

Reinforcement of Waterborne Polyurethane Films with Poly(acrylic acid)-Modified Palygorskite Fibers

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Abstract: Palygorskite (PAL) is a natural fibrous clay mineral which attracted tremendous attention as reinforcing agent to polymers. In this paper, a facile and environmental friendly modification process of PAL by poly acrylic acid (PAA) via in-situ polymerization in PAL/water gel has been reported. The effects of PAA modified PAL (PAA-PAL) on the mechanical and thermal properties of waterborne polyurethane (WPU) nanocomposites have been investigated. Scanning electron microscopy (SEM) demonstrated that the dispersion of PAL has improved dramatically after PAA modification. Tensile tests showed that PAA-PAL has a significant reinforcement effect on WPU matrix. Addition of 10 wt% PAA-PAL, the tensile strength and the Young's modulus of WPU composites increased 235 % and 388 %, respectively. Furthermore, the thermal stability of WPU also has been distinctly improved via addition of PAA-PAL.

Keywords: Waterborne polyurethane, Palygorskite, Poly(acrylic acid), Mechanical property

Introduction

Waterborne polyurethane (WPU) has been widely used in coatings, inks, adhesives, leather finishing agents and other fields because of its advantages for environmental issues [1-3]. Compared with solvent-based polyurethane, however, WPU still has some shortcomings, such as poor water resistance, slow drying speed, poor thermal and mechanical properties, etc., which severely restricts the further application of WPU.

Inspired by the pioneering work of Toyota automotive corporation on nylon modification by clay [4], using nanoparticle additives became an effective way to alter and strengthen the aforementioned properties of WPU. According to the literature, the modification of WPU has been successfully carried out by adding titanium dioxide [5,6], zinc oxide [7,8], halloysite [9], carbon nanotubes [10-12], carbon black [13,14], graphene [15-17], or even polymer blends [18], etc. The experimental results showed that the thermal stability and mechanical properties of WPU had been significantly improved by simply adding those nanoparticles.

Palygorskite (PAL) is a porous aluminum-rich magnesium silicate with one-dimensional crystal structure (single crystal length 1-5 μm , diameter about 20-70 nm) [19]. It has been widely used as catalyst supports [20], adsorbents [21], and rheological agents [22] in chemical industry. Its unique one-dimensional nano-fiber structure with large surface areas and aspect ratios, rich reactive hydroxyl groups on the surface lead to that PAL is a good polymer material additive

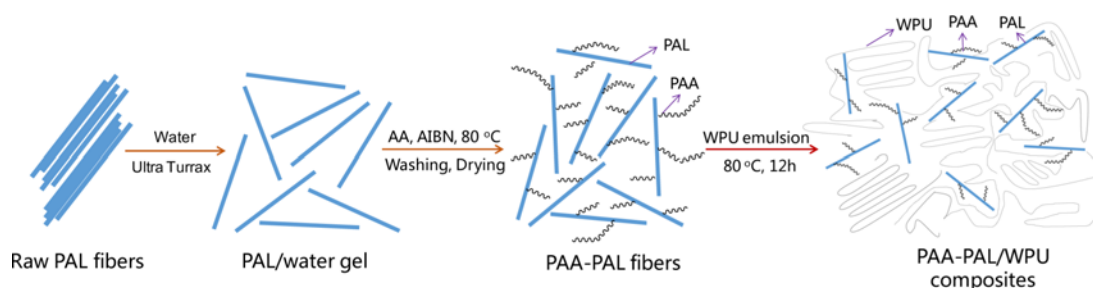
[23]. However, due to the van der Waals and hydrogen bonding interactions between the PAL intervals, the raw PAL exists in the form of micrometric aggregates and crystal bundles, which greatly impeded its applications in polymer composites [24].

