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Mechanochemical activation of cellulose and its thermoplastic polyvinyl alcohol ecocomposites with enhanced physicochemical properties

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ABSTRACT

The focus of this work is to study the influence of mechanochemical treatment of cellulose on the physicochemical properties of its polyvinyl alcohol (PVA) composites. Cellulose fibers subjected to pan-milling could be mechanochemically activated by breaking up the intra- and inter-molecular hydrogen bonds through shearing and compressing forces. Reactive hydroxyl groups were exposed on the cellulose surface, which could establish new hydrogen bonds with PVA. Moreover, the simultaneous reduction of particle size and large increment of specific surface area of pan-milled cellulose would benefit its dispersion as well as the interfacial adhesion with polymer matrix. PVA/cellulose composites were successfully processed by the melt in the presence of plasticizers containing formamide and water. Tensile tests demonstrated positive results from mechanochemical treatment. As pan-milling cycles of cellulose increased, the tensile strength of PVA/cellulose composites increased from 8.8 MPa to 16.4 MPa, while elongation at break increased from 76.8% to 374%. The composite materials also exhibited enhanced thermal stability and better biodegradability.

1. Introduction

In recent years, the petroleum shortage and environmental pollutions caused by non-degradable plastics have attracted world concerns over developing environmentally friendly materials from non-petroleum resources. Cellulose is one of the most abundant renewable natural polymers, exhibiting a number of well-known advantages, such as low cost, worldwide availability, biodegradability, high stiffness, good mechanical properties and thermal recyclability by combustion. Particular attraction is its low density that leads to high specific mechanical properties (Bledzki, Reihmane, & Gassan, 1996). These advantages make cellulose fiber a good choice as reinforcing element for composite materials where glass fiber or synthetic fiber is routinely used. Composites from petroleum based polymers like polyethylene and polypropylene reinforced with cellulose fibers have received intensive research in the past decades (Bengtsson, Baillif, & Oksman, 2007; Lei, Wu, Yao, & Xu, 2007; Marcovich, Aranguren, & Reboredo, 2001; Mulinari et al., 2009; Panthapulakkal, Zereshkian, & Sain, 2006). The combination of cellulose fibers with thermoplastic matrix encounters a considerable problem associated to incompatibility between the polar and hydrophilic fibers and the non-polar and hydrophobic matrix. Surface modification of cellulose, either physically or chemically, such as acetylation and alkali treatment, is the critical step for improving matrix-reinforcement adhesion in composites (Torres & Cubillas, 2005). It is noteworthy that these composites are only partially degradable due to the intrinsic nature of matrix polymers.

The growing environmental awareness lately has triggered interests into more environmentally friendly and biodegradable materials. Synthetic polymers with biodegradable backbones like polycaprolactone (PCL) (Siqueira, Bras, & Dufresne, 2009), poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) (Jiang, Morelius, Zhang, & Wolcott, 2008), polylactic acid (PLA) (Iwatake, Nogi, & Yano, 2008), polyvinyl alcohol (PVA) (Chakraborty, Sain, & Kortschot, 2006; Cheng, Wang, Rials, & Lee, 2007; Lu, Wang, & Drzal, 2008) have been investigated as potential matrix for fully biodegradable composites. PVA is the largest synthetic water-soluble polymer produced in the world (Ramaraj, 2007). It is also a versatile polymer with broad applications due to its biodegradability, biocompatibility, high tensile strength, excellent adhesive properties, chemical resistance and gas barrier properties (Chen, Li, & Wang, 2007). Furthermore, PVA is one of the few polymers that can be prepared via non-petroleum route, i.e. using natural gas as raw materials. These make PVA very important in the situation of petroleum scarcity. However, the degradation process of neat PVA is very slow, and the degradation rate strongly depends on the residual acetate groups (Corti, Cinelli, D'Antone, Kenawy, & Solaro, 2002; Pšeja, Charváatová, Hruzík, Hrncirík, & Kupec, 2006).

