

Preparation of Highly Filled Wood Flour/Recycled High Density Polyethylene Composites by *In Situ* Reactive Extrusion

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ABSTRACT: Highly filled wood flour/recycled high density polyethylene (WF/RHDPE) composites were directly prepared by *in situ* reactive extrusion using a twin-screw/single-screw extruder system. The effects of dicumyl peroxide (DCP) content on extrusion pressure, rheological behavior, mechanical properties, fractured surface morphology of the composites, and melting temperature of RHDPE in the composites were investigated. The extrusion pressure and torque of WF/RHDPE composite melt increased with DCP content. Mechanical property tests and scanning electron microscopy analysis results confirmed that the interfacial interaction of the composites was improved by *in situ* reaction. The composites show lower melting peak temperature (T_m) than RHDPE. The

cooling in profile extrusion shortened the crystallization time, resulting in decrease of crystalline order of RHDPE in the composites. There are no noticeable changes of T_m values with increasing DCP content. Comparative study on composites with maleic anhydride grafted polyethylene as compatibilizer demonstrated that mechanochemical treatment with DCP and maleic anhydride was an effective method to improve interfacial adhesion for WF/RHDPE composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5247–5253, 2012

Key words: wood plastic composites; recycled HDPE; reactive extrusion; rheological properties; mechanical properties

INTRODUCTION

Wood plastic composites (WPCs) have attracted increasing attention since the late 1980s owing to the potential ecological and economic advantage of the lignocellulosic fibers.^{1–4} WPCs are primarily produced with high filler loading. For example, the typical content of wood flour (WF) is 50–60% in commercial WPC products, which is close to the maximum packing content if the wood particles are considered solid.⁵ The utilization of natural fibers as reinforcing filler in plastics has a lot of advantages: high specific strength and stiffness, low cost, low density, renewable nature, absence of associated health hazards, easy fiber surface modification, wide availability, and relative nonabrasiveness.³ Wood flour is finely divided ground wood having a flour-like appearance. Typically, the particle size of wood flour used in WPCs is about 40 mesh, that is, about 425 μm .⁶ Much work has been done on virgin

thermoplastic and natural fiber composites, which has successfully proven the applicability of WPC to various technical fields.^{7,8} Compatibilizers are widely used to enhance the interfacial interaction and improve the mechanical properties of the composites.^{9–13}

Currently, the most common industrial process of WPC is profile extrusion, using a single, twin screw extruder, often the conical type or twin-screw/single-screw extruder system.^{4,14–16} It is not easy to process WPC with high WF content, one reason is the temperature limitation and hygroscopy of WF; another challenge to continuous profile extrusion of WPC is compounding or blending. Compounding consists of feeding and dispersion of the lignocellulosic component throughout the thermoplastic matrix. However, the continuous extrusion techniques are now established, and industrial equipment for processing highly filled WPC is available.^{4,16}

Plastics account for an increasing fraction of municipal solid waste around the world, thus, recycled plastics are becoming a potential worldwide source of raw materials. There are also economical and environmental reasons for utilizing recycled plastic as polymer matrix in WPC. Lei et al.¹⁷ prepared WF/RHDPE composites by melt compounding in rheometer chamber and compression molding, and

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then investigated the influence of coupling agent type and content on the compounding rheology, RHDPE crystallization behavior, and properties of composites. Other researchers^{18–22} also reported the preparation and properties of WF/RHDPE composites. In these studies, WF content was in the range of 30–50%, and composite samples were manufactured by compression molding or injection molding. However, the reports about preparing WF/RHDPE composites directly by *in situ* reactive extrusion are scarce.

In this study, highly filled WF/RHDPE composites were directly prepared by *in situ* reactive extrusion using a twin-screw/single-screw extruder system. A basic formulation with fixed weight ratio of WF : RHDPE : TPW604 (used as lubricant) : maleic anhydride (MAH) = 150 : 100 : 5 : 1 was used, and the emphasis was placed on the effects of DCP content on extrusion pressure, rheological behavior, mechanical properties, fractured surface morphology of the composites, and melting temperature of RHDPE in composites.

