Influence of Some Additives on the Performance of Wood Flour/Polyolefin Composites

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ABSTRACT: The main objective of this study was to investigate the effect of different additives, namely, maleic anhydride, alumina trihydrate (ATH), and a mixture of both on wood flour/polyolefin (50/50) composite samples. The polyolefins used were polyethylene (PE), polypropylene (PP), and a mixture of both PE and PP (50/50 w/w). The effects were studied in terms of the percentage water absorption, volumetric swelling efficiency, and mechanical and electrical properties. We found that the absorption of water and volumetric swelling were greatly retarded after 3 weeks in all of the wood flour/polyolefin composite samples containing various additives. It is also clear from the results that the mechanical properties were enhanced. The presence of ATH improved the electrical properties and enhanced the thermal stability of the wood flour composites. Generally, the PE composite samples gave better results compared to the PP ones. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2243–2249, 2008

Key words: additives; composites; fillers; mechanical properties; polyolefins

INTRODUCTION

The use of cheap natural wood fiber as a filler in thermoplastics contributes greatly to environmental protection.[1] In terms of energy savings, estimations show that half of the energy furnished by vegetable biomass is lost.[2] The use of this biomass as a filler in thermoplastics will allow the reduction of these scraps and waste. These biofillers exhibit a number of attractive advantages, including low cost, low density, low processing requirements, less abrasion during processing, renewability, ecofriendliness, and biodegradability.[3–5] Like other thermoplastic olefins, virgin and recycled polyethylene (PE) and polypropylene (PP) polymers have been used extensively in wood/polymer composites (WPCs).[6–8] PE and PP have gained an important position among polyolefins because of their versatile and broad range of applications.

However, the hydrophilic and aggregating nature of cellulose causes poor processability and inherent incompatibility with most hydrophobic polymers, such as PP. In the last 2 decades, many efforts have been made to improve the interfacial bonding strength between the polar wood fiber and the nonpolar thermoplastic matrix.[9] The incorporation of various additives and coupling agents[10–13] in these systems and the modification of the thermoplastics by grafting has helped to promote adhesion at the polymer–filler interface, improved the degree of filler dispersion, increased the fiber loading in the polymer, and improved the processability, moldability, and hence, the physicomechanical properties. Maleic anhydride grafted polyolefins are an important branch of reactive modified polymers. The grafting modification of low-density PE by maleic anhydride is prone to branching or crosslinking caused by radical–radical combination during the grafting reaction. Although PP can crosslink in the grafting reaction, chain scission (β-scission) is the dominant side reaction in PP when it is subjected to free radicals at elevated temperatures during processing.[14–16]

The crosslinking of PE by organic peroxides has received appreciable attention in the literature and is becoming a more widely accepted and studied method of altering polymer structure and properties. Dicumyl peroxide is a popular choice because of its favorable decomposition rate at the normal processing temperatures of PE.

The demand for WPCs in various applications, such as automotive components, building materials, and the aerospace industry, is increasing because of their ecological and economical advantages over conventional composites.[17,18] The thermal stability and the mechanical and electrical properties of polymeric composite materials, which are affected by temperature changes, play an important role in many industrial applications. High temperatures can cause the thermal degradation of these polymeric composite materials. Thermogravimetric analysis (TGA) can be used to evaluate the thermal degradation of compo-

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TABLE I
Chemical Compositions of the Wood Flour/Polyolefin Composites and the Sample Codes

Type of plastic used	Component of wood composites	Sample code
PE	PE/wood flour (50/50)	PE
	PE/wood flour (50/50) + 10% maleic anhydride	PEM
	PE/wood flour (50/50) + 10% ATH	PEA
	PE/wood flour (50/50) + 5% maleic anhydride and 5% ATH	PEAM
PP	PP/wood flour (50/50)	PP
	PP/wood flour (50/50) + 10% maleic anhydride	PPM
	PP/wood flour (50/50) + 10% ATH	PPA
	PP/wood flour (50/50) + 5% maleic anhydride and 5% ATH	PPAM
PE/PP mixture (50/50)	(PE/PP)/wood flour (50/50)	X
	(PE/PP)/wood flour (50/50) + 10% maleic anhydride	XM
	(PE/PP)/wood flour (50/50) + 10% ATH	XA
	(PE/PP)/wood flour (50/50) + 5% maleic anhydride and 5% ATH	XAM

sites. The effect of different additives, such as metallic hydroxide, on the polymer matrix can be studied by this method.[19–22]

The objective of this study was to examine the influence of additives on composite materials made from plastic wastes, especially the wastes of PE, PP, and a mixture of the two (50/50 w/w), and agrowastes as wood flour. The prepared composite samples were tested for their dimensional stability and mechanical, electrical, and thermal properties.