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A simple way to enhance the biodegradability and lower the cost of PVA is to prepare composites with more biodegradable, cheap and easily processable fillers such as cellulose. In fact, PVA is well suited for composites with natural polymeric materials because both of them are highly polar. Many kinds of PVA-based biodegradable composites have been prepared by incorporating natural polymeric materials such as cellulose fibrils (Zimmermann, Pöhler, & Geiger, 2004), pea starch (Chen, Chao, Chang, & Huneault, 2008), chitosan (Lee et al., 2009), lignin (Kubo & Kadla, 2003), wheat glen (Dong, Dicharry, Waxman, Parnas, & Asandei, 2008), algae (Chiellini, Cinelli, Ilieva, & Martera, 2008), etc. Cellulose fiber is one of the most promising materials for the modification of PVA due to its low cost and high mechanical properties.

The potential property improvement of any composite material depends on the degree of dispersion and the bonding ability between matrix and reinforcing phase (Mathew, Oksman, & Sain, 2005). Although cellulose has abundant hydroxyl groups on its molecules, direct incorporation of pristine cellulose fibers into PVA matrix cannot obtain a composite with good mechanical properties (Ozaki, Monteriro, Yano, Imamura, & Souza, 2005), because most of the hydroxyl groups in cellulose molecules have already formed either intra- or inter-molecular hydrogen bonds. They are not able to form strong interaction with PVA, leading to poor interfacial adhesion and deteriorated mechanical performance of the composites. Some researchers reported the grafting and cross-linking with desired molecules could increase the compatibility between PVA and nature polymers, and improved mechanical properties, transparency and water resistance were observed for those composites (Chen et al., 2008; Goetz, Mathew, Oksman, Gatenholm, & Ragauskas, 2009; Ozaki et al., 2005; Teramoto, Saiton, Kuroiwa, Shibata, & Yosomiya, 2001). Another possible approach is to break the intra- and inter-molecular hydrogen bonds of cellulose to establish new interaction between cellulose and PVA (Ramaraj & Poomalai, 2006). Our previous investigation on mechanochemical pretreatment of cellulose fibers by pan-milling suggested that the hydrogen bonds in cellulose can be effectively broken up to expose reactive hydroxyl groups on cellulose surface with fairly strong shearing and compressing forces (Zhang, Liang, & Lu, 2007; Zhang, Zhang, Liang, & Lu, 2008). These mechanochemically activated cellulose fibers are expected to be able to form new hydrogen bonds with PVA during the processing, leading to composites with enhanced performance. Moreover, the mechanochemically treated cellulose fibers that provide large surface area are considered to obtain better interaction between matrix and reinforcement (Mathew et al., 2005). The processability of composites and dispersion of fillers in matrix will be improved as well.

The aim of this work is to prepare thermoplastic PVA composites with plasticizers, using mechanochemically activated cellulose fibers as reinforcement to create biodegradable high performance composite materials. The influence of mechanochemically activated cellulose fibers on the composites' properties, including mechanical properties, thermal stability, biodegradability, etc., will be discussed in detail.

2. Materials and method

2.1. Materials

Polyvinyl alcohol 1799, with degree of polymerization 1750 ± 50 and degree of alcoholysis of 99%, was provided by SINOPEC Sichuan Vinylon Works, China. Analytical grade formamide was purchased from Chengdu Kelong Chemical Plant and was used as received. Cellulose fibers are bleached hardwood pulp fibers with approximately 90% cellulose content as reported by the Canadian supplier.

2.2. Mechanochemical activation of cellulose fibers

The mechanochemical activation of cellulose was achieved through high shearing and compressing forces generated by the pan-mill mechanochemical reactor. The details of the pan-mill equipment and operation procedure can be found in our previous publication (Zhang et al., 2007). Generally, granules (5–10 mm in diameter) of hardwood cellulose fibers having an easier access to pan-mill were obtained by chopping the pulp. After that, they were fed in hopper set at the middle of the moving pan. Milled powder was discharged from the brim of the pans. The discharged powder was then collected for the next milling cycle. The whole milling process at ambient temperature was controlled at a rotating speed of 30 rpm and a specific pressure.

2.3. Preparation of PVA/cellulose composites

PVA and cellulose (10:3 in weight) with plasticizers of 25 wt.% water and 25 wt.% formamide in composition (composite powder content is 50 wt.%) were first blended in a laboratory mixer and then sealed for a week prior to thermal compounding. The PVA blends were melted and mixed using a Brabender type mixer at 150 °C and 30 rpm for 10 min. The obtained pastes were left at ambient condition for 24 h. After that, the pastes were filled in a metal mold (150 mm of diameter and 1 mm of thickness) under a pressure of 10 MPa at 175 °C for 15 min.