EXPERIMENTAL

Materials

RHDPE pellets was provided by Shenyang Graceworld Composite Materials Co. Ltd (Shenyang, China). The material has a melt flow index of 0.6 g/10 min at 190°C, a density of 938.5 kg/m³, and melting temperature range from 121.6 to 134.6°C with a peak at 131.3°C with a heating rate of 10°C/min. WF with 40-mesh particle size from Harbin Yongxu company (Harbin, China) was oven-dried at 105°C for 24 h to remove moisture and then stored in sealed plastic bags prior to compounding. STRUKTOL® TPW604 purchased from Struktol Company (American) was used as lubricant. Maleic anhydride grafted polyethylene (MAPE) with grafting ratio of 0.9% was used as compatibilizer for comparative WF/RHDPE composite, which was supplied by Shanghai Sunny New Technology Development Co. Ltd. All other chemicals including DCP (used as initiator) and maleic anhydride (MAH) were used without further purification.

Preparation of composites

The processing formulations and the abbreviation used for the respective sample are shown in Table I. According to the foregoing study results,²³ a basic formulation with fixed weight ratio of WF : RHDPE : TPW604 : MAH = 150 : 100 : 5 : 1 was used. The content of DCP in the formulation was with respect to RHDPE weight in composite and varied from 0 to 0.15% (w/w). RHDPE, WF, TPW604, MAH, and

TABLE I
Formulations of WF/RHDPE Composite

Samples	RHDPE	WF	TPW604	MAH	DCP ^a (%)
MD00	100	150	5	–	–
MD03	100	150	5	1	0.03
MD06	100	150	5	1	0.06
MD08	100	150	5	1	0.08
MD09	100	150	5	1	0.09
MD12	100	150	5	1	0.12
MD15	100	150	5	1	0.15
RHDPE	100	–	2	–	–
D09	100	150	5	–	0.09
MAPE8	92	150	5	MAPE: 8	

^a Respect to RHDPE weight in composite (w/w).

DCP were mixed in a high-speed mixer at 1440 rpm for 10 min, then composite sheets were directly prepared by a twin-screw/single-screw extruder system through a rectangular die with the dimensions of 40 mm × 4 mm for testing. The processing temperature for extrusion was set at 155°C for melting zone, 170–180°C for pumping zone, 180°C for head and die zone, respectively. The rotating speed was 40 rpm for twin-screw and 30 rpm for single-screw. Extrusion pressure was monitored with PT124B-121/121T melt pressure transducer (Shanghai Zhaohui Pressure Apparatus Co. Ltd, Shanghai, China) and recorded by computer. Feeding of the mixture of WF, RHDPE, TPW604, MAH, and DCP was performed by a twin-screw dosing feeder. The tool for WPC extrusion (WPC extrusion die) and the downstream equipment was from Huangshi Hong Da Plastic Mold, Co, Ltd (Huangshi, China).

Measurements

Rheological property testing

The torque rheological behavior of RHDPE and its composites were performed in a RM-200A torque rheometer. The pellets ground from extruded composite sheets were added into the chamber of the torque rheometer, which was preheated to 170°C, and the rotor was set at a speed of 35 rpm. The content of every sample was kept at 55 g. Equilibrium torques and curves of torque versus time were recorded by computer.

Mechanical properties testing

Samples for mechanical testing were cut from extruded composite sheets (40 mm × 4 mm). Determination of tensile and flexural properties were carried out on a RGT-20A universal testing machine (produced by Shenzhen Regeer Instrument Co., China) controlled by computer, according to ASTM standards. Five specimens of each formulation were tested and the average values were reported.

