

Glass Fiber/Wood Flour Modified High Density Polyethylene Composites

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ABSTRACT: Composites of high density polyethylene (HDPE) with the reinforcements of glass fiber (GF) and wood flour (WF) have been studied in this work. High-density polyethylene-grafted maleic hydride (HDPE-g-MAH) was used as a compatibilizer. In particular, the effect of GF, WF, and HDPE-g-MAH on the overall properties of GF/WF/HDPE composites (GWPCs in short form) was systematically studied. The results indicate that HDPE-g-MAH as a compatibilizer can effectively promote the interfacial adhesion between

GF/WF and HDPE. By the incorporations of GF/WF, the heat deflection temperature can reach above 120°C, and the water absorption can be below 0.7%, also the tensile strength, flexural strength, and impact strength of GWPCs can surpass 55.2 Mpa, 69.4 Mpa, and 11.1 KJ/m², respectively. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2084–2089, 2012

Key words: glass fiber; wood flour; GWPCs; compatibilizer

INTRODUCTION

Wood plastic composites (WPCs) have attracted a number of researchers and manufacturing engineers due to the cost savings, low density, environmentally friendly merits, and good mechanical properties when compared with synthetic fibers/plastic composites.^{1–3} In particular, thermoplastic WPCs are more widely used than thermoset WPCs because the former are recyclable, more easily processed and have zero formaldehyde emission. WPCs as decorative materials including decking, window, door profiles, and automobile paneling are widely used,^{1–5} but the strength of WPCs (such as PE/wood flour composites) is still not enough for the structural or engineering constructions.⁴

The interfacial adhesion is vital to WPCs due to the chemically incompatibility between the hydrophobic matrix and hydrophilic fibers.⁵ Many physical and chemical methods have been used so far.^{6,7} Chemical coupling by using various coupling agents or polymer compatibilizers is proved the most effective way, the main function of chemical coupling is to react with the hydroxyl groups on the fiber surface, making the surface wettable by the polymer to promote covalent bonding with the matrix.^{6,8} The reinforcing effects of physical or chemical methods alone are limited, other reinforcements such as syn-

thetic fiber, metal inserts, and glass fiber^{5–10} have been added into WPCs, the advantages of one type of fiber could complement deficiencies in the others due to some physical or chemical synergetic reinforcing effects,^{6,11,12} among them, the incorporation of GF is most effective.

Cui et al.⁶ manufactured the GWPCs from recycled waste PE, waste wood flours and chopped glass fibers indicating that type L chopped GF had achieved full adhesion with the plastic matrix through the addition of maleic anhydride-g-polyethylene. Thwe and Liao¹¹ found MAPP is an effective coupling agent for PP/bamboo-glass fiber composites, and the mechanical properties increased with incorporation of GF before environmental aging. Kitano et al.¹³ studied the HDPE-based composites and found without coupling agent or compatibilizer the tensile strength decreased upon increasing the fiber content when long fiber was used. Jiang et al.¹⁴ delved into PVC-based GWPCs and found the impact strength improved upon adding 5% of L-GF but not upon adding S-GF. Rozman et al.¹⁵ evaluated GF/empty fruit bunch/PP composites indicating significant increase in mechanical properties when suitable coupling agents were used. Tungjitpornkull et al.¹⁶ studied GF reinforced WPVC, they found that the orientation angle of GF had a more pronounced effect on the impact properties. Most of researches are focused on the effects of the pattern and loading of GF as well as the interfacial adhesion between WF and matrix, but the concern of the multi-phase interfacial adhesion (GF/WF/matrix) is still handful, and the loading ratio of the

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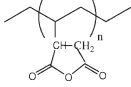
components in GWPCs is also required to be investigated further. Up to now, polyethylene (PE) is one of the most widely used thermoplastics for WPCs due to its relatively low processing temperature and good processability.¹⁷ In the previous researches of our group,^{8,18} fruitful researches on the HDPE-based WPCs have been obtained, but the deficiencies in mechanical strength and stability under heat and moisture still restrict the further applications.

