

Tensile Properties, Morphology, and Thermal Behavior of PVC Composites Containing Pine Flour and Bamboo Flour

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ABSTRACT: Composites of unplasticized poly(vinyl chloride) (PVC) blended with bamboo flour and pine flour, respectively, were prepared in a batch mixer followed by compression molding. The effects of wood flour fillers on the morphology, static mechanical properties, and thermal properties of the composites were investigated. Compared with neat PVC resin, the introduction of both bamboo flour and pine flour significantly improved the stiffness of the composites, while decreasing the tensile strength to some extent. Tensile tests showed that pine flour-filled composites exhibited better mechanical properties than those filled with bamboo flour with the same particle size at the same

loading level. Scanning electron microscopic examination revealed good dispersion and alignment tendency of short pine fiber within the composites at a lower loading level. Moreover, experimental results indicated that both bamboo flour and pine flour additions showed no obviously adverse effect on the thermal stabilities of these composites. Based on the comprehensive properties, these composites meet the need of woodlike material for use as wood structures. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1804–1811, 2004

Key words: composites; poly(vinyl chloride) (PVC); morphology; bamboo flour; pine flour

INTRODUCTION

In recent years, thermoplastic composites containing natural cellulose-based fibers such as wood flour, wood fibers, and cellulose fibers have attracted increasing research attention. The interest comes from several advantages of blending thermoplastics with natural fibers. First, natural fibers are usually characterized by relatively high specific stiffness, strength, and low density compared with properties of currently used inorganic reinforcements such as glass fibers, calcium carbonate, and mica, for instance. Second, the versatility and abundance of natural fibers, and their renewable and recyclable nature, endow such potential fillers with low cost. Third, their low hardness minimizes abrasion of the equipment during melt processing. Finally, today's environmental and

social concerns show increasing demands on forest resources, and thus the combination of wood and synthetic polymers, to produce cheap substitutes for traditional wood products, provides a promising way.

Wood is composed primarily of cellulose, a linear polymer of β -1,4-linked glucose units; lignin, a three-dimensional amorphous natural polymer containing phenylpropane units tri- or tetra-substituted with hydroxyl and methoxyl groups; and hemicellulose.¹ Having such a structure, wood flour or wood fiber exhibits a highly polar and hydrophilic nature. Much effort has been devoted to prepare composites containing polyolefins and cellulose or lignin. One of the key issues for such research work is concerned with the weak fiber-matrix interface, which results from the significant difference between hydrophobic polyolefins and hydrophilic cellulose or lignin. In this regard, different types of coupling agents or compatibilizers have been tested.^{2–5} Kokta et al. investigated the effect of silane coupling agents on the mechanical properties of thermoplastic/wood cellulose composites.^{2–4} In another study, the mechanical properties of recycled low-density polyethylene/wood flour composites were improved by using a maleated triblock copolymer styrene-ethylene/butylenes-styrene as a compatibilizer.⁵

However, the commercialization of cellulose fiber composites has been greatly limited by the availability of cellulose fibers. This situation makes wood flour a

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competitive substitute for the cellulose fibers, especially when extrusion compounding and injection molding are used as processing methods.⁶

Chen et al.^{7,8} prepared a series of maleated polypropylene (MPP) compatibilized polypropylene (PP)/bamboo fiber composites with higher tensile strength, lower density, and lower cost. The results showed that the tensile strength and the stiffness of bamboo fiber-reinforced PP composites were higher than those of the commercial wood pulp composite that was widely used in making office furniture. Feldman and Banu^{1,9} examined the influence of different lignins and lignin derivatives in polyblending with a commercial formulation of rigid PVC on the mechanical, thermal, and weathering properties. The results demonstrated that an interaction occurred between -OH groups of lignin and α -H of PVC.

PVC is a common thermoplastic that has found many applications in building and construction, for example, for window and door frames, siding, and other exterior profiles. Pine is a typical soft species and bamboo belongs to the hardwood species with a very abundant resource. Both pine flour (PF) and bamboo flour (BF) have been chosen as the reinforcements for thermoplastics. Therefore, the objective of this study was to develop a new type of PVC/wood flour composites.

