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ORIGINAL PAPER

Synergistic reinforcement of waterborne polyurethane films using Palygorskite and dolomite as micro/nano-fillers

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Abstract

In this paper, two types of reinforcement agents of fibrous palygorskite (PAL) and rhombohedral dolomite (DOL) have been used together by simply mixing in order to improve the mechanical and thermal properties of waterborne polyurethane (WPU). A great synergistic effect between 1D PAL and 3D DOL on reinforcing WPU matrix has been observed. In comparison to neat WPU, the tensile strength of such three components WPU-based composite has been significantly improved by 178% with an addition of 4 wt% PAL and 6 wt% DOL. Furthermore, its initial decomposition temperature also has been increased 55 °C. The formation of 3D conjugated filler network with 1D PAL inserted into the 3D DOL network could be attributed to such synergistic reinforcement of WPU. This work provides a good example and eco-friendly pathway for the preparation of high performance polymer composites by simply using micro/nano-fillers with different dimension together.

Keywords Waterborne polyurethane · Palygorskite · Dolomite · Synergistic · Mechanical property

Introduction

Waterborne polyurethane (WPU) is known as nontoxic, nonflammable and eco-friendly to environment [1]. Up to date, it has been widely used in coatings, inks, adhesives, leather finishing agents and other fields. However, the water resistance, thermal stability and mechanical properties of the WPU are lower than those solvent-based polyurethanes [2], which severely restrict its further applications.

Inspired by the pioneering work of Toyota research center on nylon modification by clay [3], using particle additives become an effective way to alter and strengthen the aforementioned properties of WPU. A variety of particles have been introduced into WPU as reinforcement fillers in the literature, such as silica [4], titanium dioxide [5, 6], zinc oxide [7, 8], carbon nanotube [9], carbon black [10, 11], graphene [12, 13], clay [14, 15], etc. Although the results showed that the mechanical and thermal properties have been extremely improved, unfortunately, the enhanced properties are always saturated (maximum value of mechanical and thermal properties with a best mount of reinforcement filler) due to the filler aggregation [16]. For example, it is almost impossible to further improve the mechanical properties of WPU via using graphene or clay alone.

Interestingly, Zhang et al. [17] first reported that the tensile strength and Young's modulus of nylon 6 film further increased by 150% and 290% respectively, by using one-dimensional (1D) carbon nanotubes (CNT) and two-dimensional (2D) montmorillonite clay (MMT) as binary reinforcements. In their case, CNT and MMT were oriented in different directions, resulting in optimization of stacking effect and synergistic effect of improving performance. Since then, a variety of works relating to synergistic reinforcement of polymers from two kinds of fillers with different dimensions have been reported, such as 1D/1D (CNT/halloysite [18], e.g.), 1D/2D (CNT/graphene [19–21], CNT/MMT [22–24], Laponite/graphene oxide [25], e.g.), 2D/2D (graphene/MMT [26], e.g.), 2D/3D (graphene/carbon black [27–29], e.g.). But in most cases, the binary fillers required complicated

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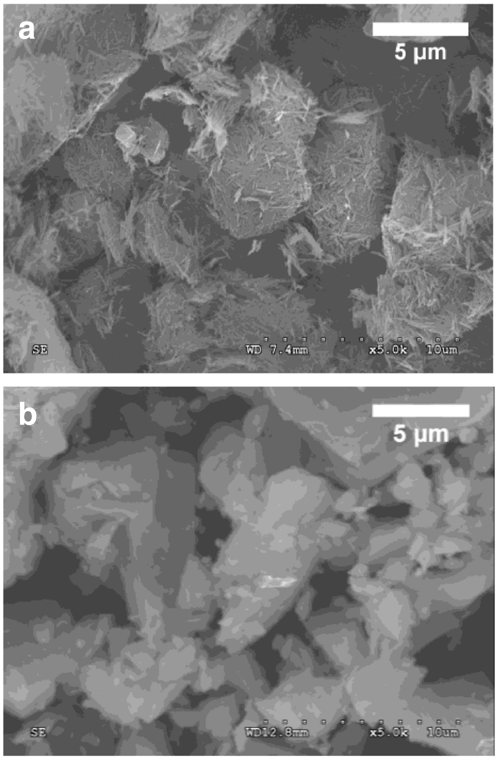

Fig. 1 SEM images of micro/nano-fillers: (a) PAL, (b) DOL

modification before use. In addition, CNT and graphene are quite expensive.

