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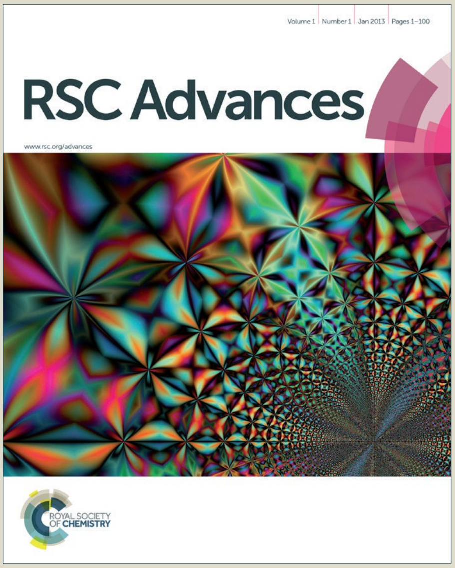

Synthesis and Properties of Nano-silica Modified Environmentally Friendly Polyurethane Adhesive

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Abstract: In this study, nano-SiO_2 modified waterborne polyurethane (WPU) adhesive with remarkably low VOC content and high adhesion performance was successfully synthesized via in-situ polymerization. The influence of nano-silica concentration on different properties of the aqueous-based adhesive and the casted films were carefully investigated. When the concentration of nano-SiO_2 was in the range of 2.0% to 2.5%, the performances of the adhesive reached the optimum. Under optimum conditions, the appearance of emulsion was milky white with blue light uniform liquid. The T-peel and shear strength of the nano-modified adhesive showed essential improvement compared with pure-WPU adhesive. The results of shear adhesion failure temperature test showed that the thermo-tolerant temperature of the adhesive was higher than 175°C. The tensile strength, elongation at break and water swelling of the casted films were about 21.3MPa, 890% and 2.7%, respectively. Finally, other properties of the water-based adhesive were characterized by FTIR, SEM, molecular weight, pH, mean particle size and solid content measurement.

Keywords: Polyurethane; Adhesives; Nano-SiO_2; Health; Storage Stability; Heat Resistance; VOC

INTRODUCTION

In the past decades, adhesives based on polyurethane, possess a unique combination of properties, including superior adhesion, excellent outdoor durability and outstanding low temperature performance, and have been widely used in leather, footwear, textile, coating, furniture, packaging, construction, automotive, military and other industry fields[1-10]. However, it is almost impossible to avoid the release of volatile organic compounds (VOCs) during the usage of traditional solvent-based polyurethane adhesives. These volatile organic compounds usually have toxic and hazardous effects to the human beings. Hence, the studies of green and environmentally friendly water-based adhesives have drawn much attention and a vast amount of researches have been done in the past few years[3, 8, 11-16].

From the environmental and healthy point of view, water-borne polyurethane (WPU) adhesives are preferred in most circumstances, due to their lower toxicity compared with solvent-borne products. Unfortunately, the utility of aqueous based polyurethane adhesives were restricted to some extent due to their inferior properties, such as lowered adhesive strength, water resistance, mechanical strength and thermal stability[12-18]. In order to improve the properties mentioned above, significant attempts have been carried out during the last decade via various approaches, such as using different kinds of chain extenders, incorporating different diisocyanates, making and cross-linking nanoparticles[13, 19-26]. It is worth mentioning that nano-modification was regarded as an effective and promising technique in this field, since it has been confirmed that with the incorporation of nano-composites into the polyurethane, the physicochemical properties of the WPU, such as solvent resistance, mechanical strength and thermo tolerance were greatly improved compared to that of conventional pure WPU[27-35]. In particular, polymer/SiO_2 nano-composites exhibit improved mechanical properties and thermal stability compared with pure polymer matrix and polymer micro-composites[34-37]. Therefore, polymer/nano-SiO_2 composites have drawn substantial academic and industrial interest, and have been employed in a variety of applications. The preparation, characterization, properties, and applications of polymer/silica nano-composites have become a quickly expanding field of research in recent years[29-37].

In this work, a series of nano-silica modified aqueous based polyurethane adhesives were successfully synthesized through in-situ polymerization. The synthesized waterborne adhesive was demonstrated by different characterization techniques. And a detailed study of the relationship between nano-SiO_2 concentration and adhesive properties was carried out. The adhesive prepared in this work featured a remarkably low VOC content (less than 0.5%) and exhibited high adhesive performance even when the operating temperature was up to 175^{o}C.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, 98% purity) and 1,4-butanediol (BDO, 99% purity) were purchased from Bayer (Germany). Modified nano-silica (99.9% purity), ethylene diamine (EDA, 99% purity) and 1-methyl-2-pyrrolidone (NMP, 99% purity) were purchased from Evonik Degussa (Germany). Poly(1,4-butylene adipate) end capped diol (PBA, number-average molecular weight = 2,000 g·mol^{-1}, 98% purity), triethylamine (TEA, 99% purity), dimethylolpropionic acid (DMPA, 99% purity) and acetone (99.5% purity) were purchased from Sinopharm Chemical Reagent (China). Anti-foaming agent BYK-028 was purchased from BYK Additives & Instruments (Germany). Catalyst, naphthenic acids, bismuth salts (NABS, 99.9% purity) was kindly supplied by Shanghai Institute of Organic Chemistry (China). Potassium bromide (99.9% purity) was purchased from Merck (Germany). Distilled water was produced in the laboratory.