EXPERIMENTAL

Materials

Poly(vinyl chloride) (PVC) (S-1000, K = 67) used in this study was purchased from Sinopec Qilu Co. (China). Several additives were added to the PVC resin to improve the melt processing before the compounding. Tribasic lead sulfate and lead stearate were used as heat stabilizer. Acrylic resins ACR-401 and ACR-ZB-21, supplied by Zibo Additive Co. (Zibo City, China), were chosen as processing aid and impact modifier, respectively. Low molecular weight polyethylene wax was selected as lubricant. γ -Aminopropyltriethoxysilane (A-1100, Nanjing Shuguang Chemical General Co., Nanjing, China) was adopted as a coupling agent to improve adhesion between wood flours and the PVC matrix.¹⁰

The wood flours used were typical pine flour (PF, which belongs to the species of *Pinus massoniana* Lamb) and bamboo flour (BF, which belongs to the species of *Sinarundinaia nitida* Nakai), obtained from a local supplier in the Guangdong Province of China. The particle size of BF was 120 mesh whereas, in the case of PF, two particle sizes (120 and 160 mesh) were used.

Preparation of composites

BF and the two types of PFs were vacuum dried at 75°C for >48 h followed by adding the coupling agent

to the fillers. A 10% aqueous solution of A-1100 silane (the added volume was equivalent to 1% silane with respect to the filler mass) was dropped at regular intervals into a mechanical mixer containing the preweighed filler. Upon finishing the addition of the required silane, the mixing continued for another 30 min. The as-treated wood flours were dried at 75°C for 48 h.

The PVC powders were initially formulated with other additives in a mechanical mixer to obtain the PVC compound. The dry PVC compound, and a certain proportion of filler, were fed into a twin rotary mixer (Haake PolyLab System, RC300P Haake Rheocord, Haake, Bersdorff, Germany) at 175°C for 7 min at a rotor speed of 30 rpm. For each sample, 50 g of materials were fed into the batch. Composites with PVC/BF(120) (the number in parentheses corresponds to the filler particle size) at weight ratios of 100/10, 100/20, 100/30, 100/40, and 100/50 were prepared, respectively. All the composites will be designated in this article in the following form: for example, PVC/10BF(120) represents PVC composite filled with 10 phr BF(120). Composites containing 10, 20, 30, and 40 phr PF(160) and 30 phr PF(120) were also prepared under the same conditions. Melt torques were recorded during the melt compounding. The PVC compound was also blended under the same conditions for easy comparison. The composites subject to blending were stored in a tightly sealed vial to prevent any moisture absorption. The mixture was melt pressed into sheets of 1 mm thickness and then cut into standard dog-bone-shape tensile bars (ASTM D638).

Mechanical properties

The tensile properties were measured at 25°C and relative humidity of 50% using an Instron (Canton, MA) Model 5566 tensile tester. The crosshead speed was set at 10 mm min⁻¹. Five specimens of each sample were tested, and the average results were reported.

Thermogravimetric analyses

Thermogravimetric analysis (TGA) measurements of the samples were performed in a Perkin-Elmer TGA-6 (Perkin Elmer Cetus Instruments, Norwalk, CT) under a protective nitrogen atmosphere. The temperatures used ranged from 30 to 500°C at a heating rate of 20°C/min. Before the analysis, the samples were dried in a vacuum oven at 75°C for 24 h.

Differential scanning calorimetry (DSC)

DSC measurements were carried out using a Netzsch calorimeter (Model 204; Netzsch-Gerätebau GmbH, Bavaria, Germany) from 10 to 150°C at a heating rate

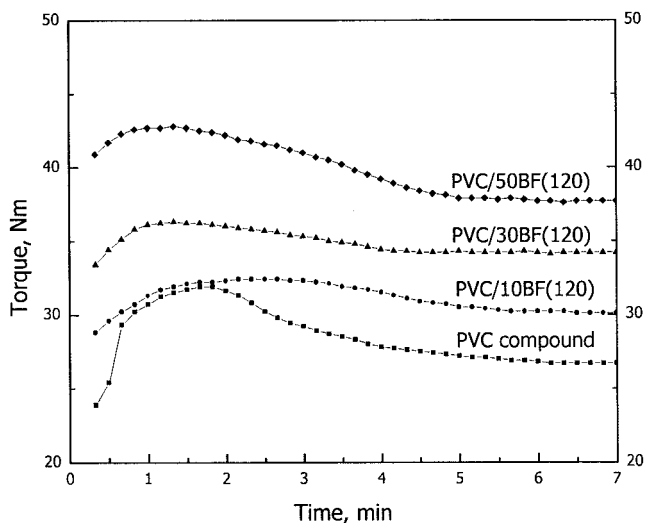


Figure 1 Torque value versus mixing time for PVC compound and PVC/BF(120) composites.

of $20^{\circ}\text{C min}^{-1}$ under a protective nitrogen atmosphere.