Herein, an effort to further improve the tensile and thermal properties of WPU has been reported by using cheap fillers of fibrous palygorskite (1D, PAL) and rhombohedral dolomite (3D, DOL) simultaneously with a simple mixing process. PAL is known as a natural fibrous clay mineral that composed of ribbons of 2:1 phyllosilicate unites with the theoretical formula of $Si_8Mg_8O_{20}(OH)_2(H_2O)_4•4H_2O$ [30]. Because of its high aspect ratios and rich reactive hydroxyl groups on the surface makes PAL attracted tremendous attention as a good reinforcing additive for polymer materials [31]. Dolomite is an inorganic mineral that composed of calcium magnesium carbonate [$CaMg(CO_3)_2$] [32]. It has rarely been used as polymer reinforcement filler [33, 34]. Up to date, no literature has been reported on using two kinds of inorganic minerals of fibrous PAL and rhombohedral DOL together as a binary reinforcing agent. In this study, PAL-DOL has been used as binary reinforcement filler in order to improve the mechanical and thermal properties of WPU-based composites. The structure, tensile mechanical properties and thermal stabilities of the WPU-based composites have been studied by various characterization techniques. In addition, a possible synergistic reinforcing mechanism by PAL-DOL binary reinforcement filler also has been proposed.

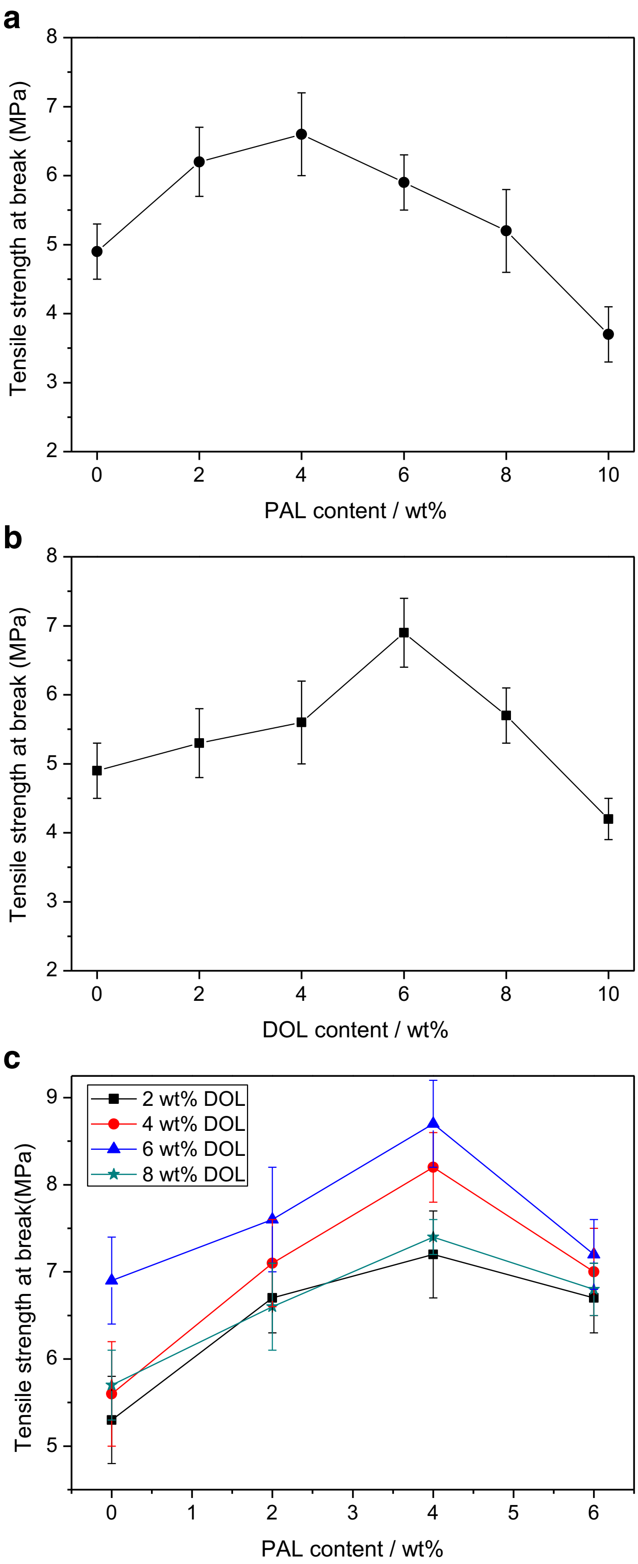

Fig. 2 Dependence of tensile strength of WPU-based composite films on the content of different reinforcement fillers: (a) PAL content; (b) DOL content; (c) PAL content with fixed DOL percentage

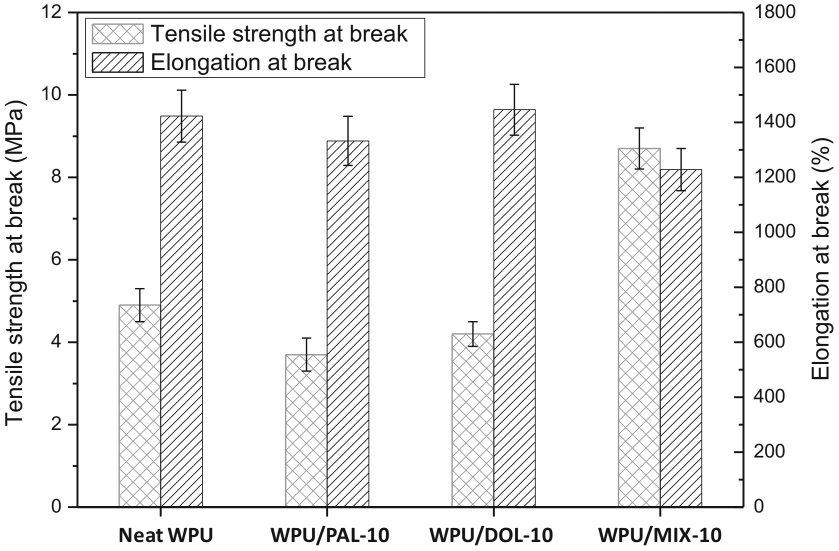

Fig. 3 Tensile mechanical properties of neat WPU and WPU-based composites

Experimental

Materials

Waterborne polyurathane (F68–20) was a gift from Jiangsu Junrui Technical Co. Ltd. (Huai'an, China). Palygorskite (PAL, > 90 wt%) was supplied by Jiangsu Zhongyuan Minerals Co. Ltd. (Huaian, China). Dolomite (DOL, > 90 wt%) was purchased from Shijiazhuang Chenxi Minerals Co. Ltd. (Shijiazhuang, China).

Preparation of WPU composites

Desired amount of micro/nano-fillers (0–20 wt.% in comparison to WPU emulsion) were dispersed into WPU emulsion with mechanical stirring for 2 h at room temperature. Then the resultant formulation was deposited on a glass substrate by wire wound bar coater. Then the films were heated to 80 °C and kept for 2 h. Finally, WPU/filler composite films were obtained. A reproducible film thickness of 40 ± 2 μm was obtained whatever the formulation composition.