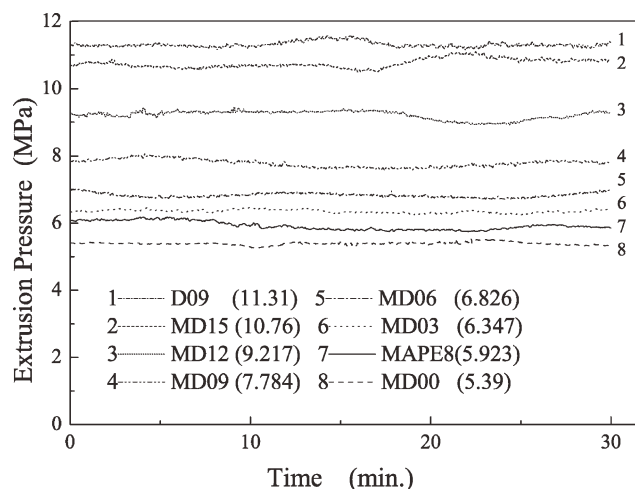


Figure 1 Extrusion pressure of WF/RHDPE composites.

Scanning electron microscope (SEM) observation

For the observation of interfacial behavior between WF and matrix in WPCs, specimens (MD09 and MD00) were fractured under liquid nitrogen condition. The fracture surface of the sample was sputter-coated with gold layer before examination, and the morphology micrographs of the composites were obtained using QUANTA200 scanning electron microscope (FEL, USA), for which the accelerating voltage was 12.5 kV.

Differential scanning calorimetry (DSC) analysis

DSC analysis was performed by DSC200 (NETZSCH, Germany) to measure melting temperature (T_m) of RHDPE in the composites. The samples of about 4 mg were weighed accurately in an aluminum pan and sealed. DSC analysis was carried out from 30 to 170°C with a heating rate of 10°C/min under an inert nitrogen atmosphere, and keeping at 170°C for 5 min to eliminate the influence of their previous thermal-mechanical histories. This was followed by cooling to 30°C at 10°C/min and keeping at 30°C for 5 min, then reheating to 170°C at a heating rate of 10°C/min. Scanning during the two heating were recorded. The values of T_m were determined.

RESULTS AND DISCUSSION

Extrusion pressure

The extrusion pressure during the *in situ* reactive extrusion of WPCs with fixed weight ratio of WF : RHDPE : TPW604 : MAH but containing different amounts of DCP and two comparative samples (MAPE8, D09) are shown in Figure 1, the values in parentheses are average extrusion pressure during extrusion. Extrusion pressure fluctuated more obviously with increasing content of DCP. To investigate the influence of DCP content on extrusion pressure,

the average extrusion pressures are plotted versus DCP content in Figure 2. It can be seen that the average extrusion pressure increases with DCP content. It is more obvious when DCP content is up to 0.09%. Figures 1 and 2 also show that extrusion pressure increased greatly without MAH (comparing MD09 with D09), even higher than that of MD15. These phenomena should be attributed to the complicated mechanochemical effects in *in situ* reactive extrusion. Like the peroxide-initiated functionalization of polyolefins with MAH in melt state,^{24,25} grafting of MAH onto PE chain can enhance interfacial adhesion between the filler and matrix, side reactions such as PE chain scission, crosslinking, and/or long chain branching may certainly alter the rheological property and processing characteristics as well as the mechanical properties of the composite system. When MAH is added and DCP content is lower in composite mixture, grafting reaction of MAH onto PE chain was dominant which enhanced interfacial adhesion between the filler and matrix; at a higher DCP content or in absence of MAH, crosslinking and/or long chain branching between PE chains became dominant which resulted in increasing extrusion pressure.

Extrusion pressure is an important processing parameter affected by many factors, such as processing temperature, die structure, extrusion output, especially the rheological properties of the composite melts. When all other conditions and parameters are kept constant, extrusion pressure varied obviously with DCP content. This implied that the mechanochemical treatment with DCP and MAH greatly altered the rheological properties of the composites.

