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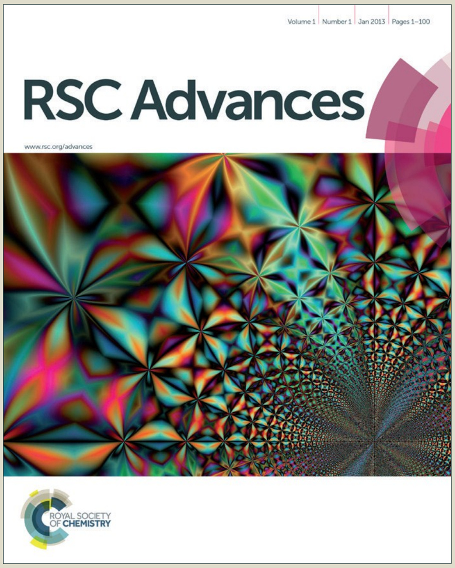

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Enhancement of water and organic solvent resistances of waterborne polyurethane film by incorporating liquid polysulfide

Yuliang Zhang, Leishan Shao, Dongyu Dong and Yinghan Wang*

State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, PR China. Email: wang_yh@scu.edu.cn; Tel: +86-028-85460823; Fax: +86-028-85460823.

Abstract: The environmentally friendly waterborne polysulfide-based polyurethane (WSPU) films have been successfully synthesized from liquid polysulfide (PSF), polytetramethylene ether glycol (PTMG), isophorone diisocyanate (IPDI) and dimethylolpropionic acid (DMPA). The chemical structures, mechanical and thermal properties of the chemical modified films have been carefully investigated by ATR-IR, gel permeation chromatography (GPC), tensile tests, dynamic mechanical analysis (DMA) and thermogravimetric analyzer (TGA). As the PSF content from 0 to 20%, after an immersion in deionized water for 96 h, the water absorption decreases from 6.2% to 3.4% and the tensile strength retention increases from 74.3% to 91.7%. The chemical resistance to organic solvent is also improved significantly. The enhanced water and organic solvent resistances of waterborne polyurethanes (WPUs) are primarily attributed the addition of PSF containing sulfur group. However, the tensile strength and thermal performance are weakened to some extent. This study produces new composite derived from polysulfide, and its high water and solvent resistance performance could contribute to the surface material areas.

Key Words: waterborne polyurethane; liquid polysulfide; composite; water resistance; solvent resistance

1. Introduction

Due to the enhancement of environmental concerns during the past few decades, aqueous polyurethane dispersions (PUDs) have attracted a lot of attention for its zero/low amount of volatile organic compounds (VOCs).[1-4] The waterborne polyurethanes (WPUs) have many excellent properties, such as adhesion, flexibility, gloss, and weatherability.[5-7] Therefore, WPUs have been one of the most rapidly growing field of polyurethane chemistry, which are widely used as adhesives, coatings and printing inks.[8,9] However, the WPUs have an inherent disadvantage of poor water resistance that limited their application, which could attribute to the insertion of hydrophilic ionic group in the structure and exhibit high hydrophilic properties compared to the solvent polyurethane.[10] A faster hydrolysis of the ester linkages would occur in the aquatic environment, resulting in a decrease on molecular weight and deterioration of physical and mechanical properties.[11] Besides, the WPU films generally have a lower average molecular weight, also exhibiting poor organic solvent resistance.[12] Therefore, improvement on these properties of WPU films has been a continuing subject and a lot of modifications have been studied.

Randhir Parmar *et al.*[13] reported the polyurethane dispersions modified with epoxy-acrylic graft copolymer (EAGD). In this study, the hot-water and salt-water resistance of the modified polyurethane dispersions was improved to some extent compared to unmodified samples. Bai *et al.*[14] introduced polysiloxane groups with low surface energy into the segment of UV cross-linkable WPU. Their water resistance and mechanical property were improved and the contact angle reached 97.80^{o}. Kim *et al.*[15] reported that fluorinated polyurethane was blended with base PU prior to dispersion in water to modify the surface of UV cured WPU. Atomic force microscopy (AFM) showed that the surface was roughened with the addition of fluorinated PU. After the addition of 9 wt% fluorinated PU, the contact angle reached 92.6^{o} and the mechanical properties were marginally altered. According to those other researches, it could be found that chemical modification by certain compound with good hydrophobic nature or water barrier property would be an effect approach to solve the poor water resistance. Consequently, the liquid polysulfide polymers with excellent resistance against solvents and chemicals will be one of the most suitable candidates.