2.4. FTIR analysis of cellulose

Transmission Fourier transform infrared spectroscopy (FTIR) was performed by means of a Nicolet 20SXB FTIR spectrometer, taking 32 scans for each sample with a resolution of 2 cm^{-1}, ranging from 400 cm^{-1} to 4000 cm^{-1}. KBr pellets of samples were prepared by mixing 2 mg cellulose powders with 200–300 mg KBr in a carnelian mortar. The 1 cm diameter pellets were prepared in a standard tool under a pressure of 4 MPa. Both cellulose powders and KBr were dried before testing.

2.5. Tensile tests

The compression-molded sheets were equilibrated in ambient environment for 7 days at a relative humidity of 75. The dumb-shaped specimens were then punched out from the sheets by a tensile specimen cutter according to ASTM D 15-54T. The stress–strain properties were measured by Instron 5567 Universal Testing Machine at a crosshead speed of 50 mm/min. At least five measurements for each composite were made.

2.6. Morphology observation

Scanning electron microscope (SEM, model JEOL JSM-5600, Japan) was used to observe the morphology of cellulose fibers and the liquid nitrogen fractured surface of composite samples prepared. Prior to SEM evaluation, the samples were sputter-coated with gold to avoid charging during the tests.

2.7. Thermal–mechanical analysis

Dynamic mechanical analysis was performed on a dynamic mechanical thermal analyzer of Polymer Laboratory (DMTA, MK II, UK) at a heating rate of 5 °C/min from 25 °C to 200 °C. The testing pieces were prepared in the same way as for tensile testing samples.

2.8. Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was conducted on TA-2000 analyzer (TA Instrument). Samples of about 5 mg were placed in an open alumina crucible. Temperature programs for dynamic adopted in this study were from room temperature to 600 °C at a heating rate of 20 °C/min. The measurements were operated under a nitrogen purge (100 ml/min). All the samples were vacuum oven dried at 100 °C for 2 h before testing.

2.9. Biodegradability measurement

Biodegradability of neat PVA and PVA/cellulose composites was evaluated by burying the samples in garden soil and measuring the weight loss. The samples were oven dried at 80 °C to constant weight prior to testing. Exposure to the soil environment continued for 60 days, at predetermined time intervals, samples were taken out from soil, carefully washed with water and dried again in oven at 80 °C. The degradability was expressed from the weight loss, which was calculated by:

$$\text{weight loss}\,(\%) = \left[\frac{W_a - W_b}{W_a}\right] \times 100\%$$

where W_a is weight of dried sample before exposure to the soil environment and W_b represents the weight of dried material after soil burial test.

3. Results and discussion

3.1. Mechanical performance of PVA/cellulose composites

PVA is a versatile polymer with a large amount of production annually. However, the intra- and inter-molecular hydrogen bonds together with the high crystallinity prevent it from melt processing. The current fabrications of PVA related materials mostly follow the wet process. This process is only able to generate simple structured products like fibers or films, which greatly limits its applications. There are only a few publications concerning melt processing of PVA composites. Cinelli, Chiellini, Lawton, and Imam (2006) reported PVA/corn-fiber composites can be injection molded in the presence of an appropriate amount of plasticizers containing glycerol, pentaerythritol and poly(ethylene glycol). Fishman, Coffin, Onwulata, and Willett (2006) have made PVA/pectin extrudable by incorporation of excess glycerol. The author's laboratory recently reported a novel technique to realize the melt processing of PVA based on inter-molecular complexation and plasticization (Chen et al., 2007). An amido-group-containing compound, which can form inter-molecular complexes with PVA through hydrogen bonds, together with water, was chosen to control the supramolecular structure of PVA, confine its crystallization, decrease its melting point and increase its thermal decomposition temperature. As a result, melt processing of PVA becomes possible. In this study, we also successfully realized melt processing of PVA composites by using formamide and water as plasticizer.