Rheological property

The torque curves of RHDPE and its composites were shown in Figure 3 (The values in parentheses

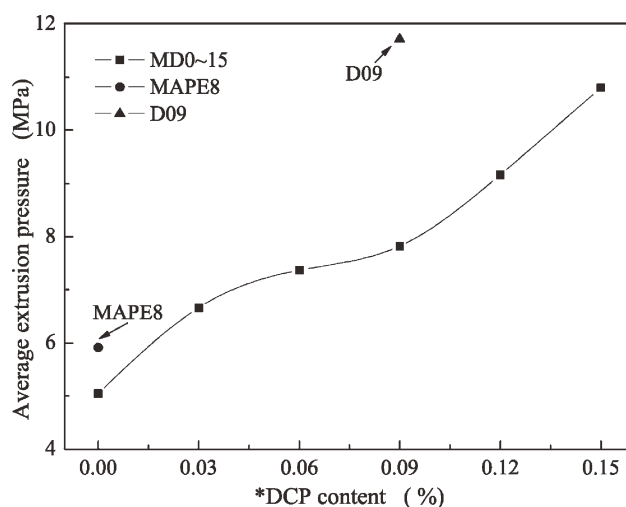


Figure 2 Variation of average extrusion pressure with DCP content.

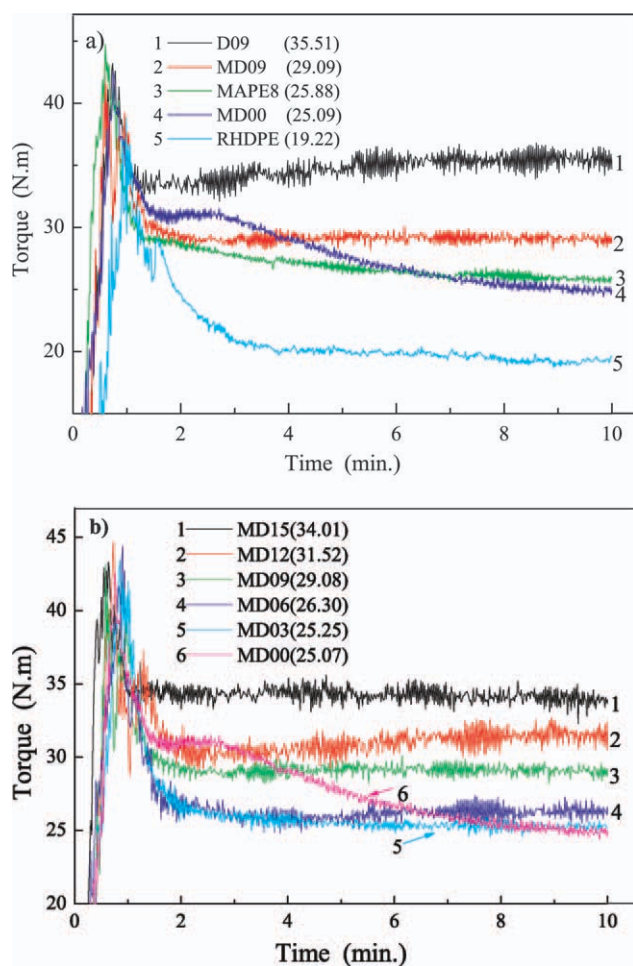


Figure 3 Torque curves of RHDPE and its composites: (a) RHDPE and its comparative composites; (b) WF/RHDPE composites with MAH and different DCP content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

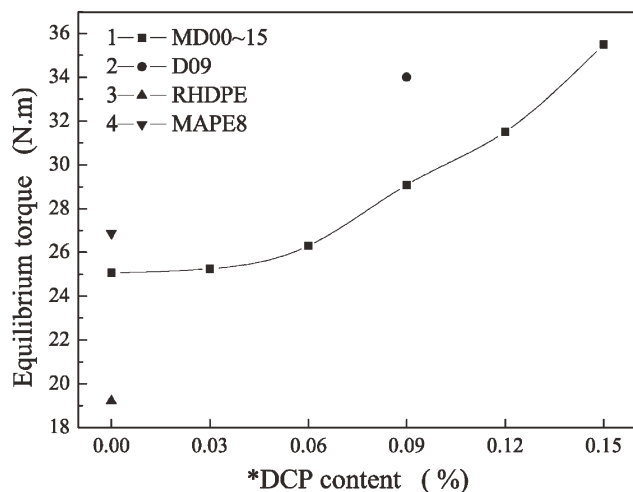


Figure 4 Variation of average equilibrium torque with DCP content.