Polysulfide polymers with low-molecular-weight have been produced since 1940. These liquid polysulfide oligomers bearing thiol end groups are synthesized by the aqueous polymerization of short chain dichloro hydrocarbons with sodium polysulfide.[16] Due to series of advantages, such as low cost, high resistance against UV radiation and environment, good low-temperature property, low water-vapor transmission, and resisted against solvents and chemicals, they have been widely applied in industries.[17]

Because of the presence of thiol end-groups, the liquid polysulfide could react with diisocyanates[18] and considerable studies have been carried out regarding the synthesis of polysulfide-based polyurethane.[19] However, to our best knowledge, the introduction of polysulfide containing S-S bonds into the waterborne PU polymer segment to improve the water and solvent resistance properties has not been so far explored. Therefore, in this research, the waterborne PU emulsions modified with different content of liquid polysulfide are prepared and characterized. The water-based polysulfide modified polyurethane (WSPU) films are synthesized and the water resistance, organic solvent resistance as well as the thermal and mechanical properties are investigated.

2. Experimental

2.1 Materials

Isophorone diisocyanate (IPDI, 98wt% purity) (mixture of cis/trans isomers) was purchased from Aladdin Reagents Co., LTD. Liquid polysulfide (PSF, $M_w \approx 1000$, SH content was 6.6%) was obtained from Changsha Chemical Research Institute and was dewatered under vacuum at 100 °C for 3 h before use. Polytetramethylene ether glycol (PTMG, M_w=1000, Xinyutian Chemical Co., Ltd) and 2,2-Dimethylol propionic acid (DMPA, Aladdin Reagents Co., LTD) were dried at 120 °C for 2 h in a vacuum oven. 1,4-butanediol (BDO) was purchased from Tianjin guangfu fine chemical research institute. Triethylamine (TEA) and acetone (dried over 4 Å molecular sieves) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. The other reagents were used as received without further purification.

2.2 Synthesis of the waterborne polysulfide-based polyurethane emulsions

Scheme 1 represents the method and conditions of synthesis of WSPU emulsions. Take the WSPU10 as an example, the PSF (6 g), PTMG (54 g), IPDI (40 g) and 0.05% of DBTDL (based on total solids) as catalyst were charged to a four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. The flask was heated at 80 °C under nitrogen atmosphere for 2-3 h.[20] The reaction proceeded until the amount of residual isocyanate(-NCO) groups reached a theoretical end point by standard N-dibutylamine back titration method. Upon reaching the theoretical -NCO value, the calculated amount of hydrophilic monomers (DMPA) (5.5 g) dissolved in NMP was added and maintained at 80 °C until the proper -NCO value was obtained. Then the obtained prepolymer was further carried out with an addition of stoichiometric BDO (2.88 g) as chain extenders at 72 °C for another 2h, and the WSPU with desired molecular weight was achieved. A certain amount of acetone was added to reduce the viscosity and prevent gelation during the cooling process. After cooling the reaction mixture to 40 °C, the obtained polymers were neutralized by TEA and stirred for about 20 min. The resultant polyurethane ionomer was then dispersed in deionized water under high speed stirring. The obtained dispersion was transferred to a rotary evaporator to remove the acetone and then the final WSPU emulsions with about 30 wt% of solid content were formed. Besides, for a better comparison of the performance between the WSPU and unmodified samples, the neat WPU was also synthesized under the same reaction condition. In this paper, the weight ratio of the PSF/PTMG was set from 0/100 to 30/70 and samples were denoted as WPU, WSPU10, WSPU20 and WSPU30 respectively.

2.3 Fabrication of waterborne polysulfide based-PU films

The WSPU films were prepared by pouring the dispersion into a teflon disc and dried under ambient conditions for 48 h. The films were then peeling off from the teflon disc and dried at 60 ^{o}C for 24 h under vacuum-drying oven to completely remove the moisture and unreacted monomer. The vacuum dried films (typical thickness: ~0.27-0.30 mm) were stored in a vacuum desiccator.

2.4 Characterization

2.41 Attenuated total reflection infrared spectroscopy (*ATR-IR*)

The chemical components of the WSPU film samples were confirmed by ATR-IR (NICOLET 560, Thermo scientific, USA). The ATR-IR spectra of the samples were recorded in the range of 4000-700 cm^{-1} using ATR apparatus at a resolution of 4 cm^{-1} and 32 scans.