PBA was dried under vacuum at 110^{o}C and 1-2 mm Hg for 2.5 h before use. Acetone, BDO and NMP were dehydrated with 4-Å molecular sieves for 5 days prior to use. Other chemicals and solvents mentioned above were used as received.

Synthesis of the nano-silica modified WPU

The nano-silica modified WPU dispersions were prepared in a 500mL glass reactor, which equipped with a nitrogen inlet, a temperature sensor, a condenser and a mechanical stirrer. An oil bath was employed for controlling the reaction temperature.

Firstly, PBA was preheated to 70^{o}C and was kept constant for 30 min, after that, nano-SiO_2 was added into the reactor at high-speed stirring (2,000 rpm). The temperature was then reduced to 60^{o}C. Then, it was slowly reheated to 80^{o}C after the IPDI and NABS catalyst were added. The temperature was kept constant for 4 h under nitrogen atmosphere. Secondly, after the NCO content was reached predetermined value, hydrophilic chain extender DMPA was added into the prepolymer. Then, the temperature was heated to 90^{o}C and was kept constant for 2 h. Thirdly, BDO was added into the reactor and the temperature was kept constant at 90^{o}C for another 2 h. After the period, the mixture was cooled to 55^{o}C and the prepolymer was neutralized with TEA. And acetone was added to reduce the viscosity, if necessary. The polyurethane dispersion of the bulk in water was performed with vigorous stirring (1,000 rpm) for 30 min. Afterwards, EDA was added into the dispersion at 25^{o}C and kept constant for 2 h to complete the chain-extension reaction between the NCO terminated groups of the prepolymer and the amino groups of the EDA. Finally, de-foaming agent BYK-028 was added into the dispersion at 40^{o}C and the product was obtained after acetone was removed under vacuum. The reaction scheme for the synthesis of nano-SiO_2 modified waterborne polyurethane adhesive was illustrated in Figure 1.

The basic formulation of the WPU dispersion was 36.0 wt.% PBA, 1.5 wt.% DMPA, 9.9 wt.% IPDI, 0.1 wt.% NABS, 0.4 wt.% BDO, 0.9 wt.% TEA, 47.0-50.0 wt.% distilled water, 0.1 wt.% EDA, 0.1 wt.% BYK-028 and 1.0-3.0 wt.% nano-SiO_2.

Preparation of the polyurethane films

The films were prepared by casting the aqueous dispersion onto a PTFE mould (14cm × 8cm) and drying the dispersion at room temperature for 3 days. The polyurethane films (approximately 0.3cm thick) were annealed at 60^{o}C for 12 h and then vacuum dried for 12 h. The vacuum-dried films were stored in desiccators at ambient temperature.

Characterization and performance testing

The viscosities of the aqueous polyurethane dispersions were tested in a Brookfield Viscometer DV-II at 25^{o}C. The molecular weight of the WPU dispersions was obtained by Gel Permeation Chromatography (GPC), using a Waters peristaltic pump model 515 HPLC and a Waters 410 refractive index detector. The mean particle size (D_{50}) of the dispersions was measured in a submicron particle sizer PSS Nicomp 380 DLS and the pH values were measured in a pH meter S700-K. Each sample was tested for 5 times, and the values were averaged.

The structure of the WPU films were analyzed by a Perkin Elmer 100 Spectrometer, provided with Fourier transform analysis (FTIR). The WPU emulsion was coated on the potassium bromide wafer with a diameter of 13 mm for the analysis. Measurements were carried out by the transmittance mode in the range of 4,000-400 cm^{-1} with a resolution of 2 cm^{-1}.

The morphologies of the WPU and nano-SiO_2 dispersed in WPU were observed by a HITACHI S-4700 Scanning Electron Microscopy (SEM) with an accelerating voltage of 10 kV. The samples for the test were prepared by casting the WPU adhesives onto a clean PTFE pan and drying it in a vacuum oven at 60^oC for 3 days. All of the specimens were coated with gold in vacuum before the SEM micrographs were carried out.

Peel resistance of the aqueous adhesive (i.e. T-peel strength, or 180-degree peel strength) was measured with an Instron 5569 machine at a relative humidity of 50 ± 2% at 25 ± 2^oC. The experiments were carried out according to ASTM D1876-08[38]. Special test panels about 300 mm wide by 300 mm long were prepared. The adhesive was applied using a roller applicator of 100μm onto the Aluminum panel and dried at 60^oC for 15 min. Then, an Aluminum-Alloy sheet was adhered at a pressure of 20MPa for 15 min to improve the contact. Afterwards, the samples were kept for 7 days at room conditions. Finally, the bonded panels were cut into 25 mm wide test specimens as shown in the standard[38]. A constant head speed of 250 $mm{\cdot}min^{-1}$ was used in the test. Each specimen was peeled over 125 mm length of the bond line after the initial peak. And the values quoted were the averages of 5 measurements.

Lap-shear test was carried out using an Instron 5569 machine at a relative humidity of 50 ± 2% at 25 ± 2^oC. The tests were carried out according to ASTM D3163-14[39]. The synthesized adhesive was deposited using a roller applicator of 100μm onto the faces of Aluminum and Aluminum-Alloy sheets and dried at 60^oC for 15min. Then, the panels were attached at a pressure of 20MPa for 15 min to improve the contact. Afterwards, the samples were kept for 7 days at room conditions. Finally, the bonded panels were cut into 25 mm wide test specimens as shown in the standard[39]. The tests were carried out by loading the specimen to failure at a rate of 10 $mm{\cdot}min^{-1}$ cross head speed. The value of each sample was reported as the average of 5 measurements.