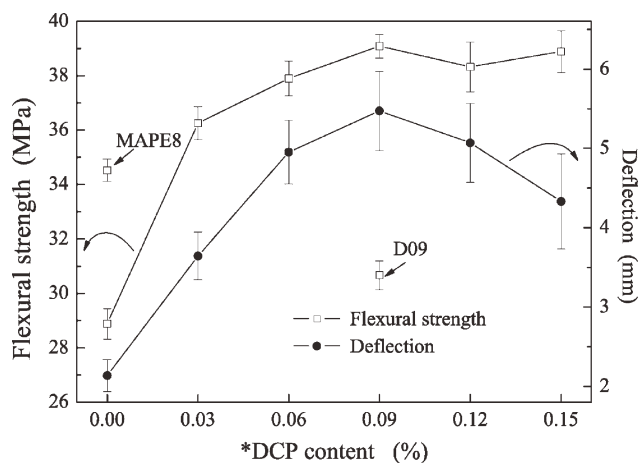


Figure 5 Flexural strength and deflection of composites versus DCP content.

were equilibrium torque between 9 and 10 min). Because the torque of the composite melt in steady-state flow fluctuated obviously with the lobed rotors rotating, the average torque between 9 and 10 min was taken as equilibrium torque (M_a). M_a values of RHDPE and its composites were plotted versus DCP content in Figure 4. Figure 3(a) shows that M_a of composites with 60% WF loading increased from 19.38 N m (RHDPE) to 25.09 N m. The addition of MAH greatly decreased M_a of the composites containing the same DCP content (comparing D09 with MD09). The torque curves in Figure 3(a) also show that the improvement of interfacial interaction made the composite plasticized easily (The torque curves leveled off in shorter time), either by addition of MAPE (MAPE8) or by mechanochemical treatment with DCP and MAH (MD09). It can be seen that M_a of the composite appears to increase with DCP content. The torque of the composites is considered to be associated with the melt viscosity of the composites.²⁶ The increased M_a of MAPE8

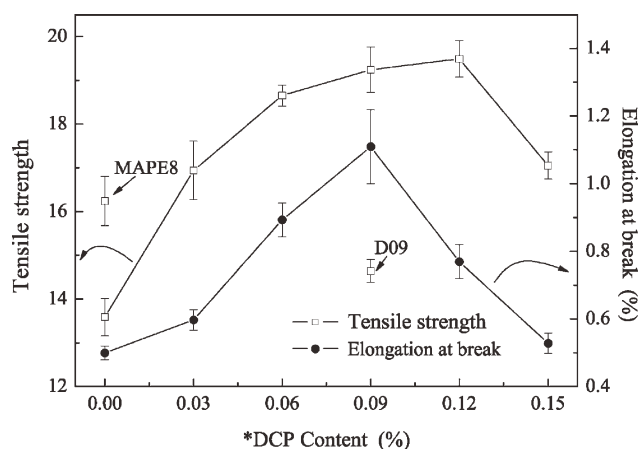


Figure 6 Tensile strength and elongation at break of composites versus DCP content.

(compared to MD00) may be most likely due to the enhanced interfacial adhesion between the filler and matrix by adding MAPE. The increased M_a of the composite melt with DCP and MAH is attributed to complicated mechanochemical effects in *in situ* reactive extrusion, as has said before.