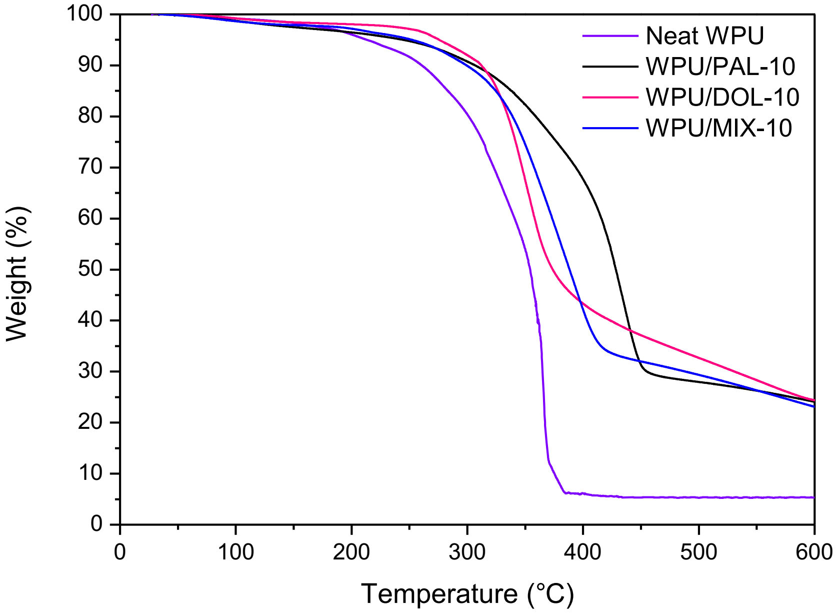

Fig. 4 TGA curves of the neat WPU and WPU-based composites under nitrogen atmosphere

Characterization

Morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi S3000 N microscope working at 25 kV). Before the analysis, the samples were coated with a 15 nm thick layer of gold to reduce the charging effect on the surface.

Tensile tests were carried out with GMET-4204 machine (SANS) at room temperature (20–25 °C). The samples were cut to 20 mm × 5 mm × 0.4 mm in size, sample length between jaws was 10 mm and the cross-head speed was set at 50 mm/min. At least 5 samples were tested and averaged for all of the data used here.

Thermalgravity analysis was carried out on a Perkin-Elmer instrument under N_2 atmosphere at a heating rate of 10 °C/min from room temperature to 600 °C.

Results and discussion

Morphologies of micro/nano-fillers

Figure 1 displays the SEM images of PAL and DOL reinforcement filler samples. Obviously, hundreds of PAL crystal fibers have been aggregated into micrometer crystal bundles (Fig. 1a). The size of such bundles is between 2 and 5 μm. Similarly, DOL also formed as micro particles with the largest size around 5 μm (Fig. 1b).

Synergistic effect of PAL/DOL fillers to WPU-based composites

Figure 2 illustrates the data of tensile strength at break of neat WPU and WPU-based nanocomposites. Remarkably, the unique synergistic effect of PAL and DOL on the reinforcing of WPU was achieved. By addition of PAL or DOL alone, the tensile strength of WPU/PAL and WPU/DOL composite films was increased along with the filler content at the beginning (Fig. 2a and b). The tensile strength of WPU/filler composite films reached maximum with 4 wt% of PAL and 6 wt% of DOL, respectively. With a further addition of PAL or DOL content, the tensile strength of the composite films decreased, which probably because of the aggregation of PAL or DOL particles. Quite interestingly, the tensile strength increased dramatically by using PAL and DOL together. The tensile strength of WPU/PAL/DOL composite films as a function of PAL content (DOL content has been fixed in 2, 4, 6 and 8 wt%, respectively) is shown in Fig. 2c. As can be seen, the tensile strength of WPU/PAL/DOL composite films was higher than the WPU/PAL and WPU/DOL composites, whatever the PAL content from 0 to 6 wt%, indicating a synergistic reinforcement effect. When the PAL content reached to 4 wt%, the tensile strength of the WPU/PAL/DOL composite film gives the maximum value in the case of DOL content was 6 wt%. Its value reached to 8.7 MPa, in comparison to the maximum value of 6.5 MPa and 6.9 MPa, respectively for incorporating PAL or DOL alone.