2.42 Gel permeation chromatography (*GPC*)

Molecular weight was measured with GPC on an Agilent 1100 column using tetrahydrofuran as the eluent and polystyrene standards as the calibration.

2.43 Dynamic mechanical analysis (*DMA*)

The dynamic mechanical properties of WSPU film samples were examined by DMA (DMAQ800, TA Instrument, USA) under a nitrogen atmosphere, at a frequency of 1 Hz and a heating rate of 3 ^{o}C min^{-1} over a temperature range, -80 to 150 ^{o}C.

2.44 Scanning electron microscope (*SEM*)

In order to identify the extent of phase separation in the composites, the morphology observations were conducted using a SEM under an acceleration voltage of 5 kV (SEM, JSM-7500F).

2.45 Thermogravimetric analyzer (*TGA*)

Thermogravimetric analyzer (TGA, Q500, TA Instruments, USA) was used to measure the weight loss of the films. The samples were scanned from 40 to 600 ^{o}C at a heating rate of 10 ^{o}C min^{-1} under N_2 atmosphere (100 mL/min).

2.46 Mechanical properties measurement

The tensile properties were measured at room temperature using a 4302 material testing machine from Instron Co. (USA). A cross-head speed of 50 mm/min was used to determine the ultimate tensile strength at ambient temperature.

2.47 Water resistance properties

The water resistance was evaluated by the measurement of water absorption of different films, which were dried completely and then immersed in water for 24 h, 48 h, 72 h and 96 h at 25^{o}C respectively. The water absorption of the different film samples was calculated with the following equation:

$$\text{Swelling (\%)} = \frac{w1-w0}{w0} \times 100 \qquad (1)$$

where $w0$ was the weight of the dried film and $w1$ was the weight of the film at equilibrium swelling.

2.48 Solvent resistance properties

The solvent resistance test was carried out with three kinds of organic solvents, including toluene, acetone and ethanol. The test consists in dipping certain size dried films (20×20 mm) into the solvents for 24h. The change in the surface appearance was monitored and the swelling of the different films was also obtained with equation (1).

3. Results and discussion

3.1. Characterization by ATR-IR and GPC

The ATR-IR spectra of the PSF, WPU and WSPU films were shown in Fig. 1. The most characteristic IR bands corresponded to the stretching vibration of -N-H in the urethane segments (-NHCOO) at 3330 cm^{-1}; The peak between 2800 and 3000 cm^{-1} was due to the -CH stretching vibrations; The band at 2555 cm^{-1} corresponded to the sulfhydryl (-SH) groups of PSF (Fig. 1(a)), and the same band disappeared in the spectra of WSPU10 (Fig. 1(c)) and WSPU30 (Fig. 1(d)) films, indicating the reaction of the sulfhydryl (-SH) groups of PSF with isocyanate (-NCO) groups of IPDI; The peak at 1691 cm^{-1} corresponded to the -C=O stretching vibrations;[21] -C-N stretching and δ N-H stretching at 1532 cm^{-1};[22] The band at 1155 cm^{-1} (Fig. 1(b)) had been assigned to -C-O-C stretching of the PTMG, while a lower intensity appeared in the spectra of WSPU10 (Fig. 1(c)) and WSPU30 (Fig. 1(d)), illustrating fewer component of PTMG in polyurethane chain segment. The peak at 956 cm^{-1}, 1026 cm^{-1}, and 1072 cm^{-1} corresponded to -C-O- stretching vibration of PSF (Fig. 1(a)); The higher intensity in the spectra of WSPU10 (Fig. 1(c)) and WSPU30 (Fig. 1(d)) further confirmed the existence of more PSF in the polymer. To get further information regarding the extent of PSF segment present in the polymer, molecular weight of different WSPU films was measurement by GPC. The detailed GPC data was summarized in Table 1. The molecular weight distribution could be defined by the polydisperse index (PDI = M_w/M_n). According to the results, the M_n and M_w of the waterborne PU films decreased to some degree with more content of PTMG replaced by PSF. This result might be due to a relatively low reactivity of -SH groups with -NCO compared to -OH, resulting in an inadequate reaction of PSF and the polymerization reaction might not have proceeded to completion as expected. On the other hand, the similar molecular weight indicated that most of PSF was chemically bonded to the PU polymer chain and the designed WSPU films were obtained.