Morphology observation

The tensile bars were fractured at room temperature and used for morphology observation with a scanning electron microscope (Model S-520, Hitachi, Osaka, Japan) operated at 15 kV. Before the examination, the fractured surfaces were coated with a thin layer of gold.

RESULTS AND DISCUSSION

Torque behavior

The torque value is generally related to the melt viscosity of the polymers or polymer composites. For the case of PVC composition, the types of PVC resin and additives have a substantial effect on the processability or the fusion characteristics of PVC composites.⁹

The relationships between the torque value and mixing time for PVC compound and PVC/BF(120) composites are shown in Figure 1. It can be seen that the torque value increased rapidly and reached a high value within the initial approximately 1.5 min after feeding the materials into the mixer batch, which is attributed to the initial melting of the PVC matrix. Thereafter, the torque value decreased gradually because of the complete melting of PVC. After about 5 min of mixing, the torque value became constant, implying that 7 min compounding was sufficient for mixing. The behavior of PVC/PF composites showed the same trend when subjected to torque measurements.

The steady-state torque values, measured at a blending time of 7 min, are shown in Figure 2. It is apparent that the melt viscosities increased significantly with increasing BF(120) content. This is a typical characteristic for the fiber-filled composites. The short fibrous BF, with its irregular shape in the composites, can perturb the normal flow of polymer and hinder the mobility of chain segments in flow. Furthermore, fiber–fiber collisions also increase the melt viscosity when increasing the fiber loading.¹¹

Tensile properties

Mechanical properties are generally dependent on such factors as filler content, particle size and shape, the degree of adhesion between the filler and the polymer matrix, and the dispersion degree of the filler within the matrix.¹² To improve the adhesion between wood flour and the PVC matrix, both wood flours were pretreated with A-1100 silane under the same conditions. Two interactions occurred when the filler surface was modified with silane. One occurs between the silanol groups of silane and hydroxyl groups on the wood flour surface by hydrogen bonding, and another between the silane chain and PVC, by van der Waals bonding.¹³ Such treatment of the filler is anticipated to result in the improvement of mechanical properties for the composites. The BF was treated with different silane-coupling agent levels of 0.2, 0.5, 1.0, 2.0, and 4.0% of BF weight. The results demonstrated that the mechanical properties of the composite containing BF treated with 1.0% silane were better than those treated with other amounts of silane. Thus, the results with 1.0% silane are those reported here.

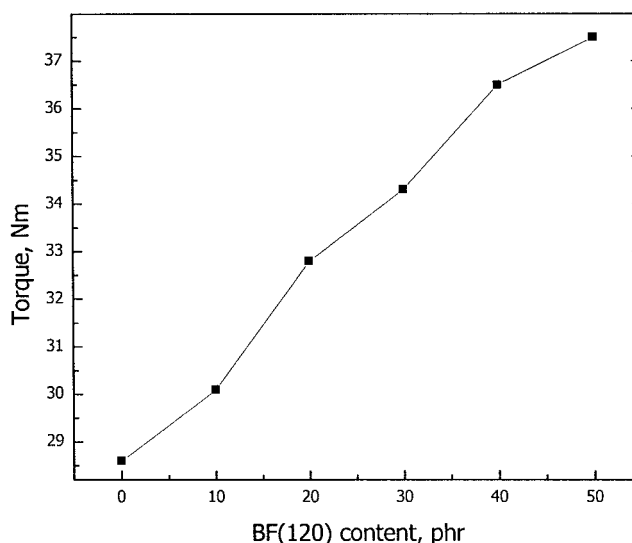


Figure 2 Torque value at 7 min versus BF(120) content for PVC/BF(120) composites.