Up to date, there are few studies reported on the PAL reinforcing WPU [25-27]. Peng *et al.* prepared a series of waterborne polyurethane/palygorskite nanocomposites by in-situ polymerization [25]. The experimental results showed that the isocyanate modified PAL fibers were uniformly dispersed in WPU. As a result, the thermal stability and mechanical properties of WPU were significantly improved. Wang *et al.* used silylated PAL to reinforce soybean oil-based polyurethane [26,27]. The experimental results showed that the tensile strength of such WPU increased by 303 % with the addition of 12 wt% silylated PAL [27]. However, complicated PAL modification process, expensive reactive agents and organic solvents, as well as limited grafting amount of organic functions onto PAL surface highly hindered their practical applications.

Herein, we report a novel and simple modification process of PAL by poly acrylic acid (PAA) with cheap acrylic acid agents via in-situ polymerization in PAL/water gel, in order to eliminate limitations of expensive modification agents and organic solvents existed in the traditional processes. Furthermore, the PAL aggregates can be separated by our modification process and the modified PAA-PAL fibers existed in isolated form due to the protection of PAA chains (Scheme 1). In addition, the dispersity of raw PAL and PAA-PAL in WPU composites and their effects on the tensile mechanical as well as thermal properties of the PAL/WPU composites were investigated by various characterizations.

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Scheme 1. Schematic illustration of preparation process for PAA-PAL/WPU composites.

Experimental

Materials

Waterborne polyurethane (F68-20) was a gift from Jiangsu Junrui Technical Co. Ltd. (Huaian, China). Palygorskite (PAL, >90 wt%) was supplied from Jiangsu Zhongyuan Minerals Co. Ltd. (Huaian, China). Acrylic acid (AA, >99 %) was purchased from Sinopharm Chemical Reagent Co. Ltd. 2,2'-Azobisisobutyronitrile (AIBN, 99 %) was obtained from Aladdin Chemical Co. Ltd.

PAL Modification

Modifications in PAL/water gel were performed by first dispersing 5 g of PAL into 245 g of water (2 wt% of solids) by means of a lab dissolver (IKA T25) operating at 10000 rpm for 20 min. Then acrylic acid (AA, 30 mmol) and 2,2'-Azobisisobutyronitrile (AIBN, 15 mg) was added into the mixture and refluxed for 12 h at 80 °C under magnetic stirring. After that, the mixture was cooled down and centrifuged (8000 rpm for 5 min, HITACHI CT15E), washed with deionized water for 4 times (200 ml each) and dried in vacuum at 40 °C for 12 h to obtain the final products of PAA-PAL.

Preparation of PAA-PAL/WPU Nanocomposite Coatings

Desired amount of PAA-PAL fibers (0-20 wt.% in comparison to WPU emulsion) was 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. The films were heated to 80 °C and kept for 12 h. Finally, PAA-PAL/WPU nanocomposite films were obtained. A reproducible film thickness of 40 ± 2 μm was obtained whatever the formulation composition.

Characterization Techniques

Fourier transform infrared spectroscopy (FTIR) of the samples were recorded via a Nicolet 5700 spectrophotometer (Thermo Electron Co., USA) with a resolution of 4 cm^{-1} from 4,000 to 600 cm^{-1} . For the PAL sample powders, they were characterized by using KBr pellet technique.

The carbon contents of the organically modified PAL samples were performed on an Elementar Vario III element

analyzer under He atmosphere. Each value was obtained by the means of three replicates with an error of less than 0.1 %.

The XRD patterns were recorded on an X-ray power diffractometer (D8Discover, Bruker AXS, Germany) using Cu-K α radiation (0.15406 nm, 40 kV, 40 mA). Data were collected from 5 to 40 ° (2 θ) with 0.5 s $^{-1}$ step.

Morphology of the samples was characterized by Scanning electron microscopy (SEM, Hitachi S3000N microscope working at 25 kV). Before analysis, the samples were coated with a 15 nm thick layer of gold to reduce the charging effect on the surface.

Tensile measurements were carried out with GMET-4204 machine (SANS) at room temperature (20-25 °C). The samples were cut to 20 mm \times 5 mm \times 0.04 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.