3.2 DMA analysis of WPU and WSPU films

To investigate the influence of PSF on physico-mechanical properties of WPU, the DMA measurement was examined. The storage modulus (E') and dissipation factors (tan δ) curves as a function of temperature for the neat WPU and the PSF modified films was shown in Fig. 2(a) and (b), and the glass transition temperature was summarized in Table 1. The storage modulus vs. temperature curves of the WPU and WSPU films was presented in Fig. 2(a). It could be recognized that all the modified films presented high E' with the introduction of PSF. Specially, E' of WSPU films increased with increasing the PSF content and a sharp decrease at about 50 °C was noted, associated with the glass transition. Also, inconspicuous dissipation of E' after 100 °C could be seen in the case of the pristine WPU, which might be associated to the hard domains transition (Fig.

2(b)).[23]

As was presented in Fig. 2(b), the broad peak of tan δ could be accounted for intermixing by part of hard segment on the soft-segment phase. T_g of the neat WPU and modified samples slightly shifted to the higher temperature from 45.34 to 52.06 °C with an increase of PSF content. The phenomenon can be connected to the incorporation of PSF that reduced the content of soft PTMG segments and provided slight cross-linking in the system. Generally, PSF polymer always contained difunctional or trifunctional segment and slight branched structure, which might result some slight cross-linking structure into the polymer.[24] Moreover, as shown in Table 1, the decrease of molecular weight caused a relatively higher content of the hard segment, also resulting a slightly increase in the glass transition temperature. Otherwise, a conspicuous peak around 110 °C could be observed in the case of the pure WPU, which might be associated to the hard domains transition. However, the peak disappeared with increasing the PSF content at the same location. It might be due to a further phase separation caused by the incorporation of the PSF, which led to a decrease of the compatibility between the soft segments and hard segments. A further proof was evidenced in the SEM imagine. As a result, the temperature of the hard domains transition shifts to a higher one.

3.3 Morphologies and phase structure of WPU and WSPU films

SEM micrographs taken from fracture surfaces of WPU, WSPU20 and WSPU30 were shown in Fig. 3. It was seen that neat WPU film exhibited relatively smooth fracture surfaces, as shown in Fig. 3(a) and (a′). However, the fracture surfaces of WSPU composites were different compared with that of neat WPU, as shown in Fig. 3(b) and (b′) as well as Fig. 3(c) and Fig. 3(c′). With the addition of PSF content, the fracture surface of WSPU20 and WSPU30 became relatively rough and exhibited slight phase separation, which might attribute to the thermodynamic incompatibility of PSF and PU segment. Specially, compared to the WSPU30, WSPU20 showed much lower phase separation. The presence of amorphous PSF segment might weak hydrogen bonding interactions between the soft segment of PTMG and hard segment. These results suggested a weak interfacial interaction between the soft and hard segment and might cause a lower mechanical properties.

3.4 Water resistance and Tensile properties

The water absorption of the WPU and WSPU films was shown in Fig. 4. The data showed that WSPU films exhibited an obvious decrease in the water absorption compared with the neat WPU from 24 h to 96 h (Table 2(a)). As the PSF content increased from 0 to 30%, the water absorption decreased first and then increased. Specially, when the content was 20%, the film showed a lowest value of 3.4% (96 h), with a decrease of 45.2% compared to the pure WPU, which was 6.3%. This result attributed to the introduction of S-S bonds in the main chain, which decreased the water-vapor transmission.[17] With the addition of PSF in PU chain, excellent osmotolerant properties were provided into the film, caused a difficult diffusion for water into interior. Therefore, a visible descent on the water absorption was observed. However, when the content of PSF was over 20%, a poor water resistance appeared.

This might result from a worse compatibility between PSF phase and polyurethane, as mentioned above. The further phase separation might result in worse anti-permeability of the film. Consequently, the water absorption increased again.

For a further observation about the influence of PSF on the water resistance of WPU, the effect of PSF content on mechanical properties of the WSPU films under different soaking time was studied. As shown in Fig. 5, the tensile strength of neat WPU decreased from 26.5 MPa to 19.7 MPa after immersing for 96h, with a final retention of 74.3%. Meanwhile, the modified films only had a slight decline. Specially, when the content of PSF was 20%, the tensile strength retention reached 91.7%, showing excellent water resistance. The detailed performance was also presented in Table 3(a) and (b). The enhanced tensile strength retention can attribute to the limited hydrolysis of urethane bond. The added PSF chain hindered the penetration of moisture, and delayed the process of decomposition reaction. The specific stress-strain curves of different films without immersed and immersed for 96 h were shown in Fig. 6, and an obvious change of neat WPU in tensile strength and elongation at break was found. In addition, it was also noted that the tensile strength decreased with increasing PSF content (Fig. 6(a)), as well as the elongation at break. The mechanical behavior should attribute to the worse mechanical properties of liquid PSF, which had been reported by others.[25,26] A subsequent modification based on the system was also needed in the future work.