Mechanical properties

The flexural and tensile performance were measured using the extruded samples. The values for tensile strength, elongation at break, flexural strength and deflection are represented graphically in Figures 5 and 6, respectively. The mechanochemical treatment with DCP and MAH showed significant effects on

flexural and tensile performance of composites. The tensile strength, elongation at break, flexural strength, and deflection of WF/RHDPE composites were obviously enhanced by mechanochemical treatment. Mechanical properties reached the maximum increase when DCP content was in the range of 0.06–0.09%. Comparing with control sample (MD00), tensile strength represented an increase of 41.6% (from 13.59 MPa to 19.24 MPa). Elongation at break showed an improvement of 122% (from 0.5% to 1.11%, Fig. 5). Flexural strength exhibited an increase of 35.7% (from 28.8 MPa to 39.09 MPa), and deflection showed an improvement of 149% (from 2.14 mm to 5.47 mm). The mechanical properties reduced when DCP content was further increased. Similar

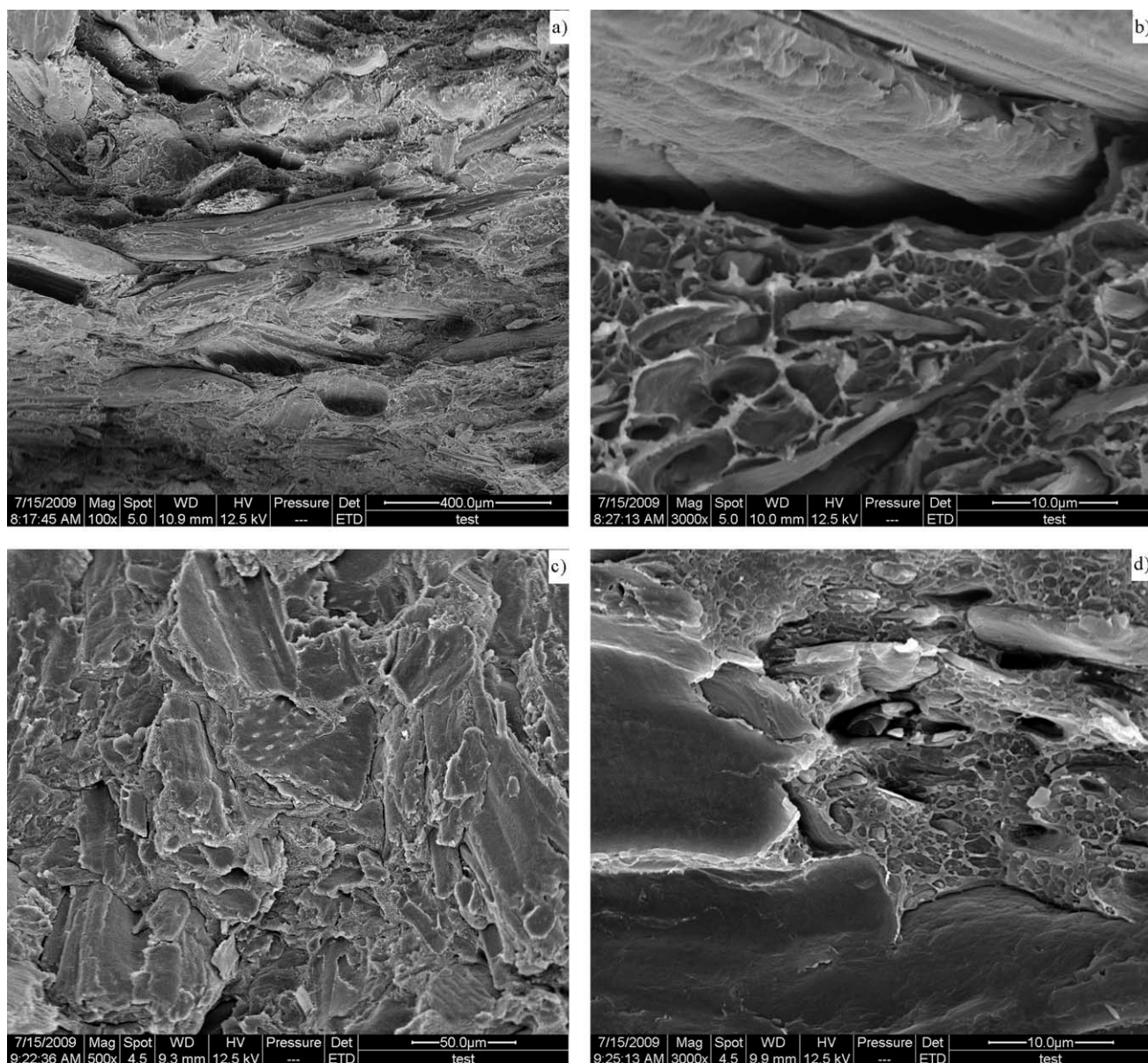


Figure 7 SEM micrographs of the fracture surface of WF/RHDPE composites: (a) MD00, $\times 200$; (b) MD00, $\times 3000$; (c) MD09, $\times 500$; (d) MD09, $\times 3000$.

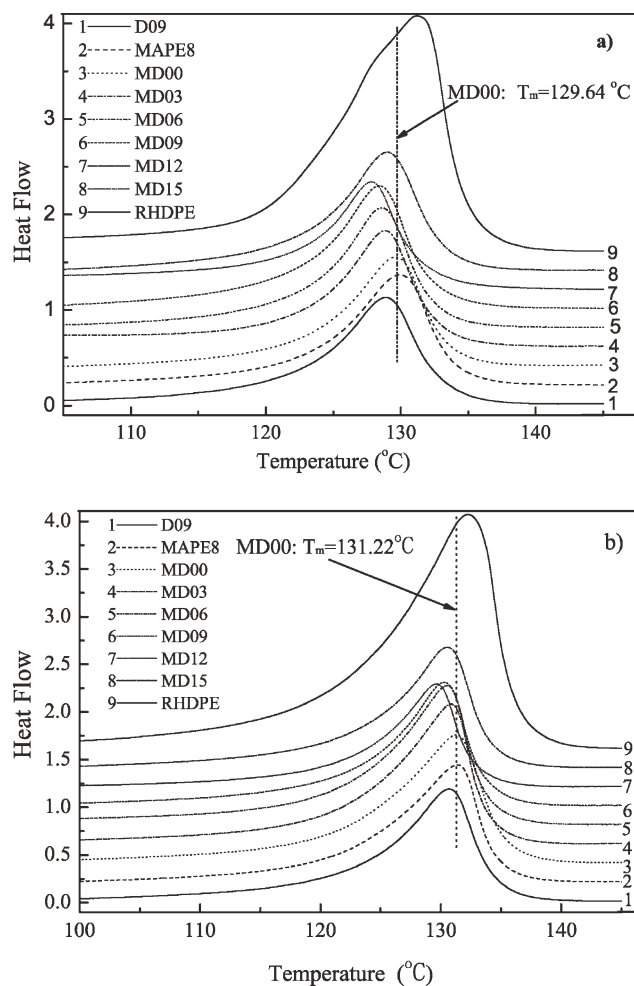