PVA/cellulose composites were fabricated by first melt mixing in Brabender mixer and then by compression molding. The weight of cellulose added was fixed at 30 wt.% of PVA used. The representative stress–strain curves of neat PVA and composites with mechanochemically activated cellulose fibers are illustrated in Fig. 1. Their tensile strength (TS), elongation at break (EL), modulus were recorded from tensile testing and are given in Table 1. During the pan-milling process, the strong shearing and compressing forces exerted by the pan-mill can defibrillate the cellulose fibers, shorten the fiber length, break up the hydrogen bond network in cellulose and release free hydroxyls groups. This claim is supported by FTIR analysis of cellulose as shown in Fig. 2. The O–H stretching vibration peak at 3417 cm^{-1} becomes stronger and narrower after 40 cycles pan-milling, indicating the breakage of hydrogen bonds in cellulose main chains. Also, the sharp decline of 2890 cm^{-1} peak, which is the C–H stretching vibration peak characterizing the hydrogen bonds between cellulose chains, suggests the breakage of inter-molecular hydrogen bonds after pan-milling. The resulting free hydroxyl groups are expected to establish new hydrogen bonds with PVA molecules during the compounding process, leading to a more robust interfacial interaction between the two phases and improved mechanical properties of the composites.

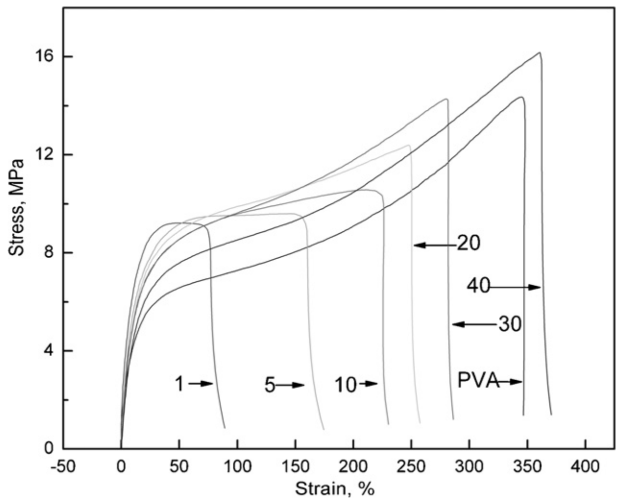

Fig. 1. Stress–stain curves of PVA and PVA/cellulose composites prepared by compression molding, the numbers beside the curves indicate the milling cycles of cellulose added in PVA.

The SEM images showing the morphological development of cellulose fibers before and after pan-milling are provided in Fig. 3(A) and (B). The original belt-like cellulose fibers were effectively pulverized into small particles after 40 cycles of pan-milling. Laser particle size analysis further demonstrated (not shown) that the volume-mean particle size decreased to 21 μm. Meanwhile, significant amount of fresh cellulose surface, covered by reactive hydroxyl groups, was generated at the cutting edge, which would benefit the interfacial interaction with PVA.

Cellulose undergoing more milling cycles has greater reinforcing effect than that with less milling cycles, as drawn from tensile

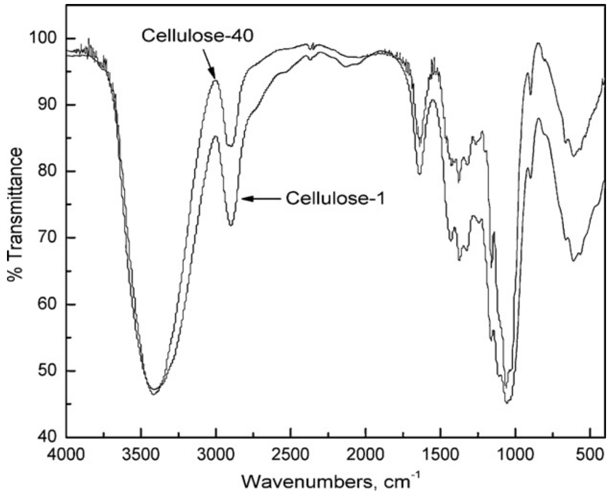

Fig. 2. FTIR analysis of cellulose after pan-milling.

Table 1
Mechanical properties of PVA and PVA/cellulose composites.