EXPERIMENTAL

Materials

The polyolefins used in this study were low-density PE (Cabco 474) with no additives and a homopolymer PP (GM10) supplied by el-Nassagon al Sharquion Co. (Cairo, Egypt). The material properties as given by the supplier are as follows: for PE, specific gravity = 0.920 g/cm^3 and melt flow index = 4 g/10 min, and for PP, specific gravity = 0.9 g/cm^3 and melt flow index = 9 g/10 min. Maleic anhydride, dicumyl peroxide, and other analytical-grade chemical reagents were obtained from Aldrich-Sigma (Darmstadt, Germany). A fine grade of alumina trihydrate (ATH; $Al_2O_3{\cdot}3H_2O$) supplied by E. Merck (Darmstadt, Germany) was used. The filler used was wood flour obtained from Sweden Wood with a particle size of around 100 μm. Plywood (MDF) was obtained from Shouguang Li Sen Board Co., Ltd. (Shanghai, China).

Compounding

The wood flour was dried for 4 h at 105°C to a moisture content of about 0.9% (based on dry weight) before the compounding process. With all of the mixing conditions the same, the polyolefin and wood flour (50/50 w/w) were mixed without and with 10 wt % maleic anhydride, ATH, or both in a Brabender Plasticorder (NJ) at a rotor speed of 100 rpm for 5 min in the presence of dicumyl peroxide (1 wt %). The temperature of the mixing zone was maintained at 190°C for PP and at 160°C for PE. After the mixing was completed, the mixes were compressed under a pressure of 4 MPa at the same mixing temperatures and then molded. The investigated samples were cut and prepared with dimensions that best suited each testing technique. The chemical compositions of the wood flour composites under investigation and their codes are illustrated in Table I.

Methods of analysis and testing

To determine water absorption and dimensional changes,[23] specimens 2 × 2 × 3 cm^3 were used. The samples were oven-dried at 105°C for 4 h, weighed, and then submerged in water for different time intervals. At the end of each time interval, the samples were surface dried with blotting paper, and their weights were recorded. The percentage water absorbed and percentage volumetric swelling was calculated according to the following equations:

$$\text{Water absorption } (\%) = (W_1 - W_o)/W_o \times 100$$

where W_o is the dry weight and W_1 is the weight after submerging in water.

$$\text{Total volumetric swelling } (\%) = (V_1 - V_o)/V_o \times 100$$

where V_o is the volume before and V_1 is the volume after submerging in water.

The density measurements were performed according to ASTM D 792 specifications with an electronic balance (Mettler Toledo AB 204-S) (Switzerland).

The mechanical properties under compressive loads were measured at room temperature with a universal testing machine (Hounsfield 100 KN, England) with a crosshead speed of 3.0 mm/min. The cylindrical samples were cut with an aspect ratio