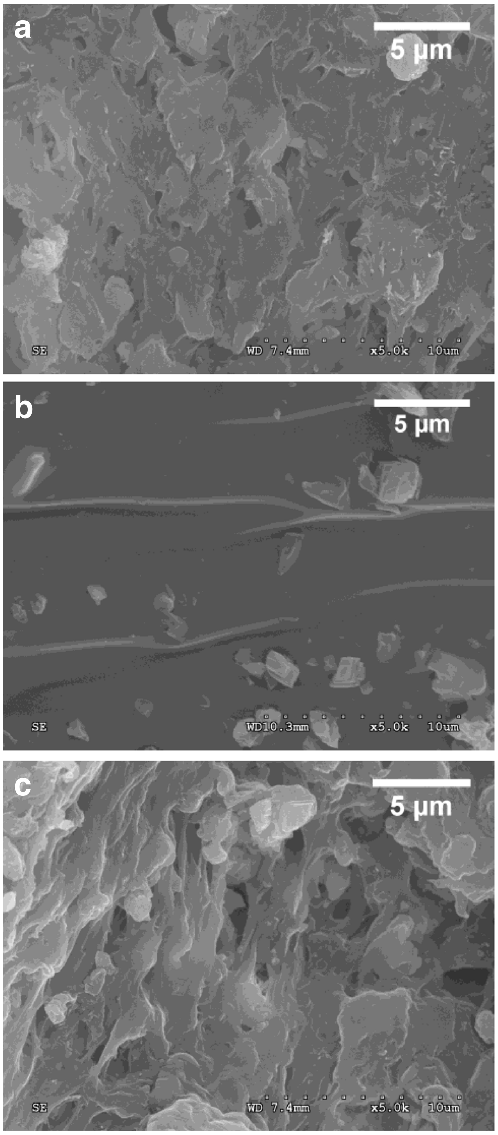

Fig. 5 SEM images at cross-cut of WPU-based composites with 10 wt% of reinforcement agents: (a) WPU/PAL-10, (b) WPU/DOL-10 and (c) WPU/MIX-10

Furthermore, it is worth noting that the tensile strength of WPU/PAL/DOL composite films is much higher than the WPU/PAL as well as WPU/DOL in the same content of fillers. Figure 3 provides tensile mechanical properties of neat WPU and WPU-based composites with 10 wt% of filler content. In comparison to neat WPU, the addition of either 10 wt% of PAL or DOL alone into WPU dropped its textile strength and elongation properties slightly. This decreasing is produced most probably because of the formation of aggregates of fillers

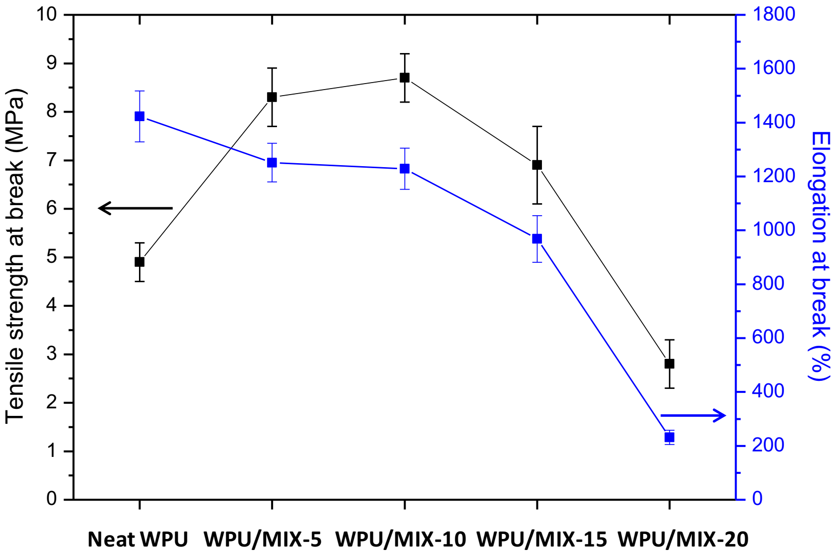

Fig. 6 Tensile strength and elongation at break of WPU/MIX composites with different amount of MIX fillers

in the composites that for such a high filler content. However, with the addition of 10 wt% of PAL-DOL mixture (4 wt% PAL, 6 wt% DOL, denoted as MIX), the tensile strength of the WPU/MIX ternary composite was increased 178%, from 4.9 to 8.7 MPa. This finding is quite interesting. Because the mechanical strength of the composite increased dramatically, even higher the best value with PAL or DOL alone (saturated value), while maintain the high filler content (10 wt% in this case) just by simply replace partially fillers of DOL by PAL (10 wt%). The insertion of PAL fibers into the WPU/DOL network created a much locked structure combined by hydrogen bond. Such structure largely enhanced the tensile strength of the WPU. Further, this much jammed structure induced by the addition of PAL has been proved by its lower value of elongation at break in comparison to neat WPU, WPU/DOL-10 and WPU/PAL-10 composite.