Heat-fail temperature showed a limiting temperature above which the adhesive was not to be exposed in service under shear load. In this study, the shear adhesion failure temperature (SAFT) test was employed to define the thermo-tolerant temperature (i.e. maximum usage temperature) of the synthesized waterborne adhesive according to the study of Sardon[15]. For each adhesive sample, 5 specimens were measured and the values were averaged. The procedure to perform the SAFT test was as follows: the adhesive was spread on the Aluminum panel and Aluminum-Alloy sheet at a thickness of 100μm by using a roller applicator. After drying it for 15 min at 60°C, the joint was placed under a pressure of 20MPa for 15 min. Then, the samples were kept at ambient temperature for 7 days. Finally, a lap joint measuring 25 mm × 25 mm inside two strips of standard substrate was prepared for test. And standard weights (500g) were positioned and the counter was turned on until all specimens failed. SAFT was measured using a temperature ramp of $0.5^{o}C\cdot min^{-1}$ from 20°C to 200°C.

The tensile properties of the casted polyurethane films were measured at room temperature using an Instron 5569 machine following the specification of ASTM D638-10[40] with a crosshead speed of $100\ mm\cdot min^{-1}$. Dumbbell specimens were cut from the casted films by a sheet-punching machine as shown in the standard[40]. The value of each sample was reported as the average of 5 measurements.

The determination of the VOC content of the synthesized WPU adhesive was used an Agilent 6890 N Network Gas Chromatograph System interfaced with a 5973 Network MSD according to the specification of ASTM D3960-13[41]. And the VOC content percentage was determined as the follow equation[41]:

$$VOC\ content\ (\%) = \frac{M_o}{M_s} \times 100 = \frac{M_v - M_w - M_{ex}}{M_s} \times 100$$

Where M_o is the weight of organic volatiles, M_v is the weight of total volatiles, M_w is the weight of water, M_{ex} is the weight of exempt volatile compound and M_s is the weight of solids.

For the swelling study, the WPU films (7cm × 7cm) were immersed in distilled water for 24h at 25°C and the water swelling percentage was determined from the weight increase as follows[4, 25]:

$$Water\ swelling\ (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

Where W_1 is the weight of the dried film and W_2 is the weight of the film at equilibrium swelling.

The solid content of the WPU was determined from the weight decrease before and after solvent evaporation. About 2-3g waterborne polyurethane dispersion was placed in a weighing bottle, then kept it in an oven at 110°C until constant weight was reached. And the solid content percentage was determined as the follow equation[14]:

$$Solid\ content\ (\%) = \frac{G_2}{G_1} \times 100$$

Where G_1 is the original weight of WPU and G_2 is the dried weight.

The value of VOC-content, water-swelling and solid content of each sample was reported as the average of 5 measurements.

RESULTS AND DUSCUSSION

Physical properties of the nano-silica modified aqueous based polyurethane adhesive

Table 1 shows the physical properties of the nano-SiO_2 modified waterborne polyurethane adhesive. Under ideal conditions, the storage life of the adhesive is more than 9 months, and the appearance of it is milky white with blue light uniform liquid. The pH value of the product is in the range of 6.5-7.5. Number average molecular weight (M_n) and mean particle size (D_{50}) of the WPU adhesive are approximately 55,000 g·mol^{-1} and 800 nm, respectively. The Brookfield viscosity of the adhesive is about 150 mPa·s (25°C) and the solid content is in the range of 50-52%. The VOC content of the nano-SiO_2 modified water-based polyurethane adhesive is less than 0.5%.

FTIR analysis of nano-silica modified WPU

The typical functional groups of the SiO_2-modified WPU (nano-silica content = 2.0%) are characterized by FTIR as shown in Figure 2. As can be seen in the spectrum, the absence of bands at 2,250-2,270 cm^{-1} confirmed the absence of a free NCO group in the polymer structure, which indicated the completion of the reaction. The bands observed between 3,300 and 3,600 cm^{-1} are attributed to the N–H stretching vibration of urethane[22]. The bands in the range of 2,800-3,000 cm^{-1}

are connected to the aliphatic C–H stretching vibration of $–CH_2$ and $–CH_3$[29]. The characteristic absorption peak of C=O of urethane is in the unique range of 1,710-1,760 cm^{-1} and the bands at 1,020-1,120 cm^{-1} are attributed to the Si–O–C and C–O–C stretching vibration absorptions[20, 31]. The absorption peak around ~470 cm^{-1} is assigned to the strong Si–O–Si bending vibration from silica, proving that the nano-SiO_2 is successfully incorporated into the polyurethane chains. Other strong characteristic absorption bands of silica are overlapped with the existing bands of WPU groups, such as 1,100-1,020 cm^{-1} (Si–O–Si stretching vibration)[32].