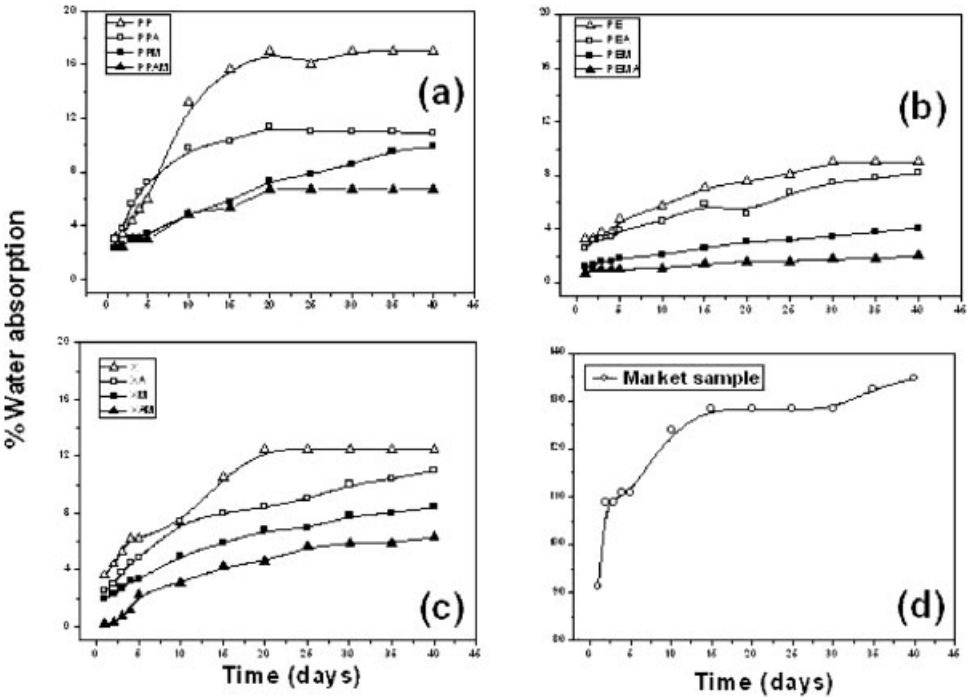

Figure 1 Effect of additives on the percentage water absorption for the wood flour/polyolefin composites and market sample.

kept at nearly 1.5 according to ASTM D 695-96. Three-point bending tests were carried out with the same crosshead speed, and the samples were cut from plates 10 mm in width, 8 mm in thickness, and 70 mm in length. The span taken was 40 mm according to ASTM D 790-92.

Dielectric measurements were carried out at room temperature (±25°C) at a frequency of 100 Hz. The permittivity (ε′), dielectric loss (ε″), and conductivity (σ) were measured with an inductance capacitance resistance (LCR) meter type AG 4311B (Ando Electric, Ltd., Tokyo, Japan). A guard ring capacitor type NFM/5T (Wissenschaftlich-Technische Werkstatten Gmbh, Weilheim, Germany) was used as a measuring cell. The cell was calibrated with standard samples with known ε′ values.[24]

TGA was performed with a Shimadzu-TGA-50H analyzer (Kyoto, Japan). The samples were heated from 25 to 600°C at heating rate of 10°C/min under a dry nitrogen (N_2) atmosphere. The temperature at the initiation of degradation (T_i), the temperature at 50% weight loss (T_{50}), and the temperature at the maximum degradation rate (T_{max}) were determined.

The microstructures of the samples under investigation were examined with a Leica optical microscope (Tokyo, Japan).

RESULTS AND DISCUSSION

The effects of maleic anhydride and ATH as additives and the type of the polyolefin used on the physical, mechanical, and thermal properties of the following composites were studied:

1. Wood flour/PE.
2. Wood flour/PP.
3. Wood flour/PE and PP mixture.
4. A sample from the market (MDF) used for comparison.

Water absorption

One of the most important roles played by the formulation of WPCs and by the chemical modifications of wood or polymer is the reduction of swelling by water, that is, an increase in the dimensional stability. The dimensional stability is most easily evaluated with the water soaking method, in which the measured results are expressed as percentage water absorbed and percentage volumetric swelling.

The results, illustrated in Figure 1, show a gradual increase up to 40 days in the water absorption percentage. This percentage was retarded after 20 days in all of the wood flour/polyolefin composites with additives as compared to that in the composites without any additives. As is apparent in Figure 1(a–c), the water uptake was reduced to the lowest values for the samples containing a mixture of ATH and maleic anhydride followed by samples containing maleic anhydride only. The reduction was in the following order: Mixture of ATH and maleic anhydride > Maleic anhydride > ATH. When the results