Figure 4 displays the TGA curves of neat WPU and WPU-based nanocomposites containing 10 wt% of different fillers under nitrogen atmosphere. In comparison to the neat WPU, the thermal stability of WPU-based nanocomposites is much better no matter what kind of fillers have been incorporated into WPU matrix. The initial decomposition temperature of WPU is located at 265 °C. With 10 wt% loading of fillers, this temperature becomes 330, 295 and 320 °C, respectively for PAL, DOL and the PAL-DOL mixture. But because of the compatibility issue between DOL and WPU matrix, the decomposition of WPU/DOL-10 composite is quite faster than WPU/PAL-10 after 325 °C. It is worth to note that the

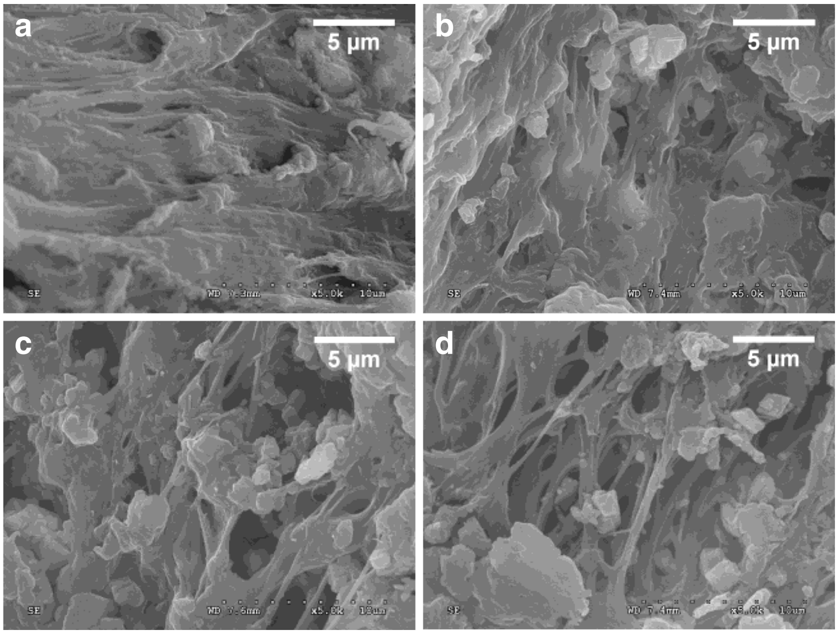

Fig. 7 SEM images of WPU/MIX composites with different amount of MIX micro/nano-fillers: (a) 5 wt.% MIX, (b) 10 wt.% MIX, (c) 15 wt.% MIX, (d) 20 wt.% MIX

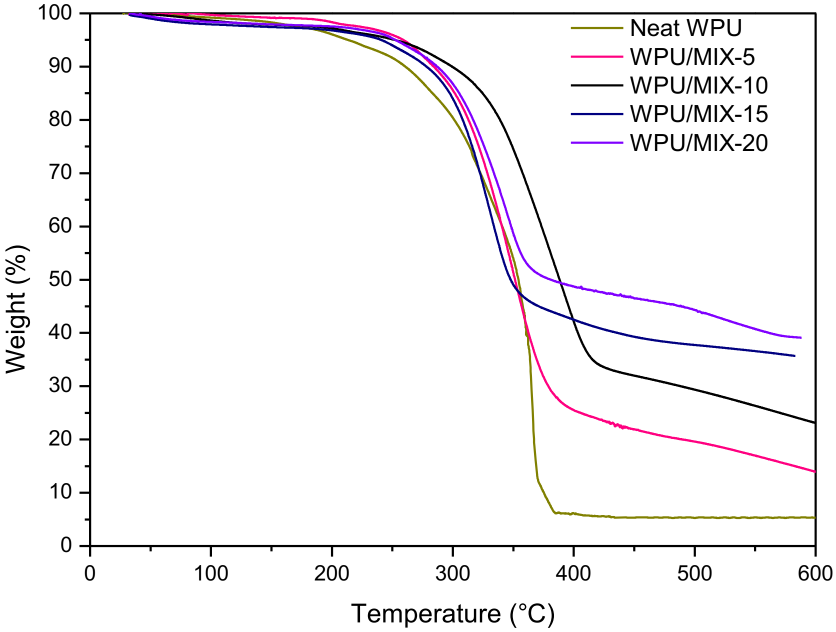

Fig. 8 TGA curves of the neat WPU and WPU/MIX composites with different amount of binary micro/nano-fillers under nitrogen atmosphere