The main objective of this study is enhancing the mechanical strengths of HDPE-based WPCs and its dimensional stability at high temperature. The detailed works contain: (i) to investigate the effects of GF and compatibilizer (HDPE-*g*-MAH) on WPCs; (ii) to find the ideal loadings of the HDPE-*g*-MAH and WF; (iii) to characterize the microstructure of GWPCs.

EXPERIMENTAL

Materials

HDPE was purchased from Sinopec (DMDA8008 with the melt index of 7.6 g/10 min at 190°C/2.16 kg and density of 0.955 g/cm³). Wood flour (WF) (Whangee, average particle size is 175.7 μm and particle size range is 93.4–227.7 μm, moisture content of 5.00%, density ~ 0.35 g/cm³) was purchased from Lin'an Mingzhu Wood Flour Factory, China. Acetone (AR) was purchased from Shanghai Lingfeng Chemical Solvent, China. Silane coupling agent 3-glycidoxypropyltrimethoxysilane (Epoxy-silane, $\text{H}_2\text{C}(\text{O})\text{CH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) was from Shanghai Yao-hua Chemical Solvent, China. Glass fiber (ER13-2000-910, Epoxy-silane treated untwisted rovings) was purchased from Jushi, China. Maleated polyole-

fins (HDPE-*g*-MAH, , MFR = 2.0 g/10

min at 190°C/2.16 kg, $T_m = 132^\circ\text{C}$, tensile strength is 28.4 ± 1.0 MPa, and grafting degree is 1.2 wt %) were made by our group, HDPE, MAH, initiators, solvent, and comonomers were simultaneously introduced into the twin-screw extruder after dry blending, which was similar to the preparation of ABS-*g*-MAH.¹⁹

Sample preparation and processing

WF was firstly dried to remove the moisture and volatiles at 100°C for 24 h, and then treated by the silane coupling agent (Epoxy-silane) in a high-speed mixer (Epoxy-silane was dissolved in 95% ethanol aqueous solution, the ratio of Epoxy-silane to ethanol is 1 : 9, the silane coupling agent content is 5% by the weight of WF). After that, the treated WF was activated at 120°C for 2 h ready for use. The mixing

of HDPE, treated WF, GF, and compatibilizer was carried out with a TSE-35 twin-screw corotating extruder (Ruiya Company, Nanjing, China), the screw speed was 120 rpm, and the barrel temperatures ranged from 140 to 175°C. With air cooled, pelletized and dried at 80°C, test specimens were obtained by compression molding (XLB-D, Shunli Plastic Machinery company, Huzhou, China), hot pressing at 185°C for 10 min.

Characterization

Mechanical properties

The tensile test specimen of 4 mm in width and 1 mm in thickness was dumb-bell shaped, and carried out according to ASTM D882 by an Instron4465 (Instron, USA) machine under 50% humidity at 23°C and testing rate at 20 mm/min. The flexural test specimen with the dimension of $63.5 \times 12.7 \times 3$ mm³ and tested according to ASTM D6109 at the speed of 2 mm/min by the Instron4465 machine. The Izod notched impact strength test was conducted according to ASTM D 256 (the sample was $63.5 \times 12.7 \times 3$ mm³, and the notch depth was 2 mm) using an Izod notched impact machine (Ray-Ran Polyttest, UK). At least eight replicates for each group.

Water absorption

Specimens (dimension: $63.5 \times 12.7 \times 3$ mm³, about 20 g each) were first dried at 80°C in a vacuum oven to a constant weight and then soaked in water at room temperature (25°C) for 5 weeks, and measure the initial weight (M_0) and real-time weight (M). The water absorption is calculated by the formulation (1).²⁰

$$\text{Water}(\%) = \frac{(M - M_0) \times 100}{M_0} \quad (1)$$

Morphology

The sample was fractured after cooling in liquid nitrogen. The surfaces of samples were dried under vacuum and then gold was evaporated. Scanning electron microscopy (SEM) S-2150 (Hitachi, Tokyo, Japan) was used to observe the fractured surface morphology.