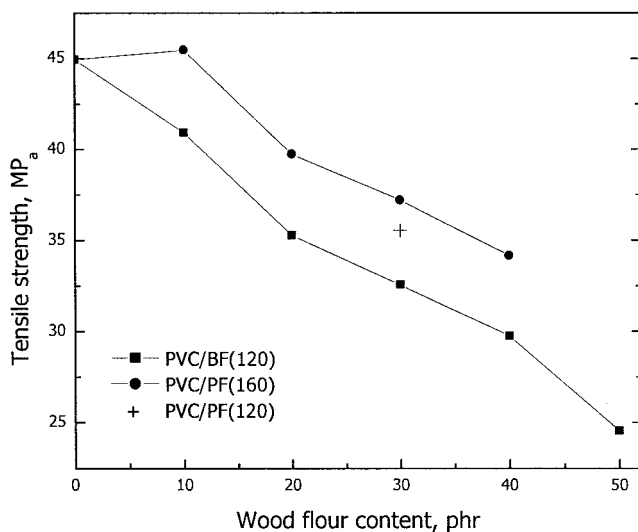


Figure 3 Tensile strengths versus wood flour content for PVC/BF(120), PVC/PF(160), and PVC/PF(120) composites.

Figure 3 shows the filler content versus the tensile strength of PVC/BF(120) and PVC/PF(160) composites. For the purpose of comparison, the results of tensile strength for PVC/30PF(120) composite are also shown in the same figure. Feldman et al.¹ reported the existence of proton donor–proton acceptor interactions between PVC and lignin chains. Such interactions occurred between hydroxyl or carbonyl groups of lignin and α -H of PVC. For wood flour, however, it contains only about <25wt% of lignin, much less of which can be distributed on the surface of filler particles. Consequently, the effect of the aforementioned interaction on the mechanical properties of wood flour-filled PVC composites may not be so pronounced. It can be seen from Figure 3 that the tensile strength for the PVC/BF(120) composites decreases with increasing BF(120) content. For the PVC/PF(160) composites, the tensile strength increases initially with increasing PF(160) content up to 10 phr and, with further increasing PF(160) content, the tensile strength decreases with the same trend as for PVC/BF(120) composites. These outcomes mainly resulted from decreasing interfacial adhesion and homogeneity with increasing wood flour loading because the filler particles tend to form agglomerates as a consequence of the presence of lignin and the OH group on the cellulose. These agglomerates then behave as larger size particles, thus reducing the effective adhesion surface.¹³ Also from Figure 3, the tensile strength of the PVC/30PF(120) composite is slightly lower than that of the PVC/30PF(160) composite because of the smaller particle size of PF(160).

Tensile moduli for the PVC compound and both PVC/BF(120) and PVC/PF(160) composites are shown in Figure 4. One obvious observation is that the moduli of both PVC composites are higher than that of

the PVC compound. The results are attributed to the stiffening effect of the wood flour particles. The Halpin–Tsai equation,^{14,15} which is commonly used to predict the modulus of a discontinuous short fiber-reinforced composite from the moduli of the individual components, explains the above results. The equation has the general form

$$E_c = E_m \left(\frac{1 + \xi \eta \phi_f}{1 - \eta \phi_f} \right) \quad (1)$$

where E_c and E_m are the moduli of composite and matrix, respectively, and ϕ_f is the volume fraction of short fibers. The constants ξ and η are given by

$$\xi = 2(L/D) \quad (2)$$

$$\eta = \frac{R - 1}{R + \xi} \quad (3)$$

where L/D is the aspect ratio (length/diameter) of the reinforcing fibers and R is the ratio of the filler modulus to the matrix modulus. It is well known that wood flour has a much higher modulus than that of commonly used thermoplastics so, in this work, the parameter R is >1 and, consequently, $\eta < 1$. Then it is apparent that the value of E_c is greater than E_m and increases with increasing ϕ_f .

For polymeric composites, the addition of the immiscible component to a ductile polymer matrix generally decreases the elongation properties considerably, despite the state of the interface between different phases.^{16–18} As expected from Figure 5, the

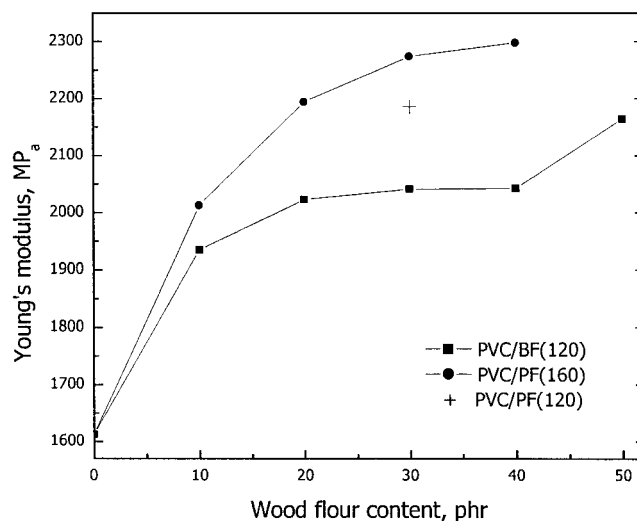


Figure 4 Variations of tensile modulus of PVC/BF(120), PVC/PF(160), and PVC/PF(120) composites with wood flour content.