SEM analysis of nano-silica modified WPU

Figure 3 shows the SEM micrographs of the (a) pure-WPU and (b), (c) nano-modified WPU having 2.0 wt.% nano-SiO_2 loading. As can be seen in Figure 3(a), the cross-section of pure-WPU shows a relatively smooth, glassy surface and there are almost no cracks. Comparatively, in Figure 3(b), the WPU/SiO_2 nano-composites show much rougher fractured surfaces. It is well known that nanopartciles dispersion and adhesion with the polymer matrix are very important to improve the properties of nano-modified WPU[20]. Uniform distribution of nano-silica as fillers in the matrix played an important role in the mechanical properties and thermo-tolerant performance of the nano nano-SiO_2 modified WPU[27], which will be discussed in the following sections. In Figure 3(c), we cannot find obvious agglomeration of the nano-silica, which indicates the dispersion capability of nano-silica particle in WPU adhesive in this work is pretty good. It is believed that the nano-silica incorporation of nano-SiO2 groups into the polyurethane chains is kind of hybrid and graft copolymer[29], and this statement is proved or partly proved by the SEM image of the WPU as is shown in Figure 3(c).

Effect of nano-silica content on the appearance and storage stability of WPU

Table 2 shows the effect of nano-SiO_2 concentration on the appearance and storage stability of the WPU adhesive. With the increase of nano-silica content, the appearance of emulsion is gradually changed from micro-blue transparent to milky white with blue light. When the concentration of nano-SiO_2 is in the range of 2.0%-2.5%, the appearance and storage life of the

WPU reached the optimum. Furthermore, the results show that nano-silica content has a remarkable impact on the stability of the emulsion. When the nano-silica content increases to 3.0%, the storage life of the WPU is significantly shortened (less than 6 months). The reasons may be that, after the in-situ polymerization, nano-SiO_2 groups incorporate into the polyurethane chains uniformly, which conducive to the formation of a three-dimensional network structure of the polyurethane, at the same time, enhance the hydrophobic of the polyurethane chains[19]. Excess nano-SiO_2 may leads to destabilization of the emulsion. Therefore, with the increase of nano-silica, the storage life of WPU is shortened.

Effect of nano-silica content on the Bookfield viscosity and mean particle size of WPU

Figure 4 shows the Brookfield viscosities (25°C) and mean particle size (D_{50}) of the WPU emulsions with different nano-SiO_2 contents. As shown in the histogram, the viscosity of the WPU dispersion decreases with the increase of nano-silica content and the mean particle size increases with the increase of nano-silica. When the concentration of nano-SiO_2 increases from 0% to 3.0%, the viscosity decreases from 480 mPa·s to 40 mPa·s and the mean particle size of the WPU dispersion increases from 310 nm to 3,590 nm, respectively. In general, the smaller of the particle size is, the higher viscosity of the emulsion will be, and vice versa. Considering the dispersion state of the WPU, when the emulsion particles are relatively small, water-soluble macromolecules are not in the "spherical" crimped state, but in the free-elongation low-energy state. In this condition, the macromolecules are wound and cross-linked with each other, which leads to the significantly increasing of the emulsion viscosity[21]. On the other hand, when the particles are relatively large, particles in the water dispersion are under a relatively ordered arrangement, therefore, the apparent viscosity of the emulsion is relatively low. Thus, with the increase of nano-SiO_2 content, the particle diameter of the emulsion become larger and the viscosity of the WPU become lower.

Effect of nano-silica content on the adhesion properties of WPU

Figure 5 shows the adhesion properties of the waterborne adhesive. T-peel strength and shear strength of the adhesive show a decreasing trend after the prior increase. And this trend is similar to the research of Chen[20]. When the concentration of the nano-SiO_2 is 2.0%, the T-peel strength and the shear strength reach the maximum, i.e. 4692N/m and 45.7MPa, respectively. The reasons may be that, with the addition of the nano-silica, the rigidity of the polyurethane's hard segment and the cohesion of the polyurethane adhesive are increased. At the same time, the force between nano-silica and polyurethane is greatly enhanced due to the large specific surface area of nanoparticles. Furthermore, there are a large number of active hydroxyl groups on the surface of nano-SiO_2, together with the urethane groups on the surface of the polyurethane, which formed hydrogen bonds[22]. Therefore, the adhesion properties of the polyurethane adhesive are significantly improved when the concentration of nano-SiO_2 increases from 0% to 2.0%. However, when the nano-silica content further increase to 2.5-3.0%, the adhesion properties become worse. The main reasons may be that, the excess of nano-SiO_2 caused the settlement phenomenon, and thus reduced the adhesion of the adhesive coating.

Effect of nano-silica content on the water resistance and thermal stability of WPU

Figure 6 shows the water swelling and thermo-tolerant properties of the nano-SiO_2 modified adhesive. The water swelling value decreases with increasing the nano-silica concentration as shown in the graph. It means that the water resistance of the films increases with the addition of nano-SiO_2. This might be due to the presence of the hydrophobic Si–O–Si groups of the cross-link structure[11]. The network structure of nano-SiO_2 increases the density of the film, and mitigates water penetration[33]. This barrier effect significantly enhances the water resistance of the films. The water swelling decreases from 12.1% to 2.5% when the nano-silica content increases from 0% to 3.0%. And the results are similar to the previous studies[11, 20]. On the other hand, the thermo-tolerant property of the adhesive is enhanced with the increase of nano-SiO_2 content. The reason may be that, the incorporation of nano-SiO_2 groups into the polyurethane chains increases the resistance of the rearrangement of the molecular chains. Simultaneously, the surface silanol groups of nano-SiO_2 react with the NCO groups in the WPU chains, and the formation of stable chemical linkages between the nano-silica and the polyurethane improve the heat resistance of WPU[26]. When the nano-silica content increases from 0% to 3.0%, the thermo-tolerant temperature of the adhesive is increased from 81^{o}C to 183^{o}C, respectively.