Heat deflection temperature

Heat deflection temperature (HDT) was measured as per ASTM-648 with a hot deformation test apparatus (Chengde COTS, China). Samples were heated at the rate of 2°C/min from room temperature.

Samples	HDPE(phr)	WF(phr)	GF((phr)	Compatibilizer(phr)
A-1	neat	0	0	0
A-2	100	42.9	0	0
A-3	100	28.6	14.3±2.0	0

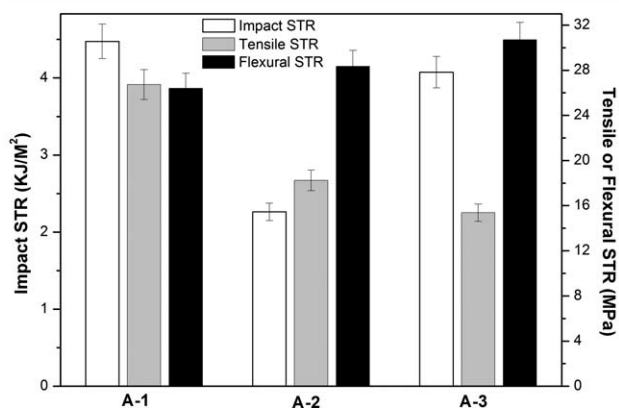


Figure 1 The effect of GF/WF on the mechanical properties of GWPCs.

Glass fiber content measurement

The content of GF was measured by burning up the specimen of GWPCs in Muffle furnace (XL-1/2, Minsheng Technology Development, China) at 600–700°C, measure the initial weight (M_0) and the weight of the remaining (M) after burning, and GF content is calculated by the formulation (2), then change the content (%) into content (phr).

$$\text{GF(\%)} = \frac{(M - M_0) \times 100}{M_0} \quad (2)$$

RESULTS AND DISCUSSION

Effect of glass fiber

Figure 1 gives the mechanical results of the reinforcing effect of WF/GF on GWPCs. As shown in Figure 1, the addition of 42.9 phr WF (A-2) lowered the impact strength of WF/HDPE sharply by 49.4%, compared to neat HDPE (A-1); and the incorporation of 14.3 phr GF (A-3) was conducive to increase the impact strength apparently compared with A-2 but failed to fully recover the loss in impact strength of the original HDPE. Besides, the addition of WF and GF decreased the tensile strength dramatically by 42.5% from 26.7 MPa for neat HDPE to 15.4 MPa for GWPCs. WF and GF cannot obviously promote the flexural strength. The explanation for such results is that the method of epoxy-silane treating could reduce the polarity of hydroxyl groups on surface of the fibers (WF/GF) to some degrees,⁸ but the fibers were still polar not compatible with HDPE well, though the epoxy-silane contained carbon-carbon bond, it was not enough to make the interfacial ad-

hesion better.^{5–7} Therefore, compatibilizer could be needed to enhance the interfacial adhesion between fibers and HDPE which will be discussed in the following part.

Figure 2 gives the SEM images of the composites without compatibilizer. White arrowhead represents WF and black one for GF. The fractured surface of A-2 (the blends of HDPE and WF) was rough and full of voids and cracks for the poor compatibility between WF and HDPE matrix. For A-3 (no compatibilizer was used), the GF or WF surface was thoroughly smooth and free of matrix, and many voids were observed, indicating that the compatibility between GF or WF and the matrix was poor allowing GF or WF to be pulled out with no pain.