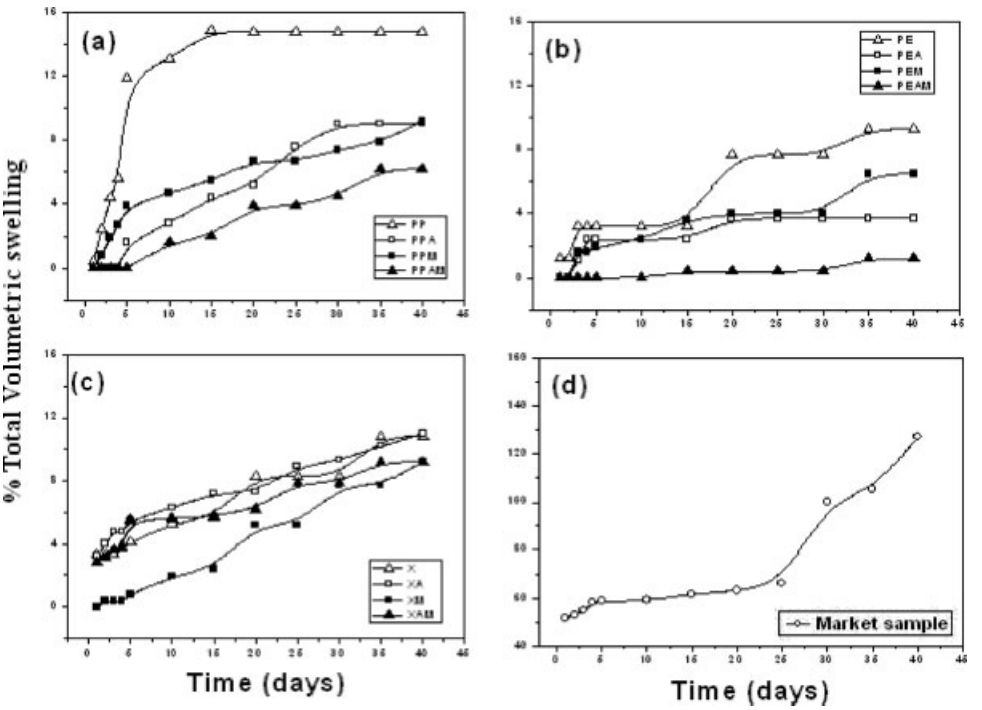

Figure 2 Effect of additives on the percentage volumetric swelling for the wood flour/polyolefin composites and market sample.

obtained for the prepared composites with the sample from the market were compared, a great difference was obtained. The water absorption percentage for the MDF sample from the market was 90% after 1 day only and reached its maximum of 132% after 40 days, as shown in Figure 1(d). The results also indicate that the PE/wood flour composites showed a lesser absorption of water than those of the PE/PP mixture followed by the PP composite samples. This may have been due to the fact that in the presence of peroxides, PE formed crosslinks whereas the β-scission of PP occurred. It is also known that PE can react with maleic anhydride in the presence of dicumyl peroxide to form maleated PE. This maleated PE could have reacted with the hydroxyl functionality on wood to form a graft copolymer, which acted as compatibilizer for the wood flour and PE. This compatibilizer may have further interacted with wood through hydrogen bonding to form a strong interface.

Volumetric swelling

The percentage total volumetric swelling for the wood flour/polyolefins is shown in Figure 2(a–c). The results indicated that the addition of a mixture of ATH and maleic anhydride suppressed the total volumetric swelling in all kinds of wood flour/polyolefin composites. Figure 2(a) showed no volumetric change for the PPAM samples for up to 5 days, and then, it increased gradually to 5% after 40 days, whereas the PEAM samples showed good dimensional stability, that is, no swelling, after 30 days. When the time was increased to 40 days, the volumetric swelling increased to 1%, as shown in Figure 2(b). This means that the crosslinking of PE in the presence of dicumyl peroxide generated lower swelling in the PE composite samples compared to those in the PP and the mixture; that is, it led to a tighter network formation. On the other hand, ATH and maleic anhydride affected the composite samples with the same trend, as found in the water absorption in the following order: Mixture of ATH and maleic anhydride > Maleic anhydride > ATH. For the market sample, the volumetric swelling increased with increasing time up to 132% [Fig. 2(d)].