3.4 Solvent resistance properties

The solvent resistance property of the different WPU films was shown in Fig. 7 and Table 2(b). The data showed that all the modified samples exhibited much lower solvent swelling compared to the pristine WPU film. Moreover, the appearance of different films before and after immersion in the solvent was shown in Fig. 8. An obvious change occurred in the neat WPU film, with a curling deformation and tacky surface. Simultaneously, the modified samples were almost unaffected. These comparisons performed significant improvement of WPU films on the resistance to solvent. Besides, with the increase of PSF content, the swelling tended to a further drop. These results could attribute to the presence of sulfur components in their backbone.[26]

3.5 TGA analysis of different WSPU films

The thermal behavior of PSF, the neat WPU as well as the modified samples was studied by TGA. Fig. 9(a) showed the TGA curves of PSF, neat WPU and WSPU films with different content of PSF, and the TGA data such as 5 wt% loss temperature (T_5), 10 wt% loss temperature (T_{10}), and 50 wt% loss temperature (T_{50}) was listed in Table 4. The TGA curve of PSF had one-weight loss stage, while WPU had two-weight loss stages and WSPU samples showed three distinct weight loss stages. The TGA data, as reported in Table 4, suggested that the thermal stability of the modified films was lower than that of neat WPU and decreased with increasing the content of PSF. The weakening performance could attribute to the relatively poor thermal stability of liquid PSF with low molecular weight, as shown in Fig. 9(a).[26] These results indicated that the introduction of PSF resulted in deterioration on the thermal stability and it would be solved in our future work.

For WSPU films, the derivative thermogram (DTG) curves clearly indicated a three-step degradation profile with an initial decomposition temperature around 210 ^{o}C (Fig. 9(b)). The smaller weight loss temperature around 140 ^{o}C might be due to the evaporation of absorbed moisture in the dispersion films. For an instant, the first-weight loss stage, in the temperature range of 210-290 ^{o}C, was attributed to dissociation of PSF component in polymer chain segment. The second weight loss stage, in the temperature range of 290-350 ^{o}C, was due to the dissociation of ether bond, alkyl chain in PTMG and PSF. The last degradation step above 350 ^{o}C corresponded to the decomposition of the urethane bonds to form isocyanates, alcohols, primary and secondary amines, olefins and loss of carbon dioxide from the urethane bond. [27]

4. CONCLUSION

Series of novel WSPU composites were successfully synthesized. It had been observed that the polysulfide chains were chemically bonded to the PU polymer, which was evidenced by the ATR-IR and GPC measurement. The water and solvent resistance as well as the tensile properties of WPU and WSPU films were characterized. When the PSF content was 20%, the resulting films exhibited significant lower water absorption from 6.2% to 3.4% compared to the pristine WPU samples, with a drop of 45.2%. The tensile strength retention ranged from 74.3% to 91.7% after soaking in deionized water of 96h. When the PSF content was 30%, the lowest solvent swelling was obtained. The above results indicated that the incorporation of PSF leaded to an excellent water and solvent stability of the waterborne PU films. DMA analysis suggested a higher T_g and incompatibility between PSF, PTMG and hard segment with the addition of PSF.On the other hand, the TGA and tensile test results showed a deterioration of the heat resistance and mechanical properties with the addition of PSF and this will be further improved in our coming research.