Impact of compatibilizer (HDPE-g-MAH) loading

Compatibilizers are added to further improve the interfacial adhesion. According to our previous works,^{8,18} HDPE-g-MAH was proved to be an effective compatibilizer for WF/HDPE composites, due to the facts: firstly, it includes the same component

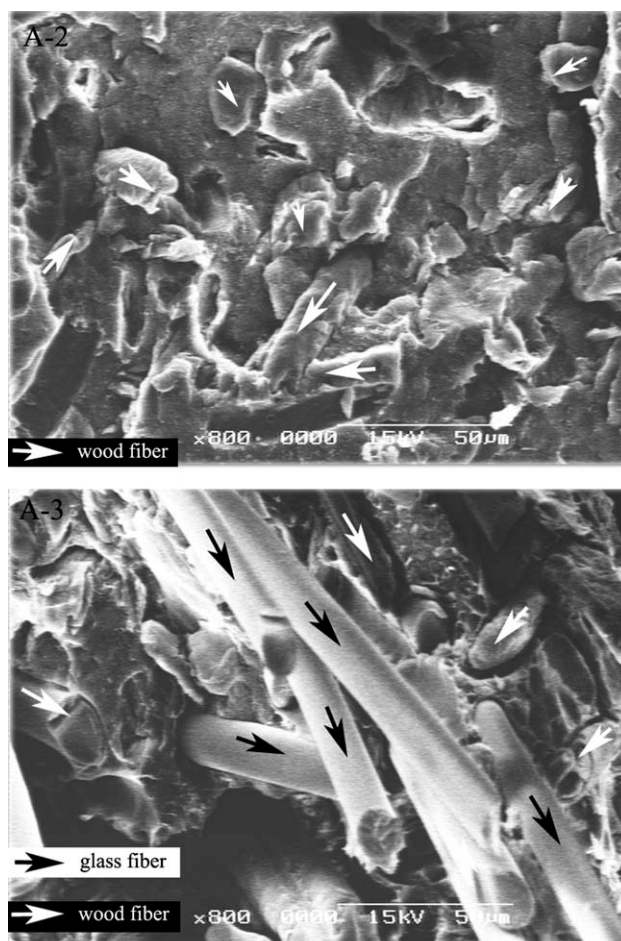


Figure 2 SEM of composites without compatibilizer (A-2 and A-3).

TABLE I
The Formula and HDT with Different Loading of HDPE-g-MAH

Samples	HDPE (phr)	WF (phr)	GF (phr)	HDPE-g-MAH (phr)	HDT (°C)
Pure HDPE	100	0	0	0	58.2 ± 2.0
B-0	100	60	0	20	63.4 ± 2.0
B-1	100	60	17.8 ± 2.0	0	100.6 ± 2.0
B-2			18.3 ± 2.0	5	115.7 ± 2.0
B-3			18.9 ± 2.0	10	116.2 ± 2.0
B-4			19.4 ± 2.0	15	117.6 ± 2.0
B-5			20.0 ± 2.0	20	118.2 ± 2.0
B-6			20.6 ± 2.0	25	120.9 ± 2.0
B-7			21.1 ± 2.0	30	121.6 ± 2.0

“HDPE” as the matrix HDPE so that it can be more compatible with the matrix; secondly, the maleic anhydride groups reaction with the hydroxyls in activated GF or WF or the epoxy groups of epoxy-silane to form ester bonds, so HDPE-g-MAH is used as a robust bridge to link both HDPE matrix and GF/WF through good distribution of GF/WF fibers into the matrix.^{8,18,21,22} Here we mainly focused on the impact of HDPE-g-MAH loading. The formula of GWPCs is listed in Table I.

Figure 3 gives the effect of HDPE-g-MAH's loading on the mechanical properties of GF/WF/HDPE composites. As depicted in Figure 3, tensile strength ascended with increasing the loading of compatibilizer and reached the peak value at the loading of 25 phr (B-6); meanwhile tensile strength improved by 286% up to 54.5 MPa (25 phr compatibilizer) comparing to the composites with 0 phr HDPE-g-MAH (B-1). Flexural strength reached the maximum improved by 111% from 31.4 MPa (0 phr, B-1) to 66.4 MPa (25 phr). The impact strength also reached the maximum (10.9 KJ/m²) at the loading of 25 phr. Proper addition of HDPE-g-MAH could enhance the interfacial adhesion between GF or WF and HDPE so that the stress transferred from matrix to GF