Density

As shown in Table II, the presence of wood flour filler increased the density of the polyolefin matrix

TABLE II
Density (g/cm^3) of the Wood Flour/Polyolefin Composites

Component	PP	PE	PP/PE (50/50)
Pure olefin	0.90	0.92	0.90–0.92
Without additives	1.09	0.99	1.10
Maleic anhydride	1.13	1.12	1.12
ATH	1.06	1.13	1.16
Mixture of both	1.13	1.13	1.11

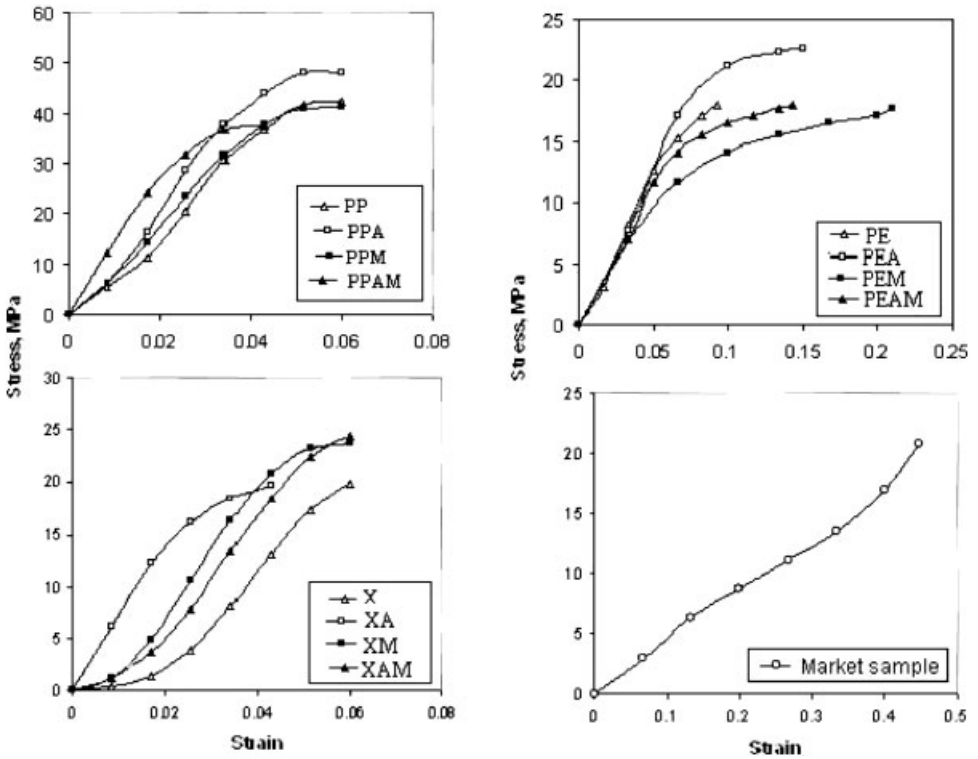

Figure 3 Stress–strain diagram of the wood flour/polyolefin composites and market sample.

composites in comparison with the pure one. However, the density of the wood flour/polyolefin composites containing different additives was higher than the samples without any additives, whereas that of the market sample was 0.83 g/cm^3.

Mechanical properties

The stress–strain diagrams for wood flour/polyolefin composites with different additives and for the local sample are shown in Figure 3(a–d).

The results of the compression test show that the compressive strength for wood flour/polyolefin generally improved when ATH was added, and the maximum value obtained for compressive strength was 47 MPa at a strain of 0.06 (6%) for the wood flour/PP composite. The slope of the elastic deformation, which represents stiffness, was 1166 MPa, whereas the compressive strength of the local sample was 21 MPa, and the slope of the elastic deformation was 37 MPa.

Table III summarizes the results of the compressive and bending strengths of the wood flour/polyolefin composite samples.

When the mechanical properties of the wood flour were compared with those of the different types of polymers and additives and with the market sample, we found that the maximum compressive strength value was observed for the wood flour/PP sample with the maleic anhydride additive (PPM). On the other hand, the bending strength of samples containing wood flour/PE with maleic anhydride and ATH additives (PEAM) showed the same bending strength as the local sample. In general, the presence of additives increased the compressive strength values in the order PP > X > PE and increased the bending strength values in the order PE > X > PP.