Thermalgravity analysis was carried out using 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

PAL Modification

FTIR is a powerful tool to characterize the organic-modification of micro/nano fillers. Figure 1 illustrates the FTIR spectra of raw PAL and PAA-PAL. The absorption bands at 3,800-3,392 cm^{-1} are belonged to the hydroxyl groups of coordinated water in the tunnels of PAL. The strong and wide peak at 1,655 cm^{-1} can be assigned to the bending vibration of zeolite water. The two sharp absorptions at 1,024 and 982 cm^{-1} can be ascribed to the stretching and the bending vibrations of Si-O-Si bonds. In comparison to PAL, new absorbance bands at 1,523 cm^{-1} (represents the COO function) and 1384 cm^{-1} (corresponds to the CH-CO groups) [28] appeared for the PAA-PAL. In addition, the adsorption at 3,400-3,100 cm^{-1} , which belonged to the stretching vibration of coordinated hydroxyl groups, became much stronger. It is probably because of the coordination of hydroxyl function of carboxyl groups from PAA. The C=O stretch band of the carboxyl group of PAA at 1,710 cm^{-1} was not visible here, probably due to the strong and wide

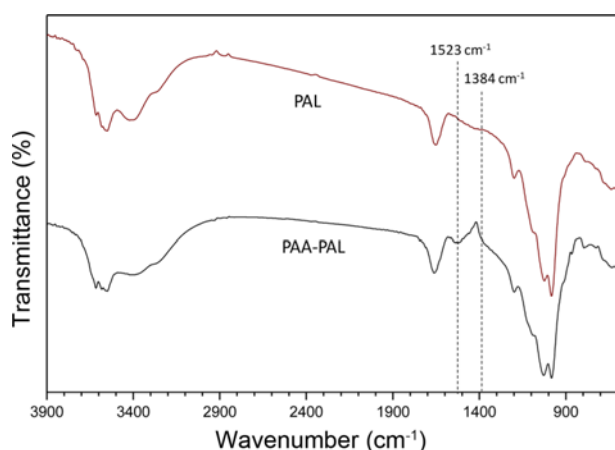


Figure 1. FTIR spectra of PAL and PAA-PAL.

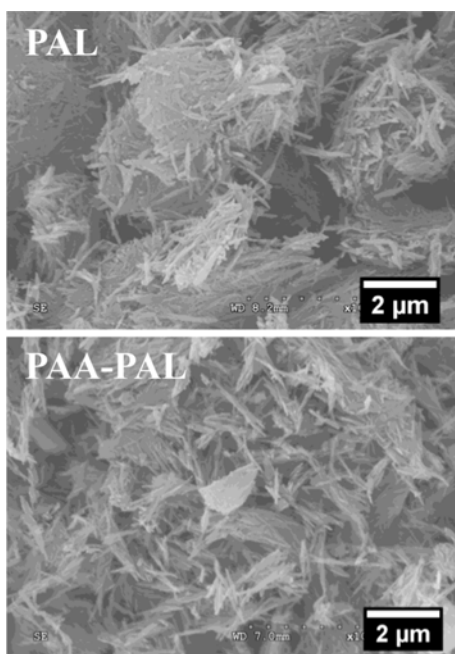


Figure 2. SEM images of PAL and PAA-PAL.

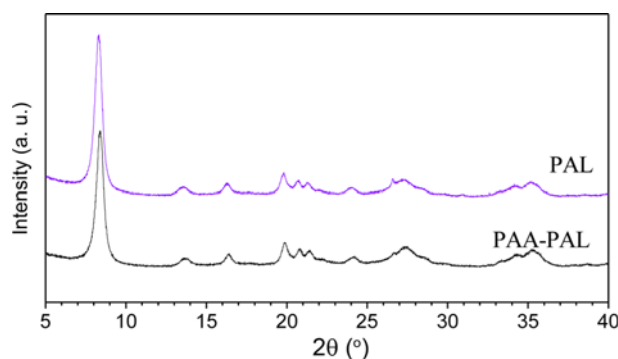


Figure 3. XRD patterns of PAL and PAA-PAL.

absorption of zeolite water of PAL at $1,655\text{ cm}^{-1}$. Nevertheless, these results indicate that the PAL fibers have been successfully modified by PAA.