Effect of nano-silica content on the mechanical properties of WPU films

The mechanical properties of the WPU films are evaluated by tensile test and the results are shown in Figure 7. As can be seen from the bar graph, the mechanical properties of the WPU films are greatly improved via added a small amount of nano-SiO_2. When the content of the nano-silica are approximately 1.5% to 2.0%, the elongation and tensile strength at break reach the optimum, viz. 890% and 21.3MPa, respectively. This might be due to cross-linking of nanoparticles in the polyurethane chain. Generally, the improvement of properties of nanocomposites as compared with parent polymers is associated with certain structural changed in a polymer matrix due to the small size and unique structure of nanoparticles[24]. When the content of nano-silica is over 2.0%, the mechanical properties decrease sharply. The reason may be that, when the nano-SiO_2 content is too high, not all of the nanoparticles could be polymerized into the main chain of the polyurethane, but agglomerated[22-23, 37]. As a result, the mechanical properties decrease. Furthermore, this may also caused storage stability and adhesive properties deteriorated.

CONCLUSIONS

In this study, using nano-SiO_2, IPDI, PBA, DMPA, BDO, TEA, and EDA as main raw materials, a series of nano-silica modified waterborne polyurethane adhesives were successfully obtained via in-situ polymerization. The incorporation of nano-SiO_2 groups into the polyurethane chains was confirmed by means of Fourier Transform Infrared Spectroscopy (FTIR). The viscosity, adhesion properties of the aqueous based polyurethane adhesive, mechanical performances and water resistance of the casted films were also investigated. The results showed that the concentration of nano-SiO_2 had significant impact on these properties.

The synthesized aqueous based polyurethane adhesive possessed good storage stability (over 9 months). The results of SAFT test showed that the thermo-tolerant temperature of the nano-SiO_2 modified adhesive was greatly improved compared with unmodified pure-WPU adhesive. The result of VOC test illustrated that the adhesive featured a remarkably low VOC content. The risk of VOCs to the human health and the environment was significantly reduced compared with conventional solvent-based adhesives. In this respect, the waterborne polyurethane adhesive that prepared in this research can be defined as healthy and environmentally friendly material.

And in the following research, a detailed characterization of this nano-modified WPU adhesive will be conducted by using NMR, TEM, AFM, XRD, TG, DTA, DSC, DMA, etc.

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Table 1. Physical properties of the nano-silica modified WPU adhesive

Parameter	Remarks
M_n	55,000±1,500g·mol^{-1}
pH	7.0±0.5
Particle size/D_{50}	800±50nm
Viscosity(25^{o}C)	150±20mPa·s
Solid content	51±1%
VOC content	0.4±0.1%
Storage stability	>9months
Appearance	Milky white with blue light uniform liquid

Table 2. The effect of nano-silica concentration on appearance and storage stability of WPU

Sample	Nano-SiO_2/%	Appearance	Storage life
WPU 0	0	Micro-blue transparent	>9months
WPU 1	1.0	Pale blue semi-transparent	>9months
WPU 2	1.5	Pale blue semi-transparent	>9months
WPU 3	2.0	Milky white with blue light	>9months
WPU 4	2.5	Milky white with blue light	>9months
WPU 5	3.0	Milky white with blue light	<6months