Figure 8 DSC heating curves of RHDPE and its composites with different DCP content: (a) first heating; (b) second heating.

results are also obtained for short sisal fibers/LLDPE composites at high DCP contents for melt pressed samples.²⁷ Excellent mixing of RHDPE, WF, and additives can be achieved with this extruder configuration,^{28,29} and the content of DCP was decreased greatly in *in situ* reactive extrusion. The results demonstrated that mechanochemical treatment with DCP and MAH was an effective method to improve interfacial adhesion for WF/RHDPE composites.

Considering the extrusion pressure, torque rheological and mechanical properties of the composites, the mechanochemical reaction mechanism of WF/RHDPE composites in *in situ* reactive extrusion may be the same as HDPE-*g*-MAH prepared in melt state.^{24,25} In the case of the RHDPE molecular chains containing a few branch chains or propylene copolymerized unites, the generation of tertiary carbon radicals by peroxide initiation is the dominating step. When DCP content is lower (<0.06%), the reaction mainly consists of initiation, chain transfer, recombina-

tion or blocking of macroradicals with MAH, and the terminated reaction of the generated succinyl radicals with macroradicals or H^{*} radicals through recombination. When DCP content is higher (>0.09%), or in absence of MAH, crosslinking and/or long chain branching between PE chains became dominant.

