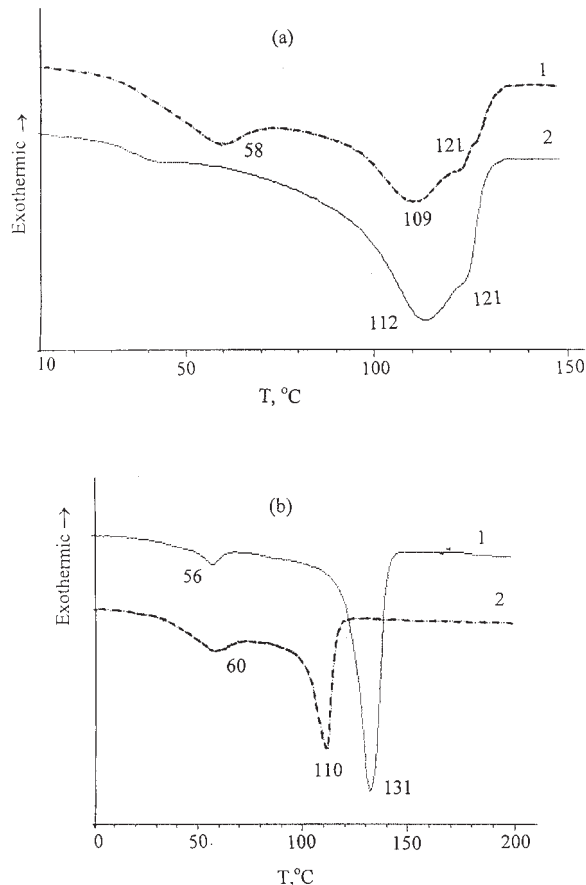

Figure 4 Effect of paraffin content on the binary PE/paraffin blends melt flow index (MFI).

Figure 5 Effect of paraffin (16 wt %) on the melting characteristics of the binary PE/PAR blends (DCS): (a) 1: WPE/PAR, 2: WPE; (b) 1: HDPE/PAR, 2: LDPE/PAR.
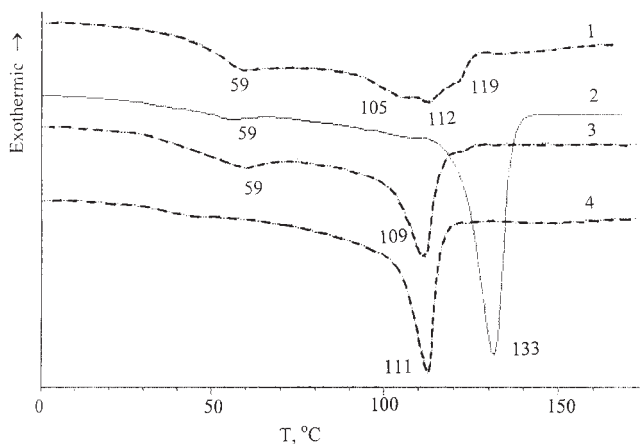
Figure 6 Effect of paraffin (16 wt %) on the melting characteristics of WF (30 wt %) reinforced composites: 1: WPE, 2: HDPE, 3: LDPE, 4: LDPE (without paraffin).

rule. Because melt flow rate is associated with melt viscosity, this rule can be also applied to MFI. Our measurements of MFI of the melt of PE/PAR blends does not confirm linear behavior (Fig. 4), indicating immiscibility of components in the molten state. Oppositely, MFI plot changes its slope at PAR content above 28%; an important increase of MFI with a further increase in PAR content of the LDPE and WPE blends was observed. If PAR was mixed with HDPE, negligible influence on MFI was observed in the investigated interval of PAR content.

For better understanding of the PAR influence on the mechanical properties of paraffin-modified polyethylenes and their composites, we studied miscibility

of these blends in the melt. It is well known that melting temperature and the shape of the endothermic peak offer information about crystal size, crystal size distribution, and degree of crystallinity of polymer.[14] In the case of binary blends, shape of their thermograms depends on the degree of the compatibility of components. The compatibility of two components at the molecular level results in a thermogram showing just a single endothermic peak. On the contrary, the incompatibility of the two components leads to a thermogram showing the corresponding two peaks of the isolated components.