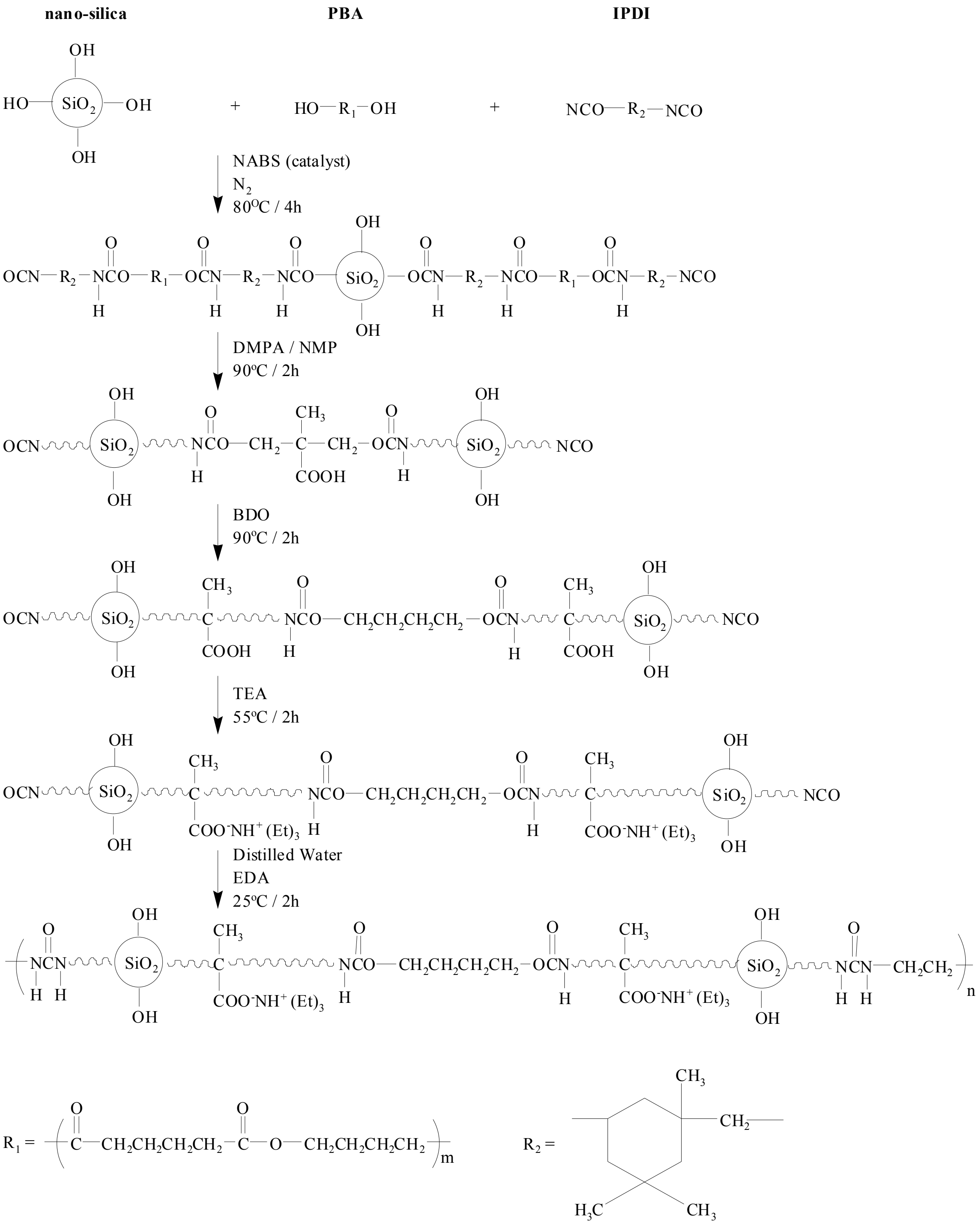


Figure 1. Synthetic scheme of nano-silica modified environmental friendly waterborne polyurethane adhesive

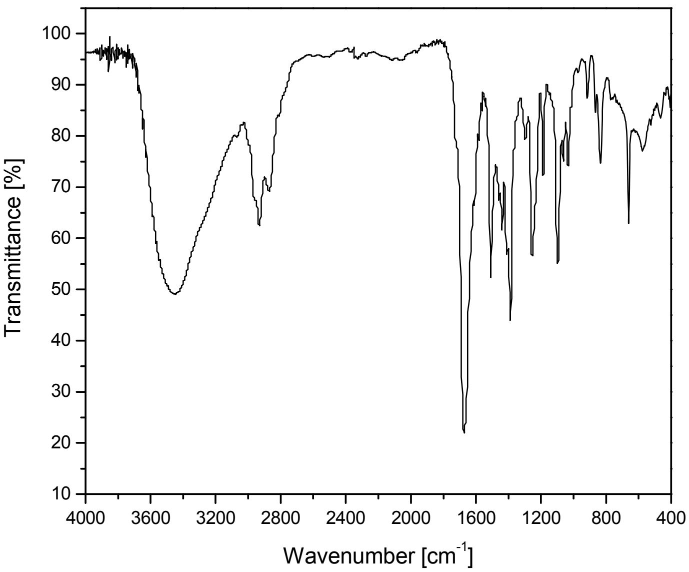
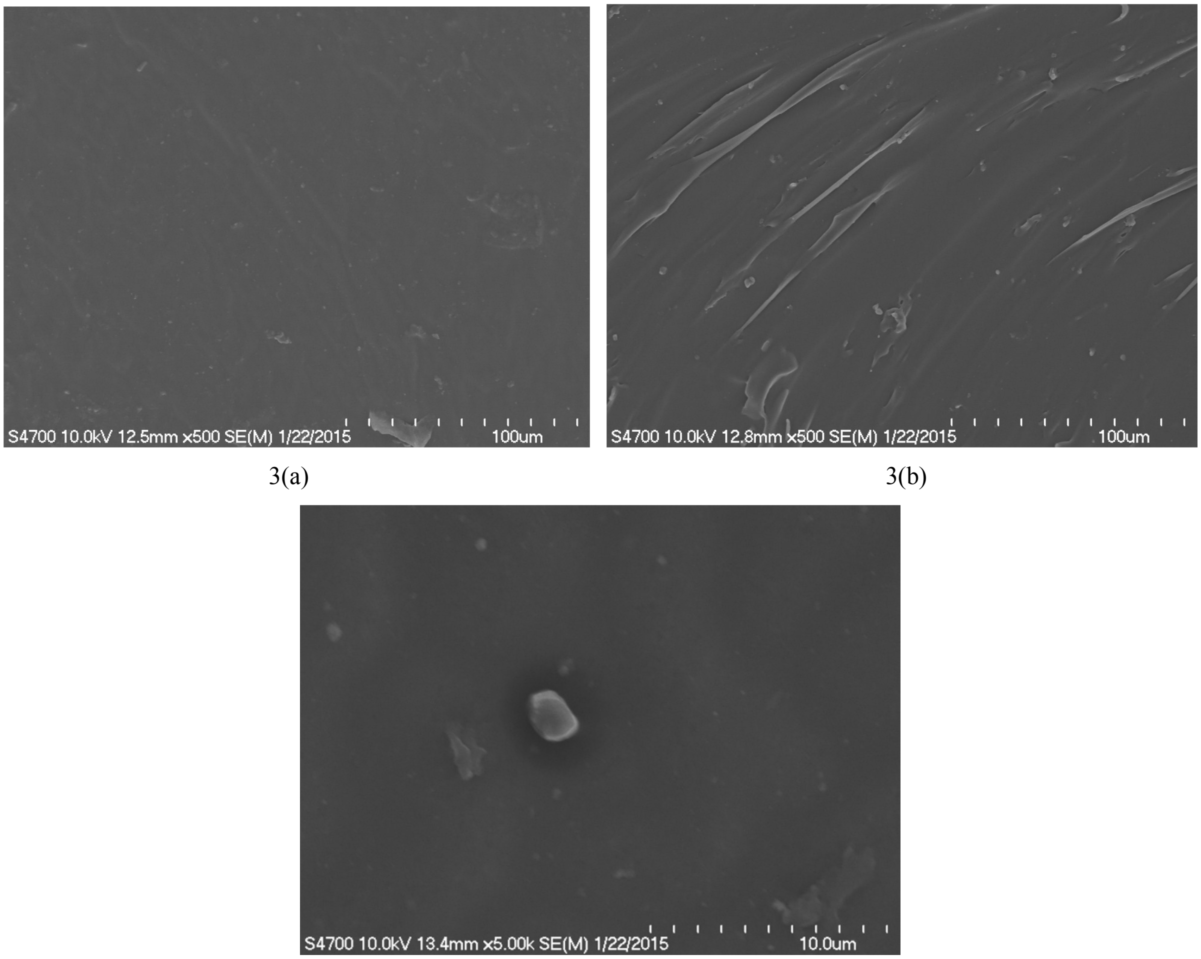