Electrical properties

It was interesting to study the electrical properties of polyolefin composites prepared in the presence of

TABLE III
Compressive and Bending Strength Values of the Wood Flour/Polyolefin Composites

Bending strength (MPa)	Compressive strength (MPa)	Code number
3.8	41	PP
4.7	37	PPA
6.9	47	PPM
4.3	34	PPAM
7.8	17	PE
8.1	22	PEA
10.0	22	PEM
12.7	21	PEAM
3.4	19.5	X
7.9	23	XA
7.0	19.5	XM
7.6	25	XAM
13.2	21	Market sample

TABLE IV
Electrical Properties of the Wood Flour Composites

$\sigma \times 10^{11}$ (ohm^{-1} cm^{-1})	ε''	ε'	Code number
5.29	0.16	7.30	PP
10.85	0.19	7.50	PPA
10.00	1.95	10.80	PPM
10.40	1.80	10.03	PPAM
6.66	0.13	6.21	PE
12.90	0.21	6.90	PEA
10.80	0.85	9.05	PEM
11.60	2.3	14.46	PEAM
4.50	0.74	8.90	X
6.79	0.50	8.20	XA
5.35	0.96	9.32	XM
6.32	1.14	12.21	XAM
1.17	0.21	7.08	Market sample

various additives. ε', ε'', and σ were measured for various polyolefin composites and for the control sample. The obtained data are listed in Table IV. As shown in Table IV, the presence of additives in the composite samples affected the values of ε' and ε'', whereas a pronounced increase was noticed in case of maleic anhydride and also the mixture of ATH and maleic anhydride. It was also clear that the highest value of σ was obtained in the case of wood flour/polyolefin composites with ATH or the ATH and maleic anhydride mixture, whereas the lowest value was obtained for the sample without additives. The sample containing wood flour/PE and ATH (PEA) had the best insulating properties, as it possessed high ε' and low ε'' values compared with all of the composite samples.

Thermal stability

Figure 4 shows the TGA curves of both low-density PE and wood flour. The mass loss steps of pure PE occurred very slowly below 500°C, but above 500°C, this process occurred very rapidly. The initial mass loss for wood flour at 100°C was due to the gradual evaporation of absorbed moisture. The second mass loss occurred from 150–500°C because of the decomposition of the three major constituents of the natural filler (cellulose, hemicelluloses, and lignin).[25] Figure 5 shows the TGA diagram for the PE/wood flour composites with different additives compared with the sample obtained from the market as an example. The thermal stability and degradation temperature of the wood flour composite samples with different additives were slightly higher than those without additives.

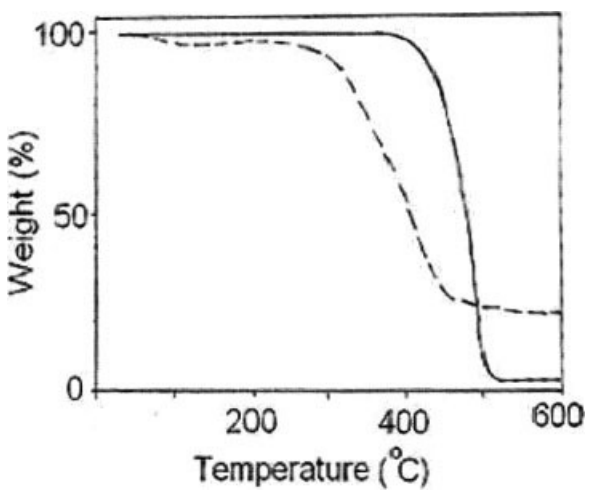

Figure 4 TGA of (—) low-density PE and (- - -) wood flour.

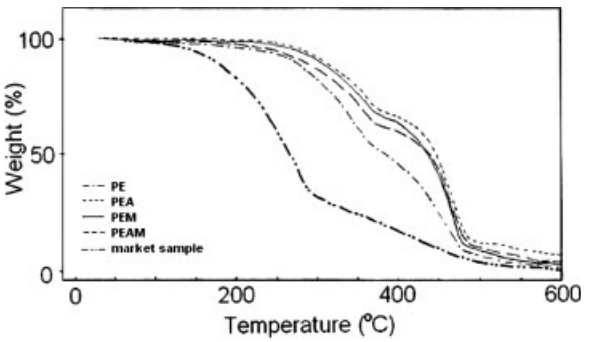

Figure 5 TGA of the wood flour/PE with various additives and the market sample.

The results from the TGA of the wood flour/PE composites are presented in Table V. As clearly shown in Table V, all of the samples had different T_i's. They shifted from 346°C for the PE/wood flour composites to 355°C for the PEM sample containing maleic anhydride to 357°C for those containing both ATH and maleic anhydride to 360°C for the PEA sample containing ATH. T_{50}, T_{max}, and the percentage char yield were higher for the PEA composite sample. This result supports the fact that the presence of ATH enhanced the thermal stability and retarded the weight loss rate, which resulted in a high char yield at high temperature.