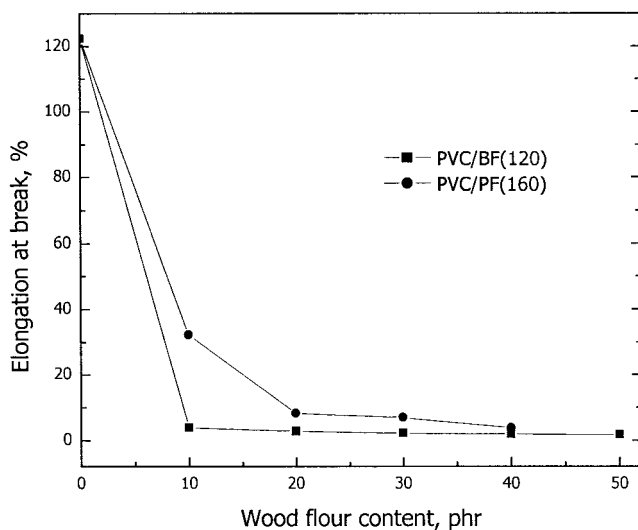


Figure 5 Variations of elongation at break for PVC/BF(120) and PVC/PF(160) composites with wood flour content.

composites became more brittle with the addition of wood flours.

Thermal behavior

Figure 6 shows typical DSC curves for the PVC compound and the PVC/20BF(120) and PVC/40BF(120) composites. Only one glass-transition temperature (T_g) for each sample in the temperature range studied can be observed, which corresponds to the T_g of the PVC matrix. The T_g values are listed in Table I. The BF(120)-filled composite exhibits a T_g close to that of

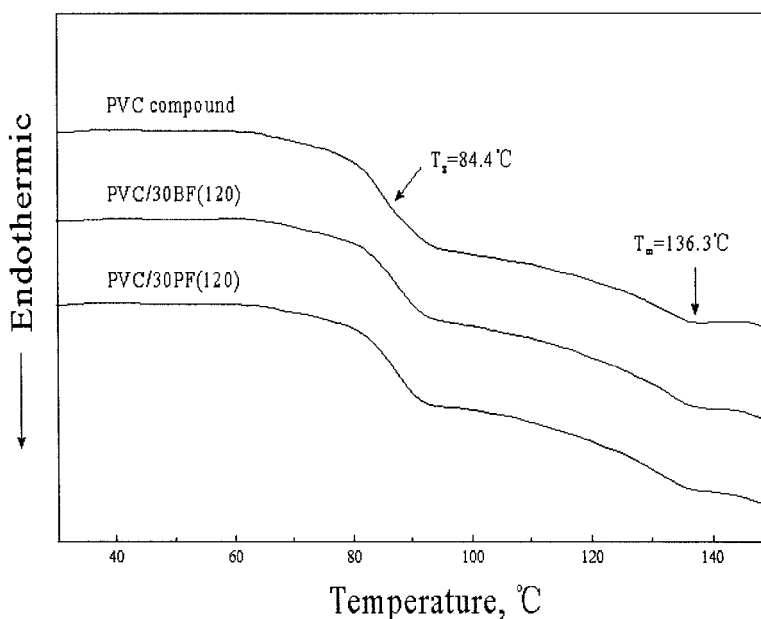


Figure 6 DSC curves for PVC compound, PVC/30PF(120), and PVC/30BF(120) composites.

the PVC compound, indicating that two phases exist in the composite. This is a direct proof for the immiscibility between the polymer and BP in the composite. In addition, the DSC curve of each specimen exhibits an endotherm region ranging from 120 to 145°C, with an endothermic peak at about 135°C (designated as T_m in Table I). This endotherm region is attributed to the crystalline melting region of PVC.^{19,20}