Further proof was provided by Elemental analysis. The exact grafted amount of PAA onto the surface of PAL was 15.2 wt%, which was determined from the carbon content of modified PAL samples (deducted 0.6 wt% of carbon content in raw PAL).

Figure 2 displays the SEM images of raw PAL and modified PAA-PAL samples. Obviously, the micrometer aggregates of raw PAL have been disaggregated into much smaller crystal bundles that composed by tens of PAL fibers or even to single fiber after modified by PAA. It demonstrated that PAA modification in PAL/water gel can partially disaggregate the PAL aggregates, which probably can beneficial the use as polymer reinforce agent.

Figure 3 shows the XRD patterns of raw PAL and modified PAA-PAL. In comparison, the position and intensity of the characteristic diffraction peaks of palygorskite crystal (8.34° , 13.74° , 16.34° , 19.83° , 27.54° and 34.28°) for both samples do not change. Apparently, this result suggests that doing PAA-modification of PAL in water gel did not destroy the crystalline structure of PAL. Only the intensity of diffraction peak at 2θ value of 26.63° , which belongs to quartz, has been decreased. This suggests that our modification procedure also has a purification function for raw PAL.

Influence of PAL Micro/nano Fillers to the Tensile and Thermal Properties of WPU

Table 1 presented the data of tensile strength, elongation at break and Young's modulus of neat WPU and WPU nanocomposites. In comparison to neat WPU, the addition of 10 wt% raw PAL into WPU decreased its tensile strength and elongation properties slightly. Quite interestingly, with the addition of 10 wt% PAA-PAL, the tensile strength of the PAA-PAL/WPU nanocomposites increased 235 %, from 4.9 to 11.5 MPa; and the Young's modulus increased 388 %, from 1.7 to 6.6 MPa. Because of the PAA modification, it created strong interfacial adhesion between the PAA-PAL and WPU matrix, which is critical for efficient load transfer and enhance the mechanical properties. The slightly decreasing of the elongation at break of WPU nanocomposites was probably because of the restricted mobility imposed by PAL fillers.

Table 1. Mechanical properties of neat WPU and WPU nanocomposites

Sample	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
Neat WPU	4.9 ± 0.4	1422.9 ± 94.2	1.7 ± 0.2
PAL/WPU	3.7 ± 0.4	1332.7 ± 89.6	3.4 ± 0.6
PAA-PAL/WPU	11.5 ± 0.9	987.8 ± 46.7	6.6 ± 0.2

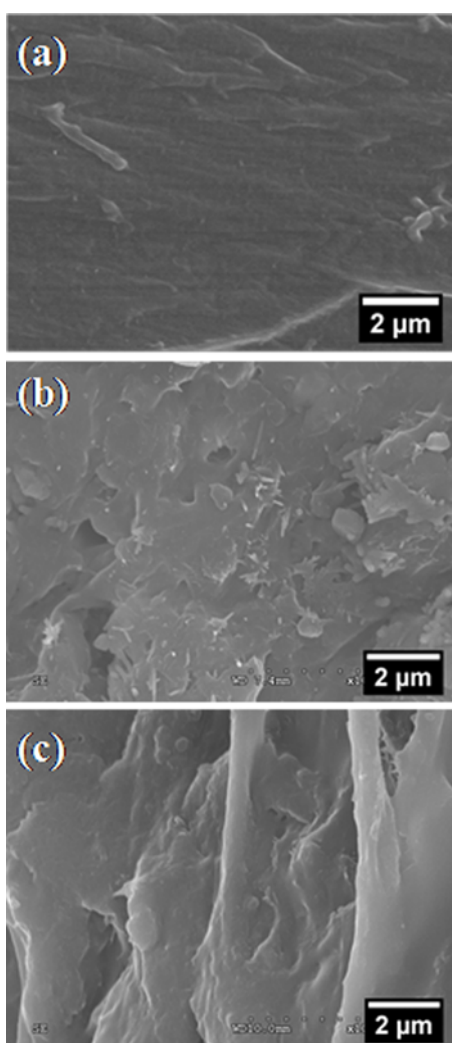


Figure 4. SEM images of (a) WPU, (b) PAL/WPU, and (c) PAA-PAL/WPU.