T_i, T_{50}, and T_{max} of the local market sample occurred at temperatures lower than those of all of the wood flour/PE samples with additives, which means that a fast degradation occurred.

TABLE V
Thermal Degradation of the Wood Flour/PE Composites

Residue (char yield; %)	T_{max} (°C)	T_{50} (°C)	T_i (°C)	Composite sample
2.7	449	380	346	PE
2.5	469	435	355	PEM
7.1	475	450	360	PEA
4.7	463	450	357	PEAM
2	458	286	120	Market sample

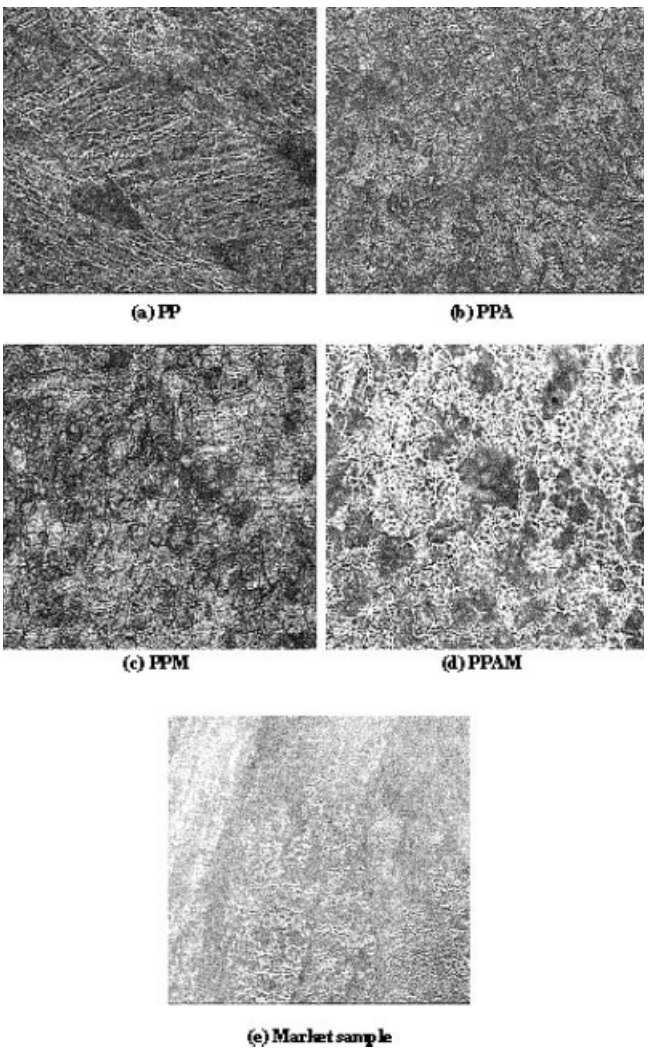

Figure 6 Effect of various additives on the microstructure of the wood flour/PP composites and market sample (100×).

Microstructure measurements

The microstructures of the wood flour/PP with and without additives were studied as an example with an electrical microscope [Fig. 6(a–d)]. The micrograph for the wood flour/PP composite sample without additives (PP) is shown in Figure 6(a). The structure had a specific fibrous texture separated by long-grain boundaries. The addition of 10% ATH to the wood flour/PP led to a change in the texture into small grains, as shown in Figure 6(b). On the addition of maleic anhydride, a circular structure was observed [Fig. 6(c)], but when a mixture of ATH and maleic anhydride was added, the structure changed into subgrains with different sizes, as shown in Figure 6(d). The microstructure of the market sample showed large grains taking a longitudinal direction, and the surface was rough [Fig. 6(e)].

CONCLUSIONS

In the previous discussion, we noted that the presence of various additives (ATH and/or maleic anhydride) in the wood flour/polyolefin composites increased the resistance of water absorption and volumetric swelling after immersion in water for 40 days. The additives also improved the mechanical and electrical properties. The presence of ATH enhanced the thermal stability of all of the composite samples. The PE composite samples gave better results compared to the PP ones. The sample from the market showed no dimensional stability with lower thermal and mechanical properties compared with the others.

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