Figure 7(a)–(c) show the weight loss and derivative weight loss curves for BF(120), PVC compound, and PVC/40BF(120) composite, respectively. From Figure 7(a), two decomposition peaks for BF(120) can be observed. The first decomposition peak (designated as T_{max}^1 in Table I) is attributed to the thermal depolymerization of hemicellulose and the glycosidic linkages of cellulose. The second decomposition peak (347.1°C) is attributed to cellulose decomposition.^{21,22} From Figure 7(b), three decomposition peaks for the PVC control can be seen in the derivative weight loss curve. They are designated as T_{max}^2 , T_{max}^3 , and T_{max}^4 , respectively, and are summarized in Table I. The T_{max}^2 and T_{max}^4 are believed to correspond to the dehydrochlorination of the PVC matrix and to the thermal decomposition of the dehydrochlorinated PVC, which consists mainly of conjugated double bonds, respectively.²³ The T_{max}^3 is attributed to the decomposition of the additive acrylic resin.

By comparing Figure 7(c) with Figure 7(a) and (b), we can see that the profile of the DTG curve for PVC/40BF(120) composite is not obtained from simply combining the DTG curves in Figure 7(a) and (b), indicating that the PVC compound and BF(120) influence each other in the decomposition process of the

TABLE I
Thermal Properties for PVC Compound PVC/BF(120) and PVC/30PF(120) Composites

Specimen	T_g (°C)	$T_{-5\%}$ (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)	T_{max}^3 (°C)	T_{max}^4 (°C)	T_m (°C)
PVC compound	84.4	269.7	—	301.0	399.5	452.5	136.3
PVC/10BF(120)	85.7	262.8	260.9	305.4	399.7	440.8	136.8
PVC/20BF(120)	84.2	266.1	264.5	305.2	406.7	439.1	135.3
PVC/30BF(120)	84.7	266.9	265.2	306.9	412.5	441.8	134.9
PVC/40BF(120)	85.7	264.3	268.9	308.0	409.2	442.3	135.6
PVC/50BF(120)	86.1	265.2	269.1	304.3	409.4	442.2	135.1
PVC/30PF(120)	—	257.5	259.9	302.1	412.0	440.2	—

composite. For the purpose of comparison, the DTG curves for BF(120), PVC compound, and three typical PVC/BF(120) composites are shown in Figure 8. From Figure 8, one can see that, with increasing BF(120) content, the decomposition peak region in the temperature range of 260–270°C for composites becomes broad and, meanwhile, the corresponding decomposition peak temperature (T_{max}^1) tends to increase. The results imply that the decomposition peak corre-

sponding to T_{max}^1 at 292.6°C for BF(120) shifted to 260–270°C for PVC/BF(120) composites. No obvious changes were observed for other decomposition temperatures shown in Figure 7.

From Table I, we can see that the 5% weight loss temperature ($T_{-5\%}$) of PVC/BF(120) composites appears to decrease slightly with increasing BF(120) content. In general, the addition of BF(120) to the PVC compound shows no significant negative effect on its