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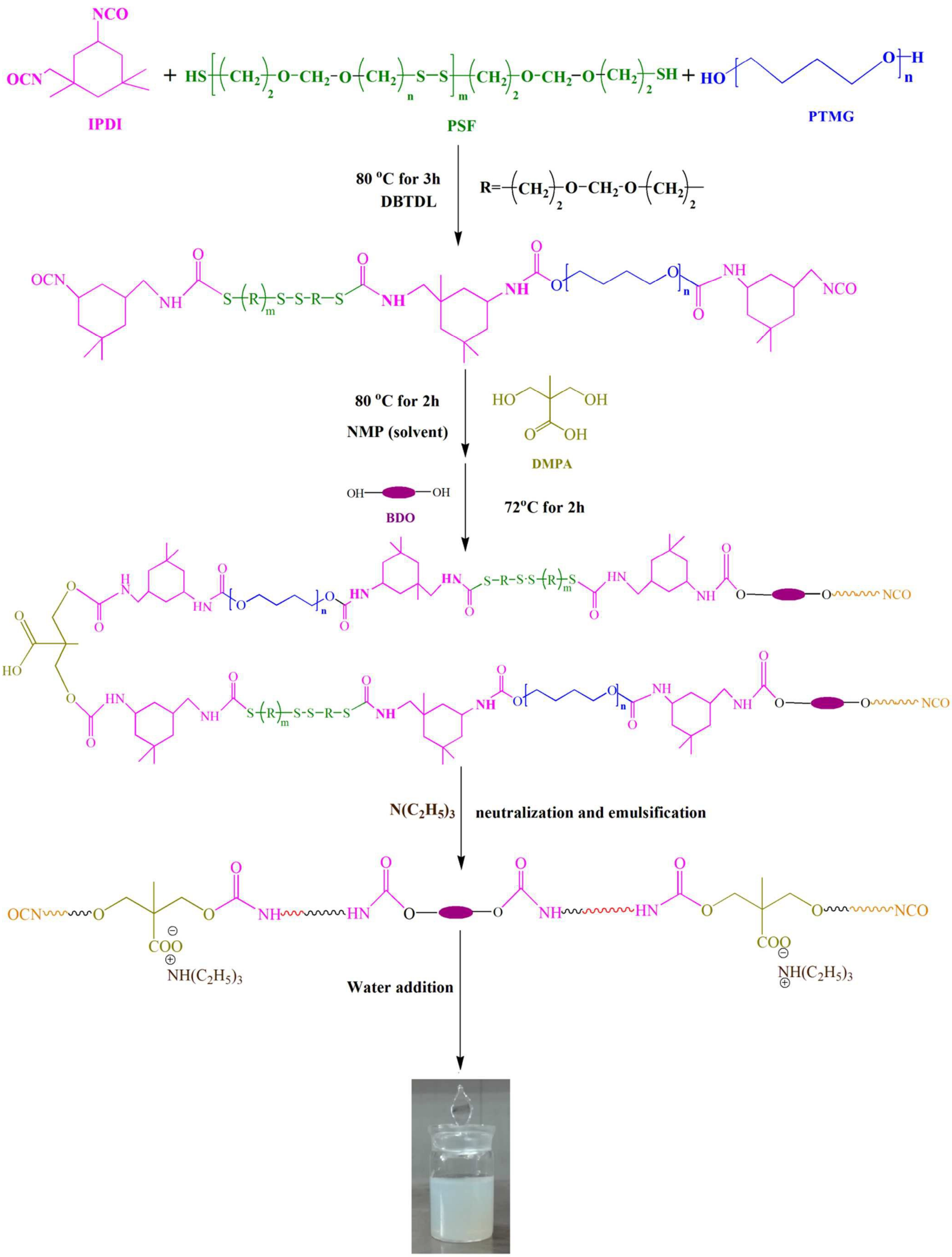


Scheme 1 Synthesis of Polysulfide-based WPU emulsfications.