Samples	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
PVA	14.0 ± 0.5	339.3 ± 10.0	44.7 ± 3.3
PVA/cellulose-1	8.8 ± 0.6	76.8 ± 7.2	96.3 ± 9.6
PVA/cellulose-5	9.3 ± 0.2	118.3 ± 6.2	90.5 ± 7.1
PVA/cellulose-10	10.5 ± 0.6	225.9 ± 20.7	78.2 ± 0.7
PVA/cellulose-20	11.6 ± 0.8	222.2 ± 22.1	70.3 ± 2.4
PVA/cellulose-30	13.3 ± 1.0	278.3 ± 15.0	68.4 ± 4.7
PVA/cellulose-40	16.4 ± 0.2	374.4 ± 6.4	55.4 ± 2.2

Note: Cellulose-1 (5, 10, 20, 30, 40) indicates the cellulose reinforcement has underwent one (5, 10, 20, 30, 40) cycle of pan-milling.

tests. With the increase of pan-milling cycles, the TS and EL of PVA/cellulose composites increased progressively, whereas the modulus showed a reverse trend. Among all the composites, PVA incorporated with cellulose of 40 milling cycles exhibited the highest TS and longest EL of 16.4 MPa and 374.4%, respectively. These values are significantly higher than those of composite combined with cellulose fibers milled for one cycle, and are even higher than those of neat PVA, suggesting a particulate reinforcing characteristic. By incorporating cellulose fibers, all the composites exhibited increased modulus as compared to that of neat PVA. Since cellulose is a rigid chain polymer with high crystallinity, it is not surprising to observe a hardening effect when cellulose was incorporated into a soft chain polymer matrix, like PVA. Cellulose of less pan-milling cycles is more effective on increasing composite modulus, due to the bigger particle size and ease of tangling in composite (Zhang et al., 2008).

3.2. *Morphology observation on the fractured surface*

Fig. 3(C) and (D) represents SEM images of liquid nitrogen fractured surface of PVA/cellulose composites. The adhesion between PVA and cellulose was strongly affected by the mechanochemical treatment of cellulose as revealed from SEM photos. Cellulose fibers subjected to one pan-milling cycle do not have satisfactory interfacial adhesion with PVA. The clear traces thereof PVA matrix due to the pulling off of cellulose fibers indicate the poor adhesion between the two phases. Although cellulose fibers are chemically compatible to PVA, the hydroxyl groups in pristine cellulose fibers are essentially within the hydrogen bond network. Therefore it is hard to connect hydroxyl groups from both components by building new hydrogen bonds in between, resulting in an inferior interfacial interaction of the composites. Additionally, the long pristine cellulose fibers tend to get entangled, and are hard to disperse well in PVA matrix during melt processing, which is also responsible for the deteriorated mechanical performance. On the contrast, cellulose fibers subjected to 40 cycles of pan-milling can be well dispersed, well coated and firmly embedded in the PVA matrix thanks to their large specific surface area and increased interfacial interaction as shown in Fig. 3(D), which provides a graphical evidence for its improved mechanical properties.

For the fiber-reinforced composite materials, a general concept is that fibers with a relatively high aspect ratio are beneficial for the composites' physical properties (Mathew et al., 2005). On the other hand, the dispersion of fibers in matrix and the adhesion between matrix and fiber reinforcement are also crucial factors for the efficient stress transfer. In our case, the aspect ratio of pan-milled cellulose fibers was significantly reduced as compared to those without treatment. Also, the crystallinity was decreased owing to the mechanical forces (Zhang et al., 2007), which may worsen the fiber strength. However, our results do reveal a positive impact of mechanochemical treatment, suggesting that the improved fiber dispersion and interfacial adhesion could compensate the negative