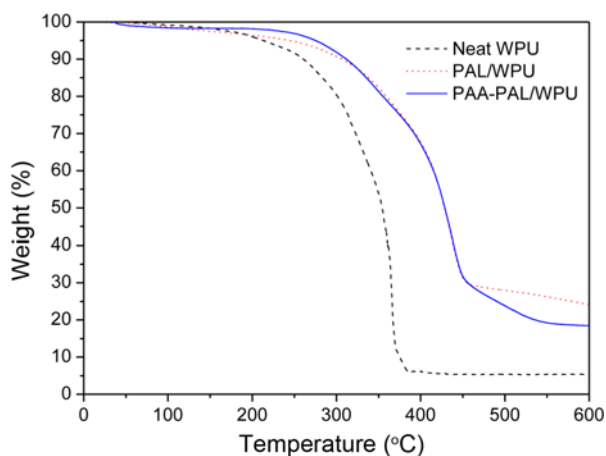


Figure 5. TGA curves of the neat WPU and WPU nanocomposites (PAL/WPU and PAA-PAL/WPU with 10 wt% of PAL, PAA-PAL nanofillers, respectively) under nitrogen atmosphere.

Figure 4 illustrates the SEM images of the WPU and PAL/WPU composite films which were filled with 10 wt% of raw or PAA-PAL. In comparison to neat WPU (Figure 4a), it can be seen plenty of PAL fibers appeared on the cross cut of PAL-WPU composite (Figure 4b), which indicates the dispersity and compatibility of raw PAL is quite poor with WPU matrix. In contrast, after PAA-modification, the PAA-PAL fibers were enwrapped by WPU completely, that can't be seen from the image (Figure 5c). Such result suggests that the PAA modification improved the dispersion ability of PAL fibers and further increased the compatibility and interfacial strength with the WPU matrix.

Figure 5 displays the TGA curves of neat WPU and WPU nanocomposites under nitrogen atmosphere. As can be seen, the decomposition temperature of 5 % weight loss for the sample of WPU, PAL/WPU and PAA-PAL/WPU is 213 °C, 244 °C and 278 °C, respectively. Obviously, in comparison to the neat WPU, the decomposition temperature of WPU increased 31 °C by incorporation of raw PAL into the WPU matrix. This result could be ascribed to PAL fibers serve as a good thermal cover layer and can avoid the direct thermal decomposition of WPU matrix while heating. One has to note that the decomposition temperature of WPU polymer even increased 65 °C by incorporation of PAA-PAL. Besides the more homogeneous distribution of PAA-PAL created better thermal insulation, the strong hydrogen bonding interactions between PAA-PAL and the hard segments of WPU matrix, which could be another reason to such improvement of thermal stability.

Effect of PAA-PAL amount on the Mechanical Properties of WPU Composites

In order to investigate the filling amount of PAA-PAL on the mechanical properties of WPU, Table 2 listed the tensile strength, elongation at break, and Young's modulus of neat WPU and PAA-PAL/WPU composites with different amount of PAA-PAL loadings. Obviously, the tensile strength increased dramatically with a small amount of PAA-PAL addition. Up to 10 wt%, the tensile strength of PAA-PAL/WPU composites reached to the maximum of 11.5 MPa. Afterwards, it was going to decrease with a higher amount of

Table 2. Mechanical properties of PAA-PAL/WPU nanocomposites with different amount of PAA-PAL nanofillers