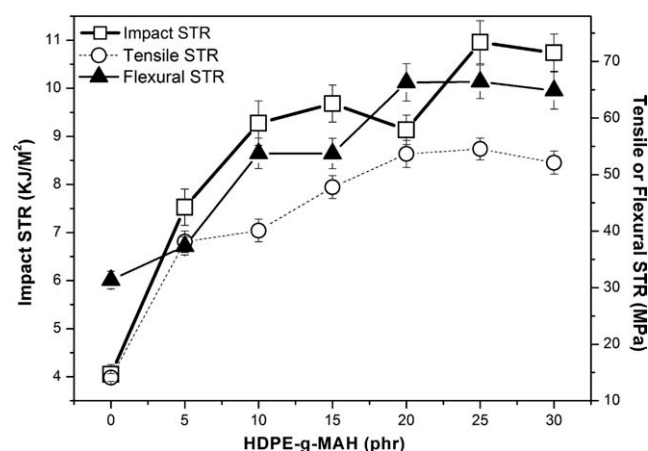


Figure 3 The effect of HDPE-g-MAH's loading on mechanical properties.

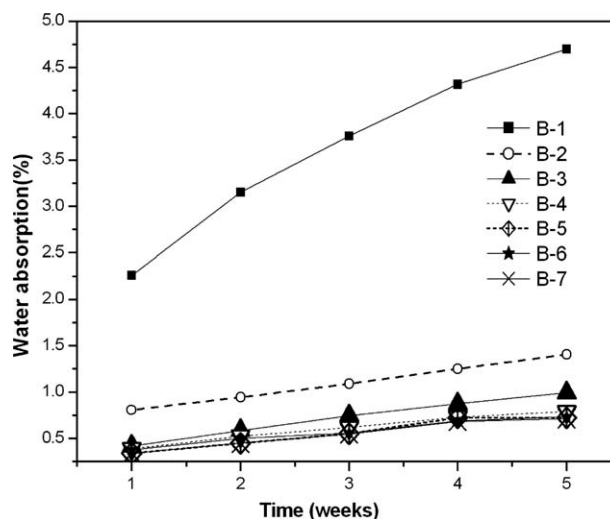


Figure 4 The effect of HDPE-g-MAH's loading on water absorption.

effectively to improve the mechanical properties.¹⁸ As the results indicating, 25 phr is the best loading of HDPE-g-MAH for comprehensive mechanical properties. More loadings than 25 phr may lead to decrease of mechanical properties due to the fact that the existence of excessive compatibilizers may enlarge the gap between the fibers and thermoplastic matrix and weaken the interfacial joint.²²

The HDT value directly affects the application of a thermoplastic material because beyond HDT the mechanical properties of the material will deteriorate.¹⁸ Table I presents the HDT of GWPCs with different HDPE-g-MAH contents. HDT of pure HDPE was only 58.2°C. The addition of WF can slightly improve HDT (B-0) to 63.4°C. When adding GF, the HDT of the composite (B-1) reached 100.6°C. Furthermore, the addition of HDPE-g-MAH can increase the HDT of GWPCs up to 121.6°C (B-7) thanks to its excellent contribution to the improvement in thermal compatibility between GF/WF and HDPE.

The water absorption results are presented in Figure 4. As shown in Figure 4, the addition of HDPE-g-MAH obviously lowered the water absorption to below 1.5% when compared with the water uptake at 4.7% in absence of any compatibilizer. At the loading of 25 phr (B-6), the water absorption was less than 1%, which is nearly negligible for the applications, because the hydrophilic fibers are effectively coated with the hydrophobic matrix and a water-resistant film is formed around the fibers.^{9,23}

Figure 5 further demonstrates the effect of compatibilizer. Sample B-3 and B-6 (blends of HDPE, WF, and GF) with HDPE-g-MAH showed fewer voids and cracks, and GF or WF surface covered with the matrix resin, suggesting that HDPE-g-MAH can improve the compatibility. More loading of HDPE-g-MAH led to better interfacial adhesion, GF in B-3