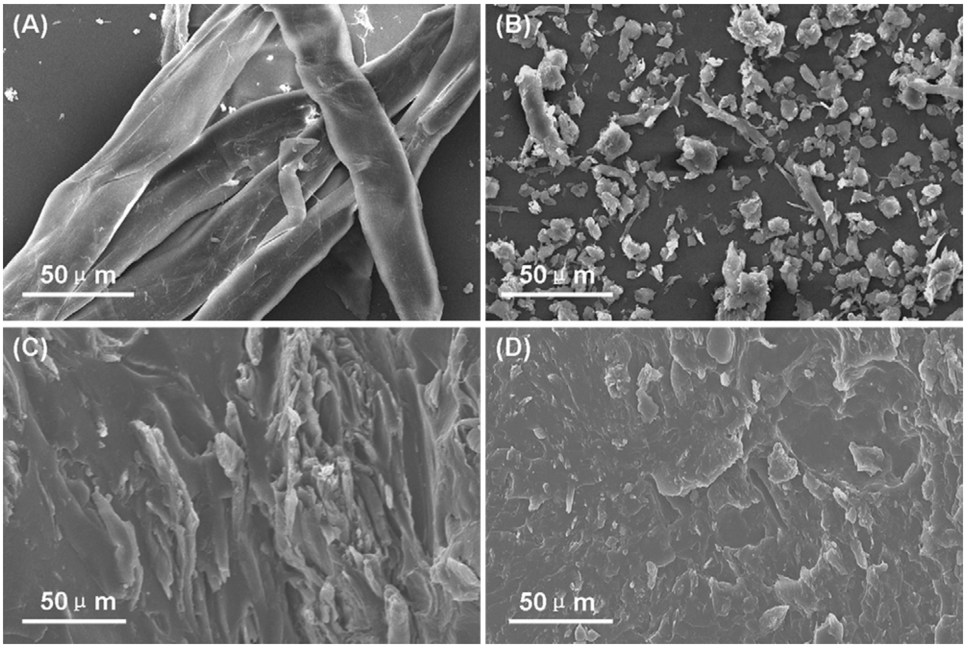

Fig. 3. SEM images of (A) cellulose fibers before pan-milling, (B) cellulose fibers after 40 cycles of pan-milling, (C) fractured surface of PVA/cellulose-1 composites, (D) fractured surface of PVA/cellulose-40 composites.

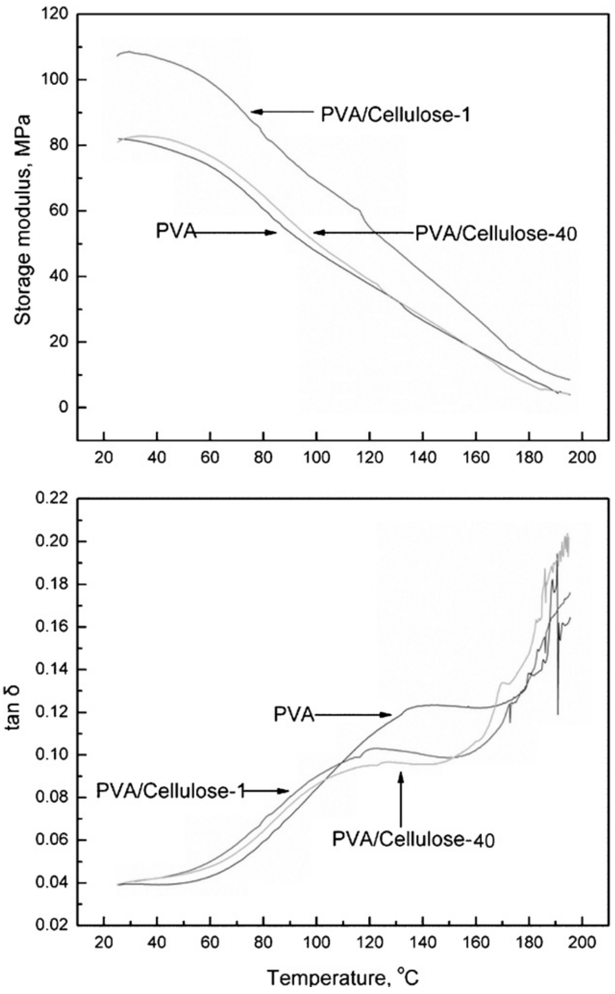

Fig. 4. DMA curves for PVA and PVA/cellulose composites. The storage modulus and tan δ are plotted as functions of temperature.

influence from milling and yield products with improved performance.