DSC curves of paraffin, PE, WF, and their blends are shown in Figures 5, 6, and 8. The melting thermograms of PAR show two peaks at 35.8 and 54.7°C, indicating melting and recrystallization, respectively [Fig. 8(a)]. Thermograms of virgin PE exhibits only one melting peak at 110°C (LDPE) and 131°C (HDPE), but WPE had two melting peaks at 112 and 121°C (as explained previously). Opposite to observations of Luyt and Kruppa,[12] who found that DSC curves of LLDPE/PAR and LDPE/PAR blends showed only one endothermic peak (therefore, they concluded that partial miscibility in the crystalline phase of components is possible), thermograms of our PE/PAR blends had two melting peaks. Consequently, our blends are immiscible. Maybe it is connected with different types of paraffins used in both experiments: Kruppa used paraffin wax of greater molecular weight (785) and higher degree of crystallinity ($d = 0.94$ g/cm^3) in comparison with paraffin used in our experiments (paraffin characteristics, see Experimental).
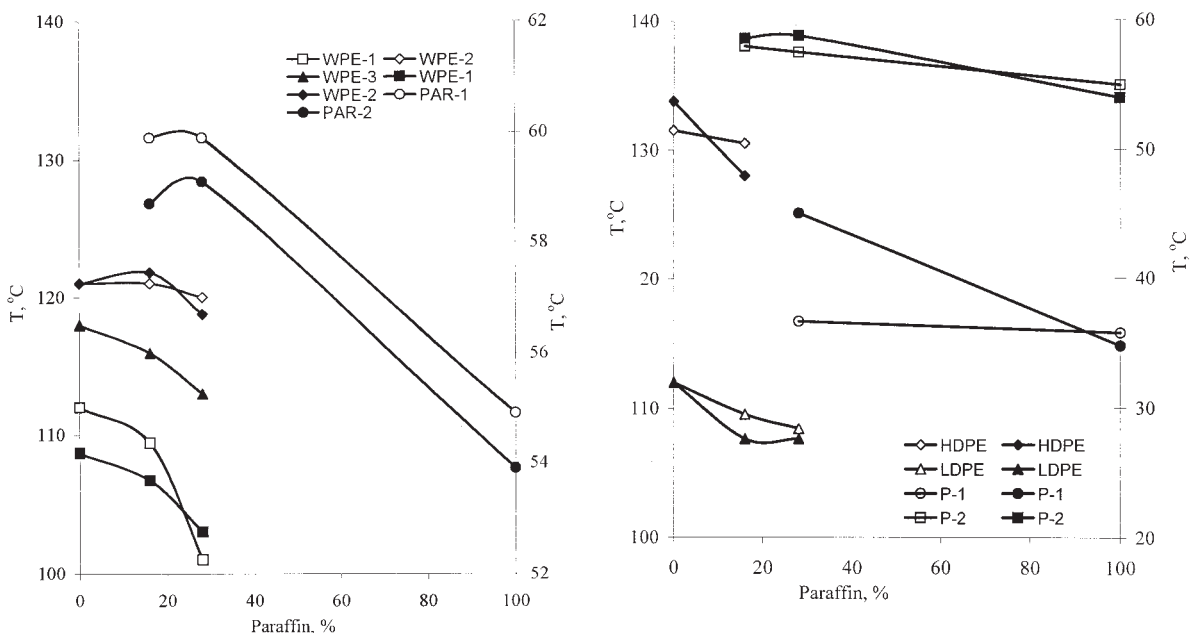

Figure 7 Variation of the melting temperatures of the PE/PAR blends with composition (from DSC curves) (open and filled symbols refer to data from the first and second run). (a) WPE/PAR; (b) HDPE/PAR (top curves), LDPE/PAR (bottom curves).

In the case of PE/PAR blends, multiple fusion peak thermograms was observed. Figure 4 illustrates DSC traces of three blends; the lower temperature peak which is associated with the PAR is broad in comparison to the higher T peak, which is related to PE. As it can be expected, thermograms of PE composites had the same shape (Fig. 6).

Figure 7 shows the plot of the melting temperature measured at the peak maximum for first and second DSC run of PE/PAR blends as a function of composition. For the first DSC run, PE peak decreases with C_{paraf} in all compositions. It is apparent that a different chain reorganization upon blending of two phase mixture, which depends on C_{paraf}, is taking place. Decrease of PE melting temperature and increase of PAR melting temperature indicate a net exchange of material from the PAR towards PE. After a second run, the PE temperature peak is reduced further with increase of C_{paraf}. This would suggest a segregation of material: in the process of blending in the molten state, the paraffin fractions with higher T_m will probably mix with PE lowering its T_m (so possibly partial miscibility in the molten state took place).