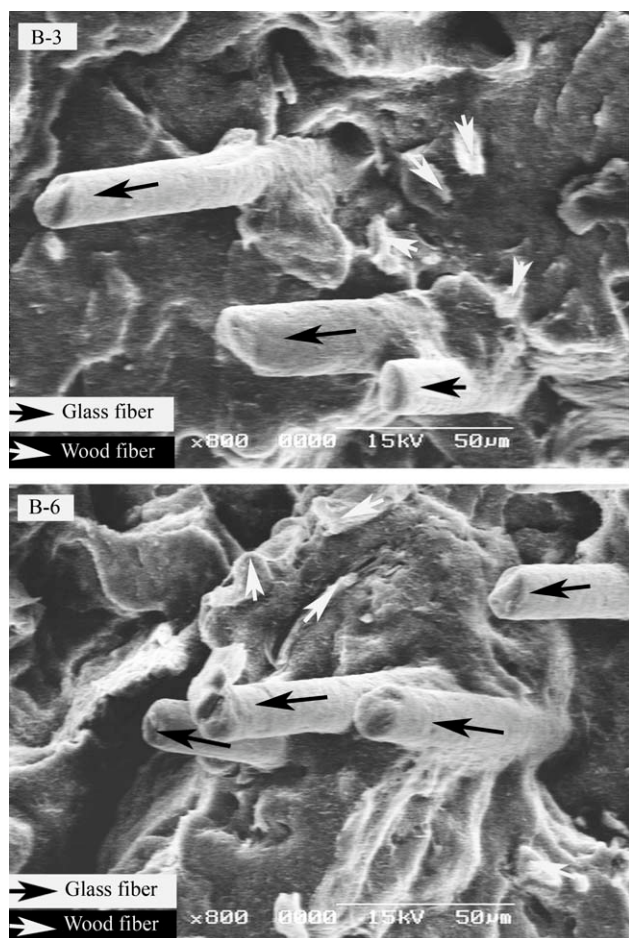


Figure 5 SEM of composites with compatibilizer (B-3 and B-6).

(10 phr HDPE-g-MAH) was partly covered by HDPE and there still existed some voids; while, GF in B-6 (25 phr HDPE-g-MAH) was almost covered by HDPE wholly. This morphology also provides a further evidence for the better mechanical properties and low water absorption of the composites.¹⁸

Impact of wood flour loading

The addition of WF can not only reduce the cost but also partly improve the mechanical properties.²⁴ The formula of WF loading is listed in Table II and the mechanical test results are given in Figure 6.

TABLE II
The Formula and HDT with Different Loading of WF

Samples	HDPE (phr)	WF (phr)	GF (phr)	HDPE-MAH (phr)	HDT (°C)
C-1	100	20	16.4 ± 2.0	27.5	107.0 ± 2.0
C-2		40	18.6 ± 2.0		109.0 ± 2.0
C-3		50	19.7 ± 2.0		113.1 ± 2.0
C-4		60	20.8 ± 2.0		120.5 ± 2.0
C-5		70	21.9 ± 2.0		119.0 ± 2.0
C-6		80	23.1 ± 2.0		119.6 ± 2.0

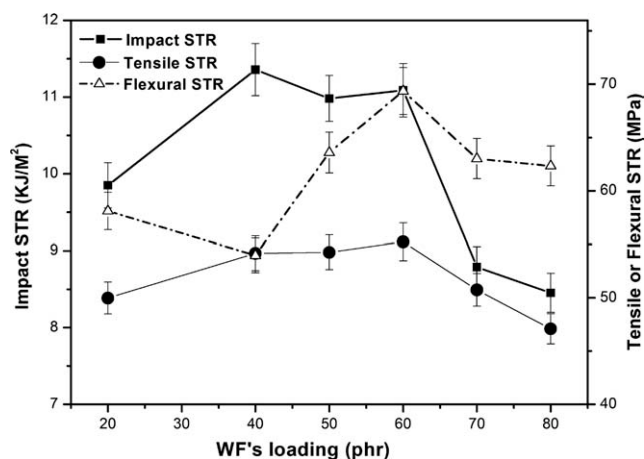


Figure 6 The effect of WF loading on mechanical properties.