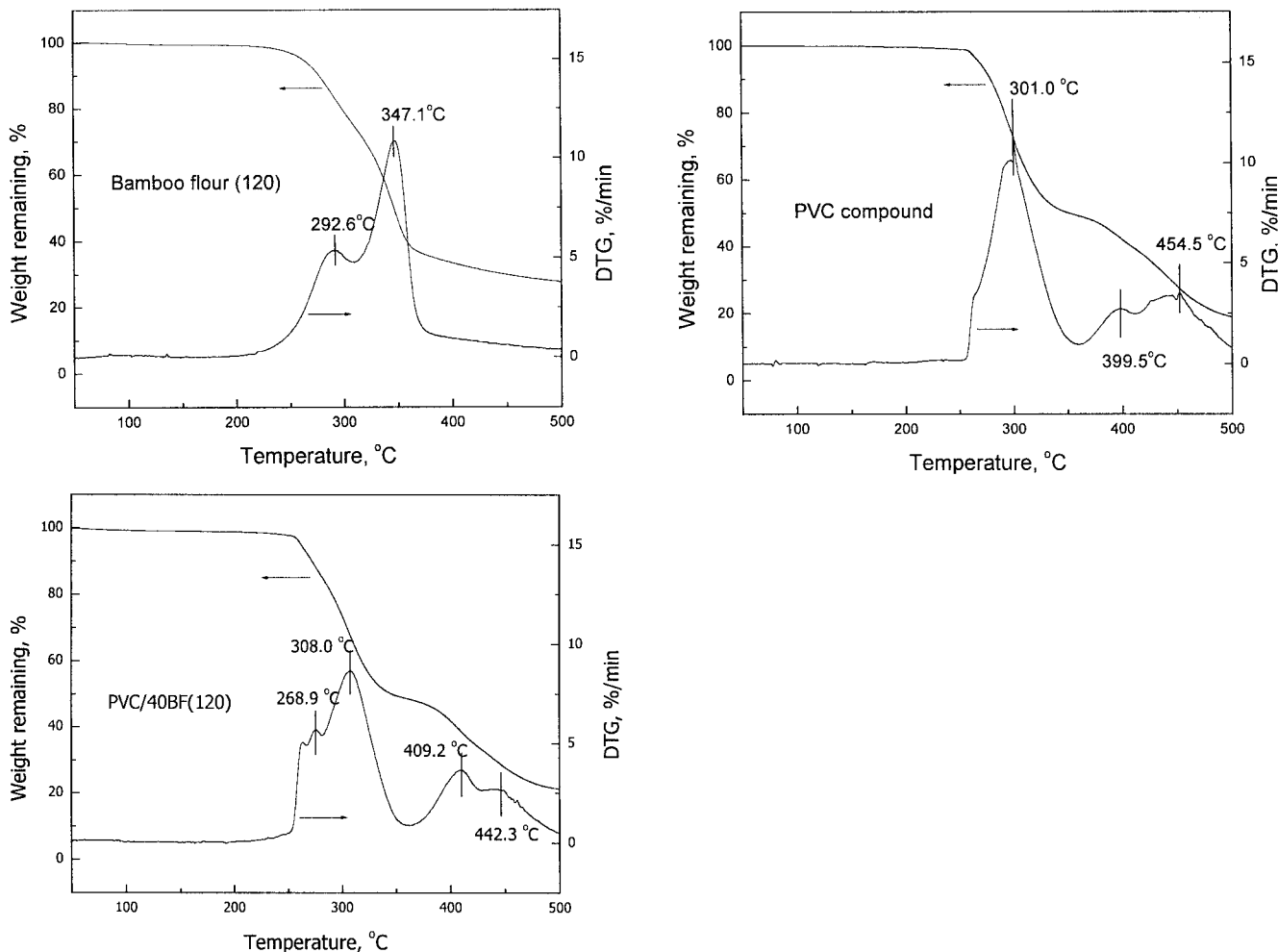


Figure 7 Typical thermogravimetric curves for (a) BF(120), (b) PVC compound, and (c) PVC/40BF(120) composite.

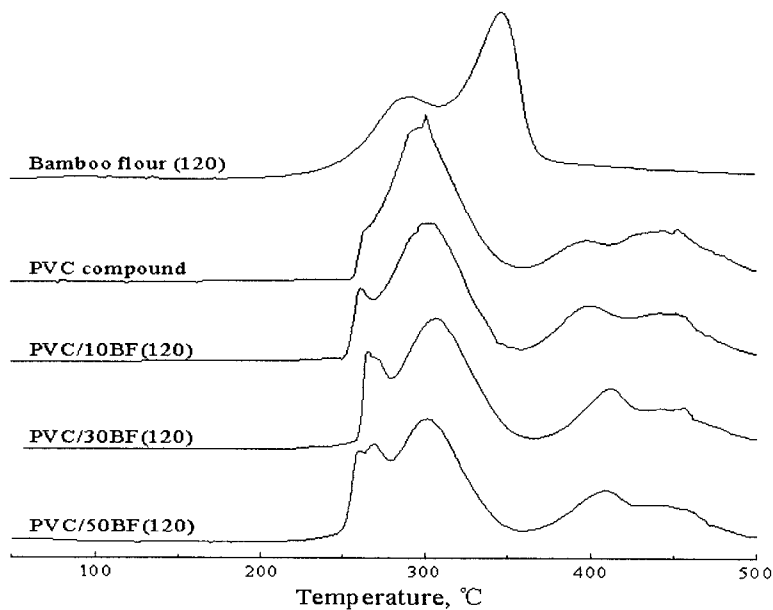


Figure 8 DTG curves for BF(120), PVC compound, and PVC/BF(120) composites.

thermal properties. In addition, by comparing the thermal properties of PVC/30BF(120) and PVC/30PF(120), one can conclude that the thermal stability of the former composite is slightly better than that of the latter.