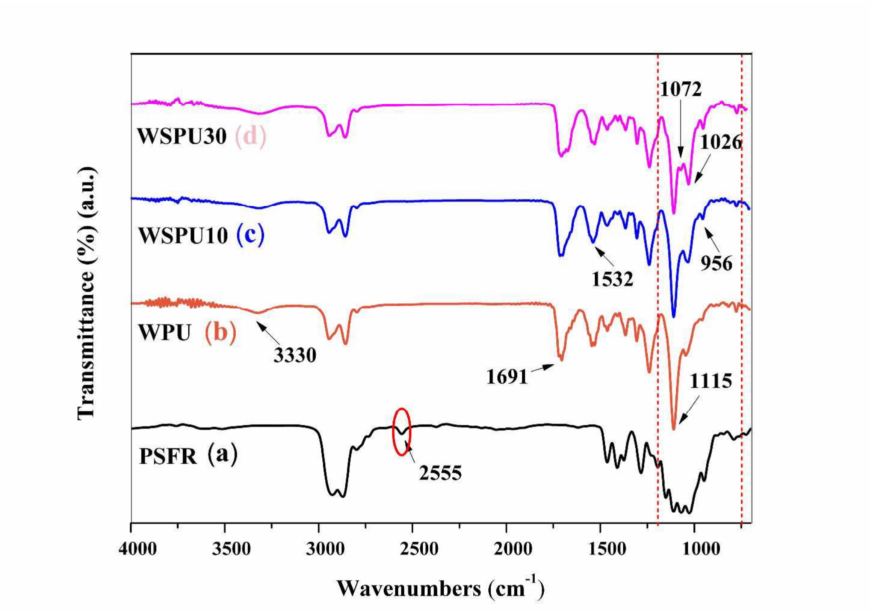


Fig. 1 ATR-IR spectra of PSF, WPU, WSPU10 and WSPU30 films

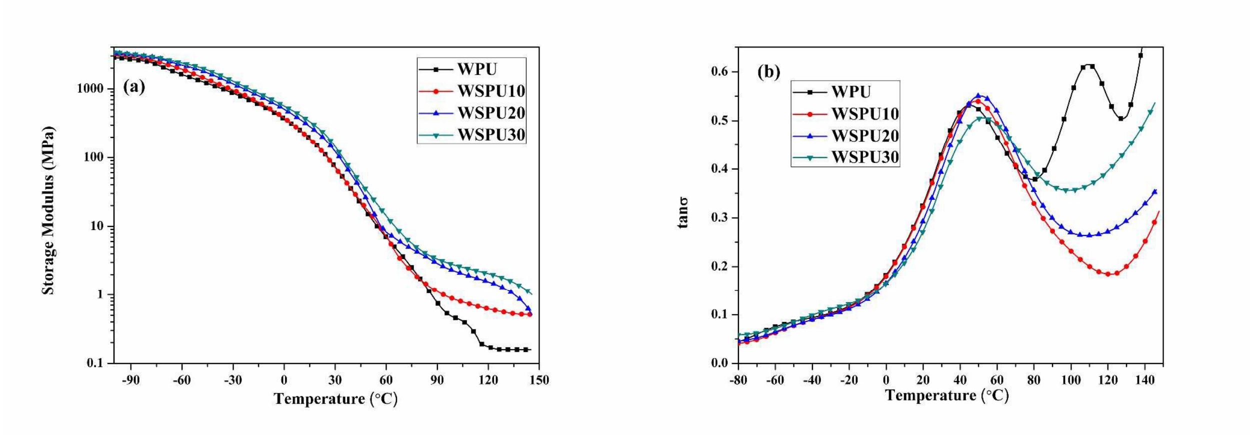
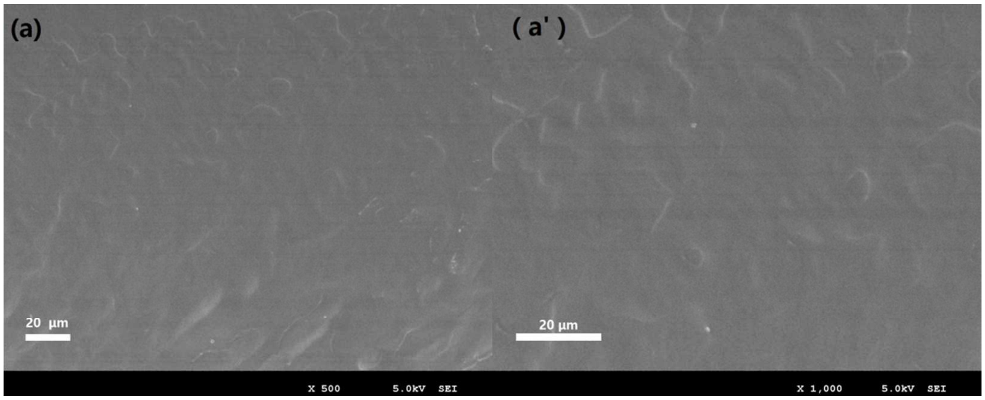


Fig. 2 The storage modulus (E') and loss factor (tan δ) as a function of temperature for WPU and different WSPU films