3.3. Dynamic mechanical analysis

Fig. 4 shows the storage modulus and tan δ versus temperature, as evaluated by DMA measurements in tensile mode for neat PVA and PVA/cellulose composites. The storage modulus of all the samples decreases with increasing temperature. The composite reinforced by cellulose fibers pan-milled for 40 cycles shows a slight increase of storage modulus as compared to neat PVA, whereas the sample filled with cellulose fibers of one cycle of pan-milling exhibits a remarkable increment of storage modulus in the entire testing temperature range, suggesting improved thermal–mechanical properties of the composites. This result is in accordance with tensile tests and is due to the volume effect of hard (cellulose fibers) phase (Jiang et al., 2008). All the samples show broad tan δ peaks in 50–150 °C, which is because of glass transition of amorphous portion in PVA in this temperature range (Teramoto et al., 2001). By incorporating cellulose fibers into PVA system, the glass transitions shift to lower temperatures. This is probably because the addition of cellulose fibers restrains the crystallization of PVA chains, resulting in a larger amorphous portion in which the polymer chains are able to move at a lower temperature. Compared to PVA/cellulose-1, the glass transition of PVA/cellulose-40 happens at a relatively higher temperature. This may be the result of hydrogen bonds between the mechanochemically activated cellulose and PVA chains, which restrict the motion of movable PVA chains.

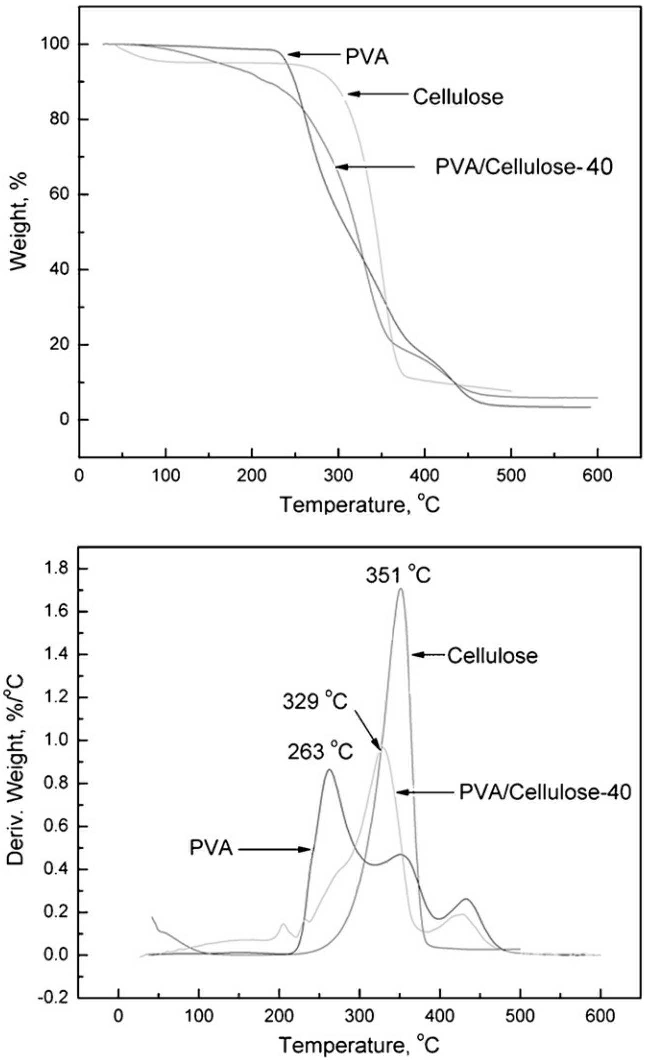

Fig. 5. TGA and DTG curves for pristine PVA, cellulose and PVA/cellulose-40.

3.4. TGA measurements

The thermal stability of pristine PVA, cellulose and PVA/cellulose composite was compared by using TGA. Both TGA and DTG data are illustrated in Fig. 5. The PVA experiences two major weight losses in the temperature range of 200–500 °C. The first one begins at 241 °C with a major degradation peak at 263 °C according the derivative curves, mainly involves dehydration and formation of some volatile products. The other one starts at 418 °C, which involves the degradation of polyene residue to yield carbon and hydrocarbon (Lu et al., 2008). The initial weight loss below 120 °C for cellulose is attributed to the loss of adsorbed moisture. There is only one degradation step for cellulose, which starts from 319 °C with major degradation peak at 351 °C. The PVA/cellulose composite shows a slow and steady weight loss before the major degradation, due to the evaporation of plasticizer in the composite. The onset temperature of its major degradation is 291 °C which is 50 °C higher than that of neat PVA, whereas the major degradation peak shifts to 329 °C from 263 °C for neat PVA, demonstrating a significantly increased thermal stability. Similar superior thermal stability was also achieved by adding chitosan into PVA system (Lee et al., 2009).