decomposition rate of ternary composite (WPU/MIX-10, 4 wt% PAL, 6 wt% DOL) can be decreased by using PAL-DOL together. On the other hand, for WPU composites, the maximum decomposition temperature changed to 437, 355, 385 °C, respectively for PAL, DOL and the PAL-DOL mixture. Compared with 367 °C for neat WPU, it is obviously that the incorporation of PAL and PAL-DOL mixture delayed the maximum decomposition temperature of WPU. The above findings indicates that when the loading amount is 10 wt%, PAL and PAL-DOL mixture significantly improves the thermal stability of WPU, which maybe because the fillers sever as physical heating barrier when homogenously dispersed in WPU matrix and slows the thermal degradation process.

Figure 5 illustrates the SEM images of the neat WPU and WPU-based composite films which were filled with 10 wt.% of reinforcement agents. There are some PAL fibers appeared on the cross cut of WPU/PAL-10 composite (Fig. 5a), which indicates the dispersion and compatibility of raw PAL is poor in WPU. Similar phenomenon can be observed in the case of WPU/DOL-10 composite, as shown in Fig. 5b. Plenty of DOL micrometer particles separated from the WPU matrix. In contrast, the binary additives of MIX are well dispersed in WPU matrix, that only few DOL particles can be seen from the SEM image (Fig. 5c). Obviously, binary fillers of PAL-DOL mixture provides better dispersion at the same level of loading (10 wt%) in comparison to PAL or DOL only. Such result is in accordance with the tensile test results.

Influence of MIX amount to WPU composites

The filling amount of MIX reinforcement agent on the mechanical properties of WPU has been further investigated. Figure 6 displays the tensile strength and elongation at break properties of neat WPU and WPU/MIX composites with different amount of MIX loadings. As expected, the tensile strength increased dramatically with a small amount of MIX addition (5 wt%), from 4.9 MPa to 8.2 MPa. The tensile strength of WPU/MIX composite reached to the

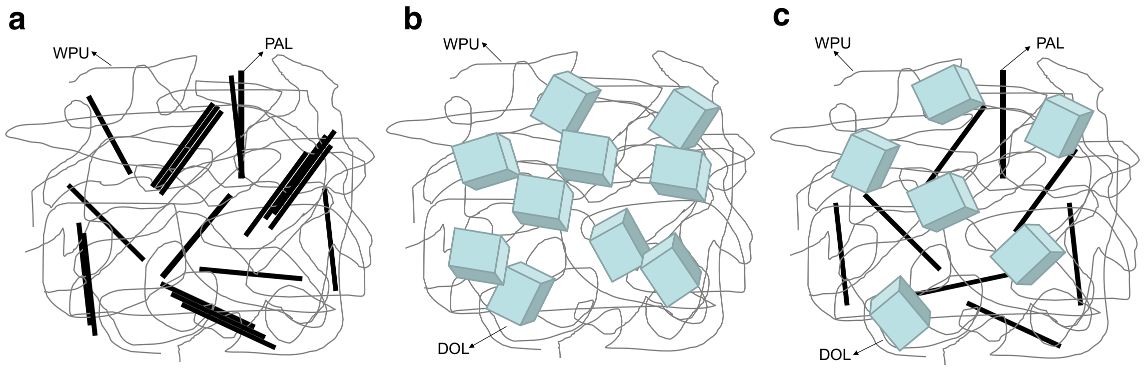

Fig. 9 Schematic illustration of PAL and DOL micro/nano-fillers in WPU composites: (a) WPU/PAL-10; (b) WPU/DOL-10; (c) WPU/MIX-10

maximum of 8.7 MPa while the MIX addition increased to 10 wt%. Afterwards, it started to decrease by further addition of MIX, which can be attributed to the aggregation of MIX in WPU matrix. However, the elongation property is quite different to tensile strength. Its value at break was decreasing simultaneously along with the increasing of MIX amount because of the restricted mobility caused by MIX fillers.