Morphology of composites

Figure 7 shows the fractured surface of WF/RHDPE composites (MD00/MD09). For MD00, there are obvious gaps between RHDPE and WF, and many voids presented around the WF [Fig. 7(a,b)], which attribute to the incompatibility between hydrophobic matrix and hydrophilic WF. For MD09, the gaps between the matrix and WF reduced [Fig. 7(c,d)]. The mechanochemical treatment significantly improved the compatibility between the matrix and WF, and the matrix was well bonded to the WF, especially via grafting of MAH onto RHDPE chain initiated by DCP in *in situ* reactive extrusion. Therefore, this result produces a positive effect on the tensile and flexural strength, which means that loads can be transferred from RHDPE matrix to the WF. The improved interfacial adhesion is in agreement with the enhanced mechanical strength as discussed before.

Melting temperature of RHDPE in composites

The melting temperature of RHDPE in composites is used to characterize the changes of RHDPE in composites in *in situ* reactive extrusion. The DSC curves for RHDPE and its composites are shown in Figure 8 (first and second heating steps). The melting peak temperature (T_m) of RHDPE in composites was determined from DSC curves, which is summarized in Table II. The T_m of RHDPE in composites determined in the first heating step are 1.5–2°C lower than those obtained respectively, in the second heating step, it is the cooling in extrusion shorten

TABLE II
Melting Temperature of RHDPE in Composites

Samples	T_m (°C)	
	First melting	Second melting
D00	129.64	131.22
MD03	128.84	130.88
MD06	128.60	130.50
MD09	128.44	130.26
MD12	127.82	129.60
MD15	129.00	130.54
D09	128.94	130.66
MAPE8	129.94	131.38
RHDPE	131.52	132.20

the crystallization time, resulting in decrease of crystalline order of RHDPE in composites. All composite samples showed lower T_m than RHDPE. The addition of high WF content (60%) in the RHDPE matrix increases the matrix viscosity at the crystallization temperature, and may reduce the diffusion rate of the polyethylene chain, which results in lowering of the crystallization rate.¹⁹ The values of T_m did not have noticeable changes with increasing DCP content (Table II).

CONCLUSIONS

In this study, highly filled wood flour/recycled high density polyethylene (WF/RHDPE) composites were prepared directly by *in situ* reactive extrusion using a twin-screw/single-screw extruder system. A basic formulation with fixed weight ratio of RHDPE : WF : TPW604 : MAH = 100 : 150 : 5 : 1 was employed. The effects of DCP content on extrusion pressure, rheological behavior, mechanical properties, fractured surface morphology of the composites and melting temperature of RHDPE in composites were investigated. The conclusions were as follows:

The extrusion pressure and torque of WF/RHDPE composite melts increased with DCP content. The equilibrium torque (M_a) of WF/RHDPE composites with 60% WF loading increased from 19.38 N m (RHDPE) to 25.09 N m. Torque rheometry and mechanical property tests revealed obvious differences between the composites adding the same DCP content with and without MAH. The improvement of mechanochemical treatment on the interfacial interaction of the composites was confirmed by mechanical property tests and SEM analysis. The mechanochemical treatment with DCP and MAH showed significant effects on flexural and tensile performance of composites. Mechanical properties reached the maximum increase when DCP content was in the range of 0.06–0.09%, being comparable with that of adding MAPE. Composite samples showed lower melting peak temperature (T_m) than RHDPE. The cooling in profile extrusion shortens the crystallization time, resulting in decrease of crystalline order of RHDPE in composites. There are no noticeable

changes of T_m values with increasing DCP content. These results indicate that mechanochemical treatment with DCP and MAH is an effective method to improve interfacial adhesion for WF/RHDPE composites.

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