It seems interesting how PAR treatment changes WF hydrophobicity and affects the water absorption behavior of treated samples in comparison with untreated samples. The sorption of nonpolar polymers containing a WF depends mainly on the nature of WF. Cellulose is the main component in WF; each fiber is hollow and contains a lumen at its center. There are
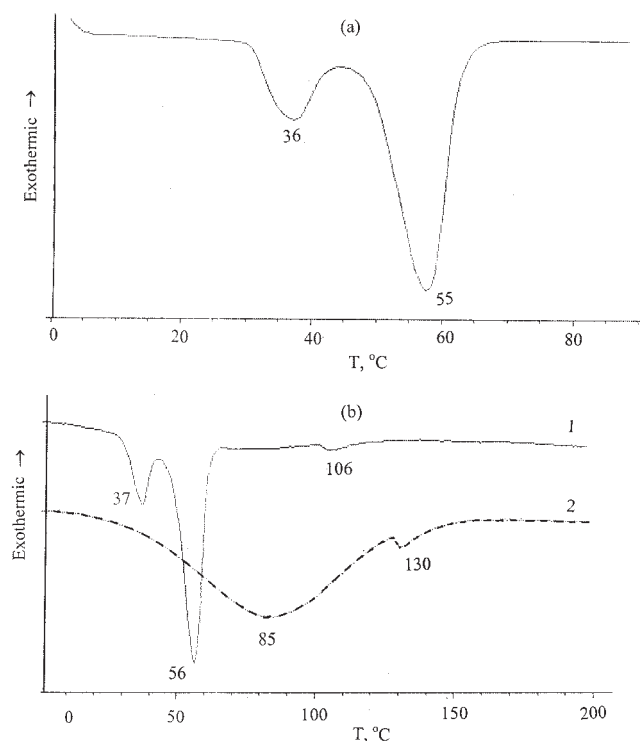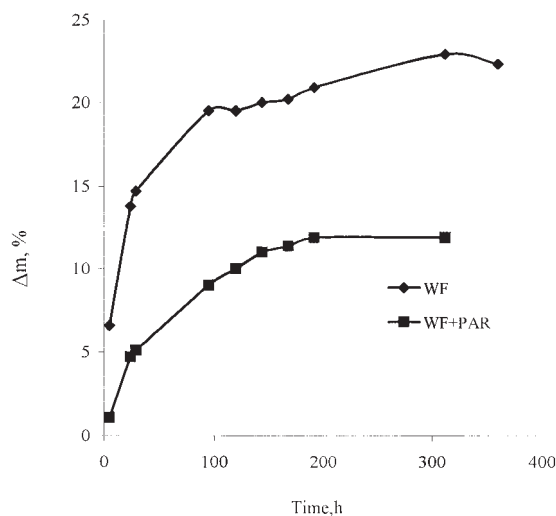
Figure 9 Moisture (RH = 99%) sorption kinetics for WF and paraffin solution treated WF.

three main regions where the absorbed water in the composite can reside: the lumen, the cell wall, and the gaps at the interface between fiber and polymer matrix in the case of poor WF wetting and lack of interfacial adhesion. These facilitate water penetration. After treatment with PAR (from solution phase), hydrophobicity was imparted to WF surface and paraffin separated the paths through which water entered from the surface to the inner regions of WF. On the other hand, due to low viscosity of PAR, it possibly can penetrate into WF pores and so blocked part of internal hydroxyl groups of WF.

Such suggestions were supported by DSC measurements. Figure 8 illustrates DSC traces of initial and PAR-treated WF; as can be seen, the low temperature peak at 85.6°C of WF (related to the presence of water) disappears after paraffin treatment and only two peaks characteristic for PAR remain. As a result, degree of moisture absorption of the paraffin-treated WF, conditioned in 99% RH, decreased if compared with untreated WF (Fig. 9).

Figure 8 DSC analysis of (a) paraffin; (b) paraffin-treated WF (1), untreated WF (2).

CONCLUSION

Wood fiber reinforced polyethylene composites containing paraffin showed reduced WF agglomeration and an increase in tensile and flexural strength and modulus, but simultaneously a decrease in elongation at break and impact strength was observed. The type of polyethylene (LDPE, HDPE, WPE) and paraffin content was found to be important, and the best results were obtained for LDPE-based composites that contain 16–20 wt % paraffin. The thermal study of PE/PAR blends reveals the material segregation in the melting process: melting temperature of PE decreases and melting temperature of paraffin increases with the

increase of paraffin loading in blend, indicating material exchange from paraffin towards PE.

References

1. Bledzki, A. K.; Sperber, V. E.; Faruk, O. Rapra Review Reports, Report 152, 2002, 13, 135.
2. Liao, B.; Huang, Y.; Cong, G. J Appl Polym Sci 1997, 66, 1561.
3. Balasuriya, P. W.; Ye, L.; Mai, Y-W. Composites, A 2001, 32, 619.
4. Gauthier, R.; Joly, C.; Coupas, A. C.; Gauthier, H.; Escobes, M. Polym Compos 1998, 19, 619.
5. Zhang, F.; Enclo, T.; Qui, W.; Yang, L.; Hirotsu, T. J Appl Polym Sci 2002, 84, 1971.
6. George, J.; Sreekala, M. S.; Thomas, S. Polym Eng Sci 2001, 41, 1471.
7. Raj, R. G.; Kokta, B. V. J Appl Polym Sci 1989, 38, 1987.
8. Raj, R. G.; Kokta, B. V. Polym Eng Sci 1991, 31, 1358.
9. Kajaks, J.; Bulmanis, V.; Reihmane, S.; Tsciprin, M. Mech Compos Mater 1997, 33, 540.
10. Park, B. D.; Balatinecz, J. J. Polym Compos 1997, 18, 79.
11. Dutra, R. C. L.; Soores, B. G.; Campos, E. A.; De Melo, J. D. D.; Silva, J. L. G. J Appl Polym Sci 1999, 73, 69.
12. Luyt, A. S.; Kruppa, I. Macromol Symp 2002, 178, 109.
13. Hlavata, D.; Krulis, Z.; Horak, Z.; Lednicky, F. Hromadkova, J. Macromol Symp 2001, 176, 93.
14. Wunderlich, B. in Macromolecular Physics; Crystal melting; Academic Press: New York, 1980; Vol. 3.