Figure 2. FTIR spectra of the synthesized nano-modified WPU (2.0 wt.% nano-silica)



3(a)

3(b)

3(c)

Figure 3. SEM images of (a) pure-WPU and (b), (c) nano-modified WPU (2.0 wt.% nano-silica)

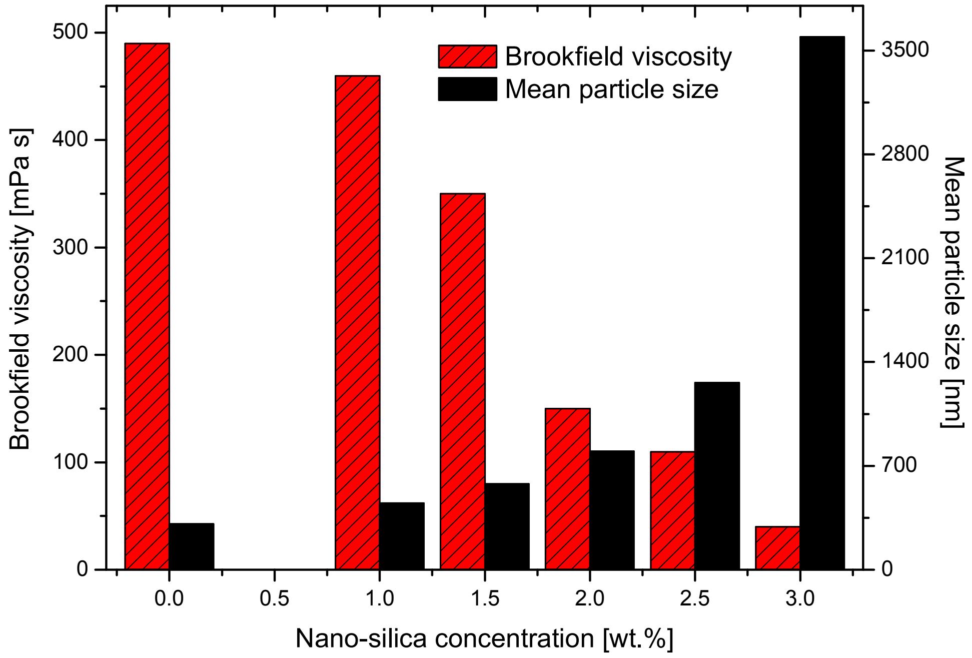


Figure 4. The effect of nano-silica concentration on Brookfield viscosity (25°C) and mean particle size (D_{50})