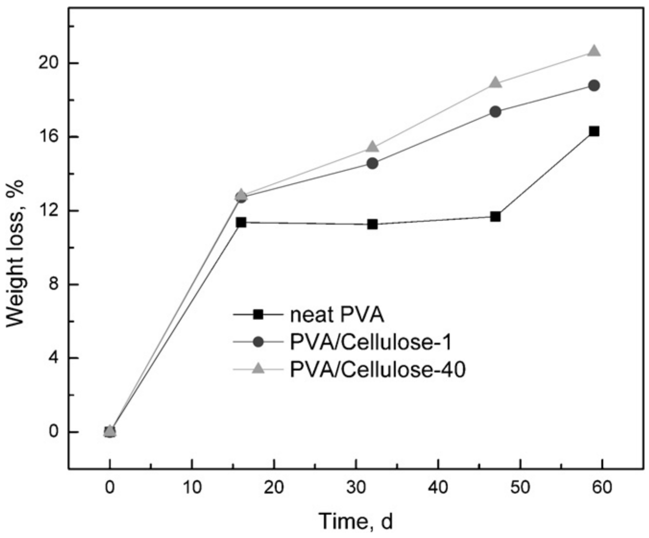

Fig. 6. Weight loss curves of PVA and PVA/cellulose composites during soil burial test.

3.5. Biodegradability in soil

The evaluation of biodegradability is mostly based on the weight loss of materials referring to the erosion of molecules from the solid phase. The soil burial test provides indirect indications of biodegradation. Compared with enzymatic test, this method is more effective if the samples are buried in suitable climatic conditions and various populations of microorganisms that are involved (Hadano et al., 2004; Shibata, Oyamada, Kobayashi, & Yaginuma, 2004). The soil used in this study was collected from the garden in SKLPME of Sichuan University, China. The tests were operated at ambient condition of temperature at 22–27 °C and relative humidity of 70–80%. As shown in Fig. 6, all the samples exhibited a quick weight loss in the first 16 days of soil burial, and the weight loss slowed down in the subsequent burial period. PVA/cellulose composites showed a higher weight loss than neat PVA, suggesting their better biodegradability. This is because cellulose is more easily biodegradable than PVA. In fact, it is very difficult to separate cellulose fibers from soil after the first 16 days of burial test attributed to their severe biodegradation under the experiment conditions. Similar result was reported for PVA/coconut-shell-powder composites (Ramaraj & Poomalai, 2006). The experiment also shows that PVA/cellulose-40 is more likely to biodegrade than PVA/cellulose-1, probably due to the reason that cellulose fibers subjected to more pan-milling cycles are smaller in size and less crystalline, which benefit the attack for microorganisms in the soil.

4. Conclusion

The potential property improvement of any composite material depends on the degree of dispersion and the bonding ability between matrix and reinforcing phase. In order to obtain PVA/cellulose composites having improved performance, cellulose fibers were mechanochemically activated prior to being incorporated into the composites. The fairly strong shearing and compressing forces exerted by the pan-mill can destroy the hydrogen bonds and release reactive hydroxyl groups that may establish new hydrogen bond network with PVA molecules. Furthermore, the processability and dispersion of cellulose in polymer matrix can be greatly improved after the mechanochemical treatment due to the small particle size and large specific surface area of pan-milled cellulose fibers. The mechanical properties of composites were significantly increased by mechanochemical treatment of cellulose fibers. The tensile strength of PVA/cellulose composite increased from 8.8 MPa to 16.4 MPa, while elongation at break increased from 76.8% to 374% when the pan-milling cycles of cellulose increased. The composite materials also exhibited remarkably enhanced thermal stability and biodegradability.

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