Figure 7 displays the SEM images of WPU/MIX composites with 5, 10, 15 and 20 wt.% of MIX addition. By addition of 5 wt% of MIX fillers (PAL/DOL = 2/3), no PAL fiber and DOL particle can be observed (Fig. 7a). Further increasing of MIX loading amount even to 10 wt%, only few DOL particles can be observed from the WPU matrix but not with PAL fibers (Fig. 7b). It suggests that the PAL fibers and DOL particles were dispersed quite homogenous throughout the WPU matrix. Unfortunately, further incorporation of 15 wt% of MIX, plenty of DOL particles as well as few PAL fibers can be observed which separated from the WPU matrix. It is quite in accordance with the results of mechanical tests.

Figure 8 shows the TGA curves of neat WPU and WPU/MIX nanocomposites with different amount of MIX loadings under nitrogen atmosphere. In comparison to the neat WPU, the incorporation of 5 wt% of MIX into WPU matrix remarkably increased the initial decomposition temperature to 295 °C from 265 °C. It is really interesting of that the initial decomposition temperature further reached to 320 °C by increasing the MIX content to 10 wt%. The maximum decomposition temperature of neat WPU is 367 °C, after incorporation of MIX, it becomes to 344, 392, 350 and 348 °C, respectively for the loading amount is 5, 10, 15 and 20 wt.%, which suggests the thermal stability of WPU can be enhanced by 10 wt.% MIX.

Accordingly, there are three ways of PAL and DOL inorganic reinforcement agents enhancing the thermal stability of WPU matrix. First, the hydroxyl group of PAL can provide strong hydrogen bonding interactions with the hard segments of WPU matrix, which could attribute partially to such improvement of thermal stability. Second, such agents can restrict the mobility of the polymer chains and provide heat insulation. Third, the PAL and DOL also can provide barrier effect to the diffusion of the volatile thermal decomposition products of the WPU. The aforementioned phenomenon can be explained by the uniform dispersion of PAL and DOL reinforcement agents with a suitable amount to give the maximum value of hydrogen bonding interactions, thermal insulation and barrier effect to gas compounds. As it is well-known, there is a maximum amount of reinforcement agents can disperse into polymer matrix uniformly. In this case, 10 wt% of MIX is the maximum value, which has been proved by SEM characterization in fig. 7.

Discussion

Figure 9 illustrates the possible dispersion of PAL, DOL and their mixture in WPU matrix at the loading of 10 wt%. As it is well known, nano/micro particles tend to aggregate in order to decrease their high surface energy. In addition, there are electrostatic and vander Waals' interaction between PAL fibers which lead them to further aggregate forming crystal bundles. Such phenomenon highly decreases the enhancement properties of fibrous PAL as well as 3D DOL on polymers (Fig. 9a and b). In WPU/MIX ternary composites, the fibrous PAL set in 3D DOL network, resulting in a much jammed and conjugated 3D PAL-DOL network (Fig. 9c). There are PAL-PAL network, PAL-DOL network, PAL-WPU-DOL bridging and WPU-WPU network in the system. The formation of such different networks as well as interactions could attribute to the observed synergistic effect of PAL and DOL on the significant reinforcement of WPU.

Conclusion

In summary, high performance WPU-based composite films have been successfully prepared by using fibrous PAL and 3D DOL together. A great synergistic effect of 1D PAL and 3D DOL on reinforcing WPU matrix has been observed. It is worthy to note that with an addition of 4 wt% PAL and 6 wt% DOL, the tensile strength of this ternary composite film has been significantly improved by 178% in comparison to neat WPU. Using 10 wt% of PAL or DOL only, the tensile strength of both WPU/PAL and WPU/DOL composite films even has been slightly decreased by 17% and 14.3%, respectively. This finding could be explained as due to the formation of 3D conjugated filler network with 1D PAL inserted into the 3D rhombohedral DOL crystal network. Such network also improves the thermal stability of the composites. However, the tensile strength as well as the thermal stability is going to decrease with a too high amount of MIX filler incorporation due to its aggregation. This work demonstrates a good example for the preparation of high performance polymer composites by simply using micro/nano-fillers with different dimension together.

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