As shown in Figure 6, with the increasing loading of WF, the mechanical properties of GWPCs first increased and then decreased indicating that there exists an optimum WF loading. At the loading of 60 phr, both the tensile strength and the flexural strength simultaneously reached the maximum values of 55.2 and 69.4 MPa, respectively. The impact strength showed the similar trend, and reached the maximum value of 11.4 KJ/m² at 40 phr WF. WF can act as a reinforcing filler to strengthen HDPE thermoplastic mainly due to its high specific strength and stiffness when the good interaction between WF and HDPE matrix is formed.²⁴ It is also worth mentioning that the properties of GWPCs are subjected to the distribution of WF, WF wetting, and HDPE penetration in the processing.³ There is a processability issue for high WF loading (more than 60 phr) because of the agglomeration of WF and increasing of viscosity in the system.^{1,3,8,18}

HDT and water absorption results are shown in Table II and Figure 7. The HDT increased with the

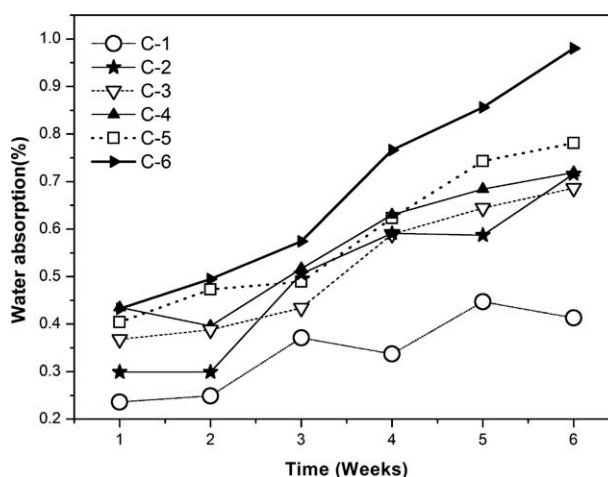


Figure 7 The effect of WF's loading on water absorption.

increasing loading of WF while 50–80 phr loading showed close HDT between 110 and 120°C, suitable for some high temperature applications. Water absorption also increased with the increasing loading of WF, but all the water absorption remained in a low level below 1% on the whole. The surplus of WF failed to interact with HDPE matrix leading to high moisture uptake.¹⁸ Therefore, it is fair to say that GWPCs with 60 phr loading of WF exhibits relatively the best comprehensive properties.

CONCLUSION

In this article, GF/WF/HDPE composites (GWPCs) were prepared through glass fiber and wood flour as reinforcements and HDPE-g-MAH as a compatibilizer. The effects of GF, HDPE-g-MAH's loading and WF content on the mechanical properties, HDT, water absorption and morphology of GWPCs were investigated. The important results are summarized as follows:

1. Simply by adding glass fiber can not play a significant role in improving the performance of WF/HDPE composites due to poor interfacial adhesion between WF/GF and HDPE through SEM.
2. HDPE-g-MAH is an effective compatibilizer to promote the interfacial adhesion between GF/WF and HDPE from SEM and enhance the properties. When the loading of HDPE-g-MAH is 25 phr, the composite possesses much higher HDT (>120°C), lower water absorption (< 0.7%), high tensile strength (54.5 MPa), flexural strength (66.4 MPa), and impact strength (10.9 KJ/m²).
3. The mechanical properties of GWPCs initially increase and then decrease with the increase of WF loading. When WF loading is 60 phr, the GWPCs exhibit relatively the best properties (tensile strength, flexural strength, and impact strength surpass 55.2 MPa, 69.4 MPa, and 11.1

KJ/m², respectively). While water absorption increases with the WF loading increasing, all the water absorption remained in a low level below 1% on the whole.

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