Morphology observation

The SEM micrographs of PVC/30PF(120), PVC/30BF(120), and PVC/50BF(120) composites are shown in Figure 9(a) and (b) and Figure 10(a) and (b), respectively. It can be seen that both wood flours exhibit the shape of irregular short fibers in the composites. Figure 9(a) shows that the PF fillers were well dispersed within the PVC matrix, whereas there was obvious agglomeration of BF(120) particles in the PVC/30BF(120) composite [Fig. 10(a)]. In addition, it should be noted that PF(120) fibers tend to align along the melt flow direction, as can be seen in PVC/30PF(120) [Fig. 9(a) and (b)]. This behavior resulted from the high melt viscosity of the PVC matrix, which accounts for PVC/30PF(120) having higher tensile strength than that of PVC/30BF(120), as discussed in the previous section. For PVC/50BF(120) composite, larger agglomerates of filler particles were observed in Figure 10(b) than that in Figure 10(a), which in turn leads to the decrease of tensile strength for PVC/50BF(120).

CONCLUSIONS

Natural pine flour (PF) or bamboo flour (BF) can be simply melt blended with rigid poly(vinyl chloride) (PVC) compound to produce cost-competitive and woodlike composites with satisfactory properties. The

tensile strengths of the composites increased with increasing PF(160) up to 10 phr, and thereafter decreased with further increasing PF(160). For PVC/

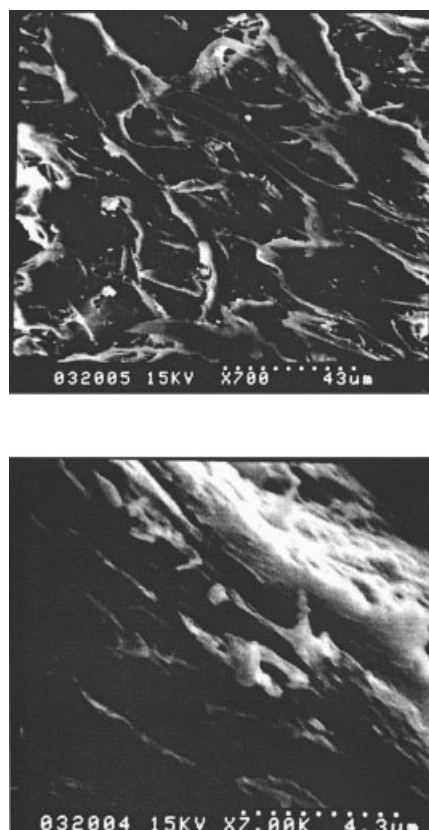


Figure 9 SEM micrographs for the PVC/30PF(120) composite at magnifications of (a) $\times 700$ and (b) $\times 7000$.

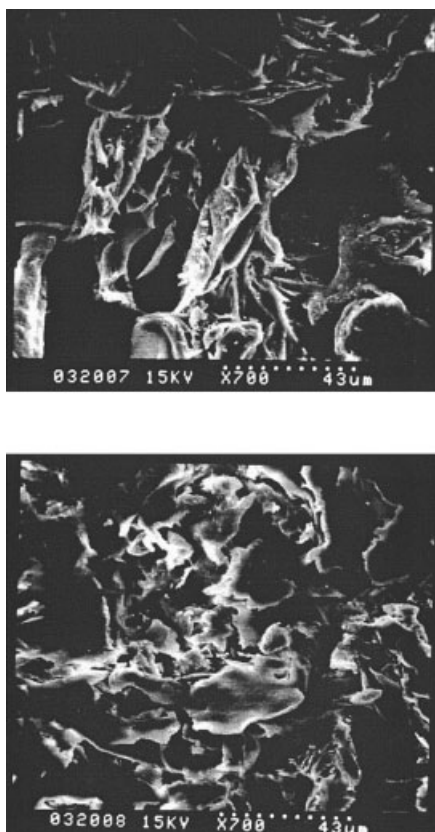


Figure 10 SEM micrographs of (a) PVC/30BF(120) and (b) PVC/50BF(120) composites.

BF(120) composites, the tensile strengths decreased with increasing BF(120) content. The stiffness of all the composites was substantially improved by filler addition. Thermal analyses indicated that the addition of BF(120) into the PVC matrix showed no obviously negative effect on its thermal properties. Scanning electron microscopic examination revealed that PF(120) was dispersed better than BF(120) within the PVC matrix at the same filler loading level. There was an obvious alignment tendency of short PF fibers in the composite at lower PF(120) content. Based on the

comprehensive properties, the PVC/30PF(120) composite can be used as a woodlike material for applications in wood structures.

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