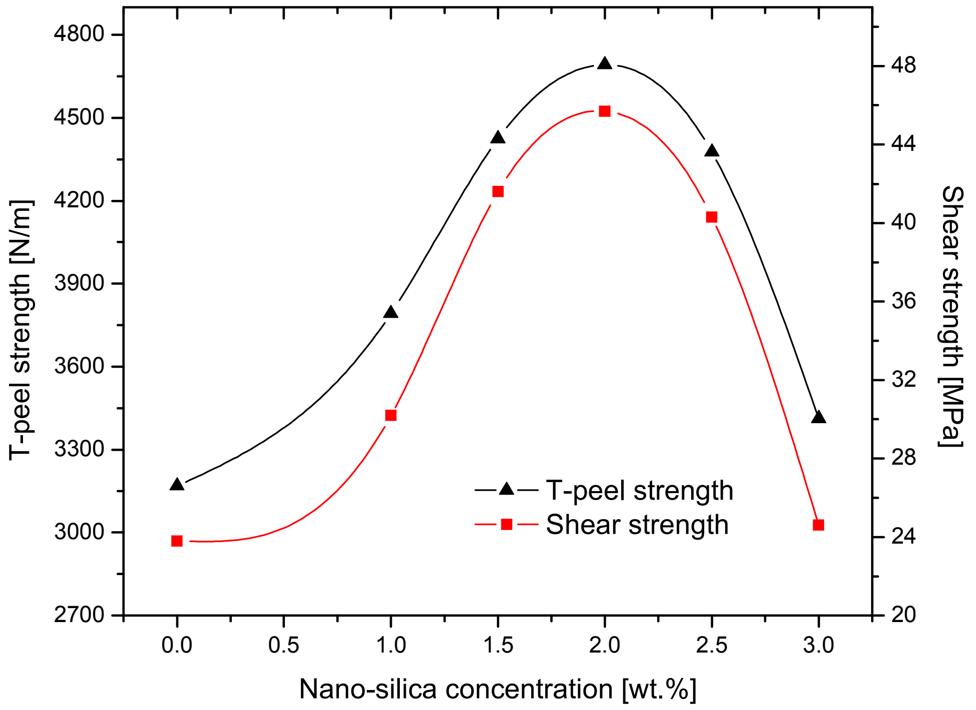


Figure 5. The effect of nano-silica concentration on adhesion properties

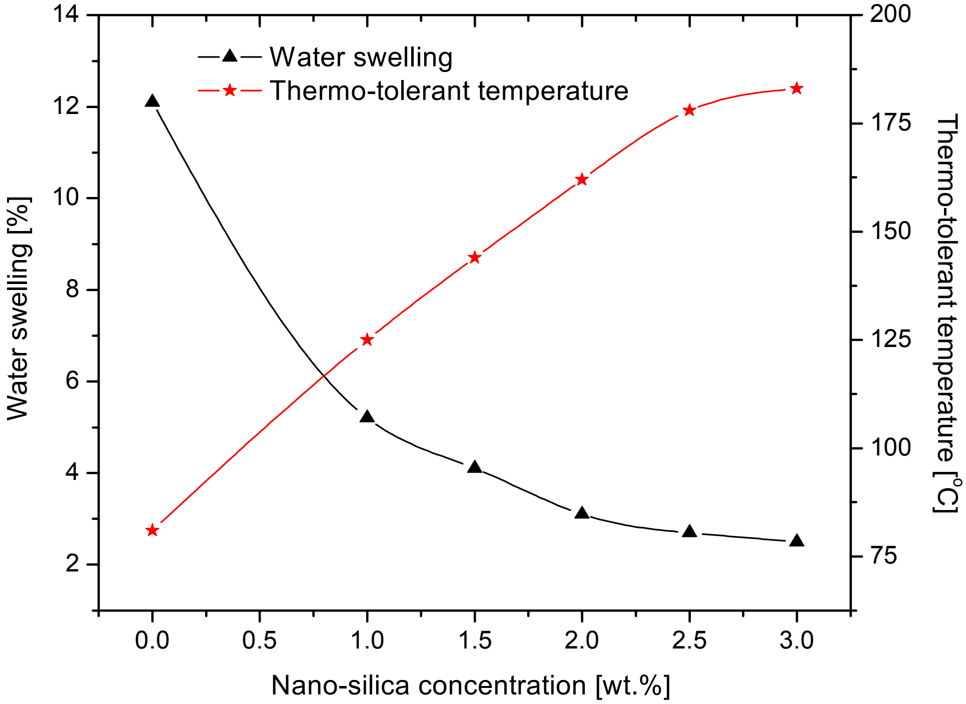


Figure 6. The effect of nano-silica concentration on water resistance and thermo-tolerant properties

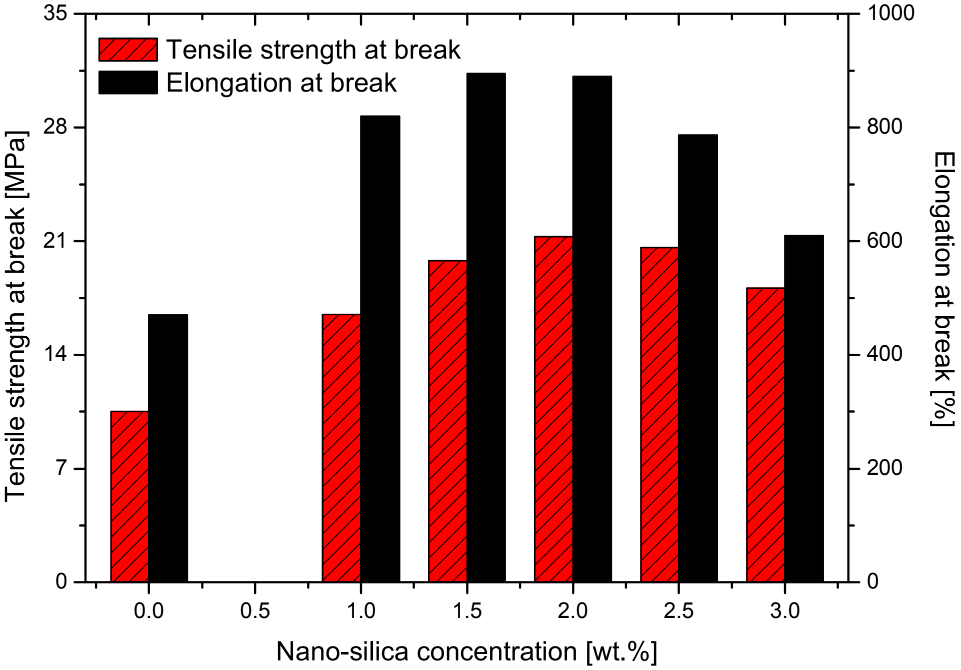


Figure 7. The effect of nano-silica concentration on mechanical properties of WPU films