Sample	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
Neat WPU	4.9±0.4	1422.9±94.2	1.7±0.2
PAA-PAL-5/WPU	8.6±0.7	1151.5±0.4	3.4±0.6
PAA-PAL-10/WPU	11.5±0.9	987.8±46.7	6.6±0.3
PAA-PAL-15/WPU	9.6±1.1	857±34.6	7.1±0.2
PAA-PAL-20/WPU	6.8±0.8	449.1±63.2	8.4±0.2

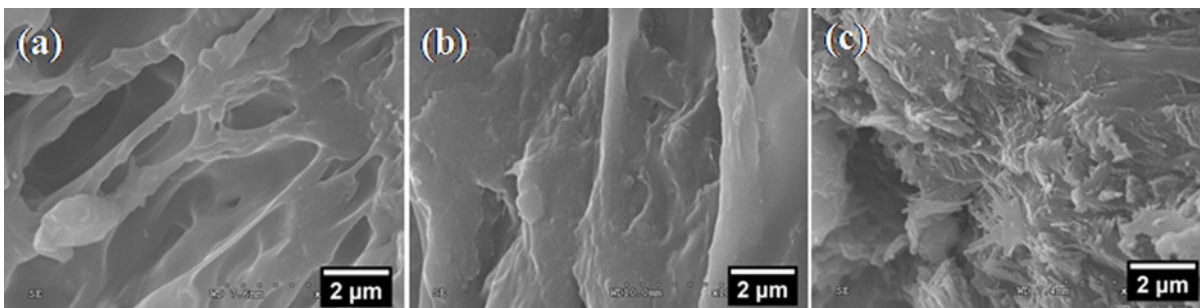


Figure 6. SEM images of PAA-PAL/WPU nanocomposites; (a) PAA-PAL-5/WPU, (b) PAA-PAL-10/WPU, and (c) PAA-PAL-15/WPU.

addition, which can be attributed to the saturated dispersion of PAA-PAL. As expected, the value of elongation at break was decreasing along with the increasing of PAA-PAL loading amount due to the restricted mobility caused by PAA-PAL.

Figure 6 displays the SEM images of PAA-PAL/WPU nanocomposites with 5, 10 and 15 wt% of PAA-PAL addition. As can be seen from the images, the compatibility between PAA-PAL and WPU matrix was quite good. Even with 10 wt% of PAA-PAL loading, very few PAL fibers can

be observed from the WPU matrix (Figure 6b). It suggests that the PAA-PAL fibers were dispersed quite homogenous throughout the WPU matrix. Unfortunately, the incorporation of 15 wt% of PAA-PAL, plenty of PAL fibers can be observed which separated from the WPU matrix. This finding is quite in accordance to the results of mechanical tests.

PAA-PAL Reinforcement Mechanism on WPU

As it is well known, PAL fibers tend to aggregate forming crystal bundles due to the electrostatic and vander Waals'

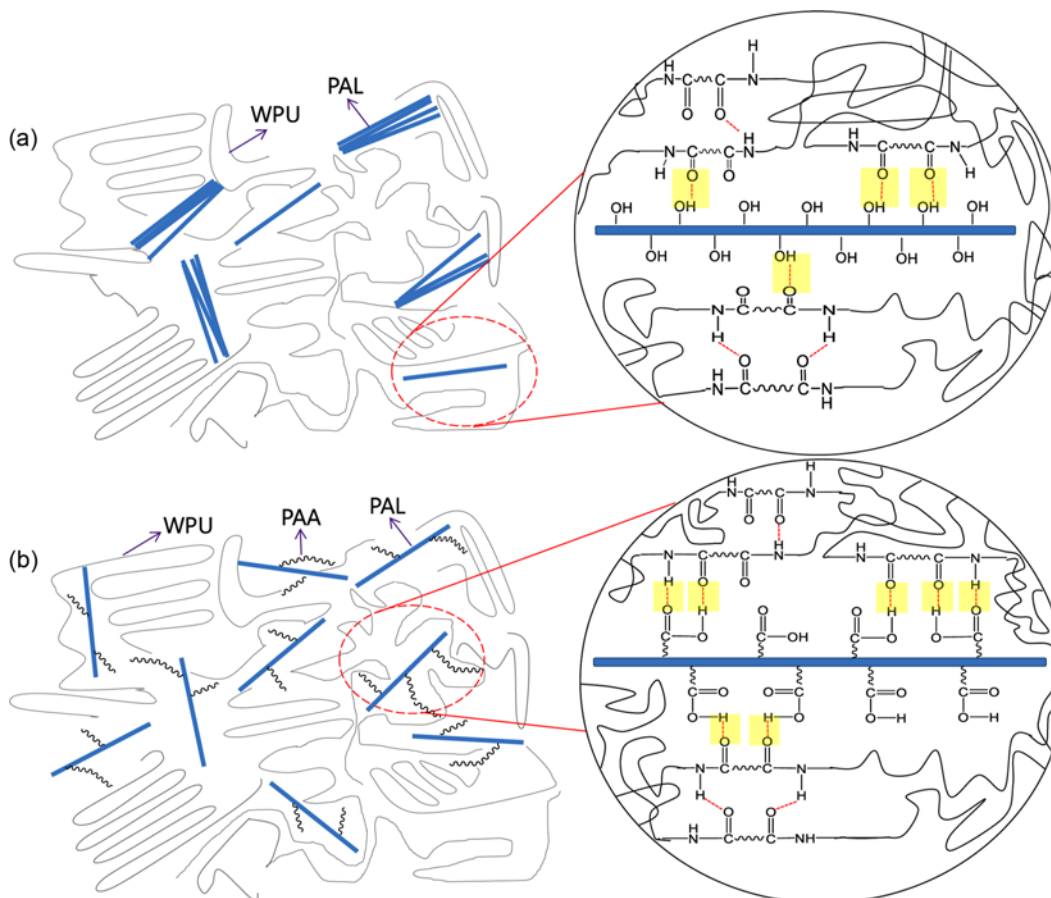


Figure 7. Schematic illustration of the PAL reinforcement mechanism on WPU composites; (a) PAL/WPU and (b) PAA-PAL/WPU.

interaction. Such phenomenon highly decreases the enhancement properties of fibrous PAL on polymers. As shown in Figure 7a, the raw PAL fibers have been aggregated into micro-aggregates in WPU matrices, which have proved by SEM characterization (Figure 4b). Besides, the silanol groups existed on the surface of PAL, probably can form hydrogen bonds with amide groups of WPU. Thus, the mechanical and thermal properties of WPU have been slightly reinforced by raw PAL. In the case of PAA-PAL, it has been disaggregated via the PAA modification, which was proved by SEM in Figure 2. Furthermore, PAA modification also improves the compatibility of PAA-PAL fibers with WPU matrix, as can be seen from the SEM image of Figure 4c. One has to note that PAA has plenty of carboxyl functions. In comparison to raw PAL, there are abundant carboxyl functions on the surface of PAA-PAL fibers. Such function may form hydrogen bond with amide group from WPU matrix. An idea dispersion of fibrous PAA-PAL crystals in WPU matrix as well as the supposed interaction between PAA-PAL and WPU matrix was displayed in Figure 7b. All of these reasons can attribute to the significant promotion of mechanical as well as thermal properties of PAA-PAL/WPU composite.

Conclusion

PAL fibers have been successfully modified by PAA via a facile and environmental friendly in-situ polymerization process in water gel, which was confirmed by FTIR. The modified PAA-PAL fibers were proved that they could significant reinforce the WPU matrix. It is worthy to note that with a 10 wt% addition of PAA-PAL, the tensile strength increased 235 % and the Young's modulus increased 388 %. SEM revealed the homogeneous dispersion of PAA-PAL in WPU matrix, indicating that the good compatibility between PAA-PAL and WPU matrix, which could provide strong interfacial adhesion. Furthermore, the thermal stability also has been improved dramatically. The decomposition temperature of 5 % weight loss for the PAA-PAL/WPU composite increased 65 °C in comparison to neat WPU.

Acknowledgements

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