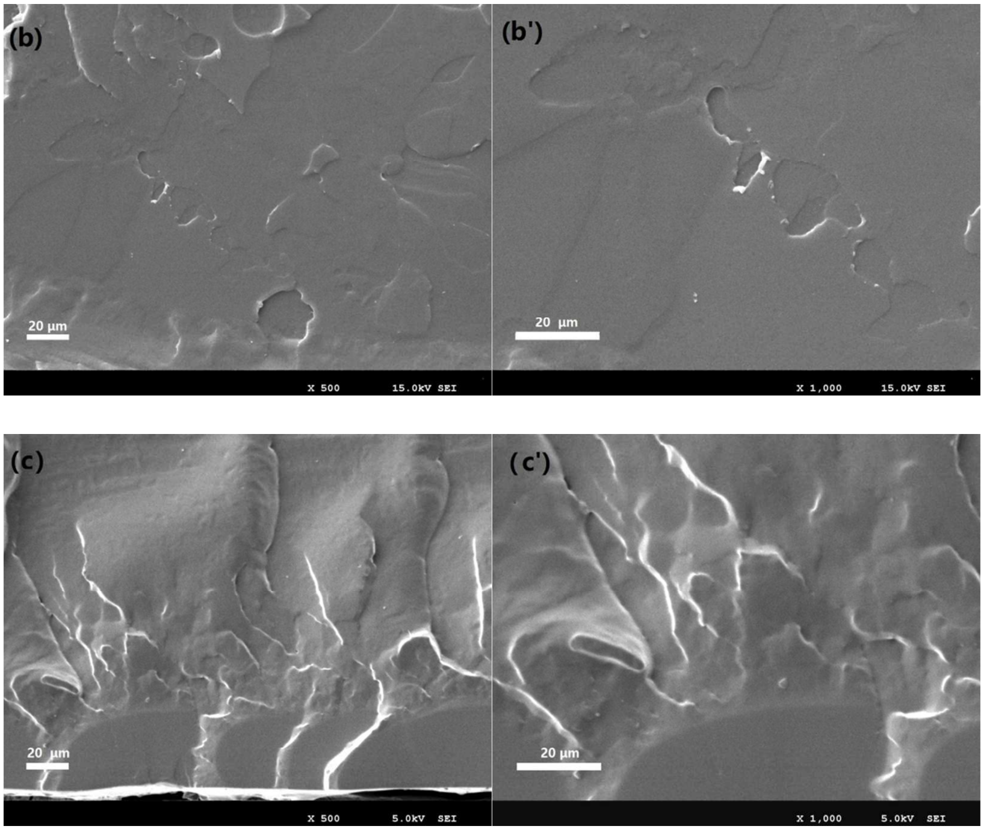


Fig. 3 SEM micrographs of fractured surfaces of WPU (a and a′), WPSU20 (b and b′) and WSPU30(c and c′) films

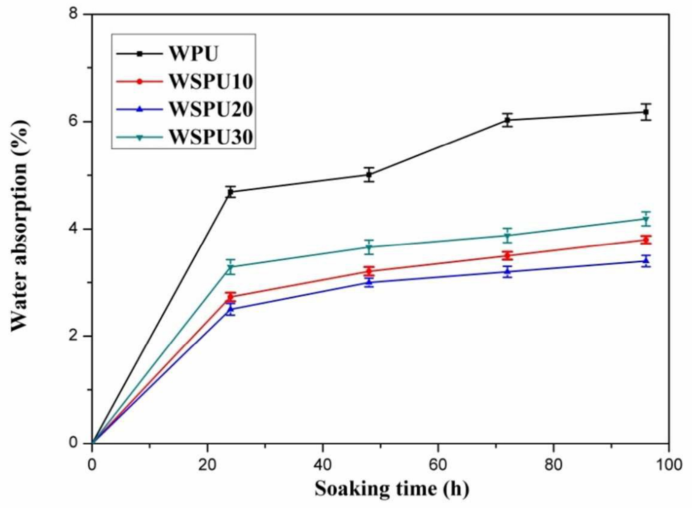


Fig. 4 Water absorption of WPU and WSPU films with different soaking time in deionized water

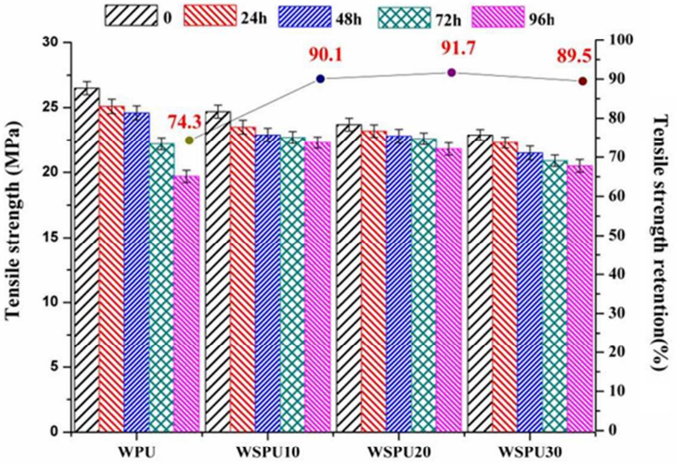


Fig.5 Tensile strength of WPU and WSPU films with different soaking time and the tensile strength retention after 96h

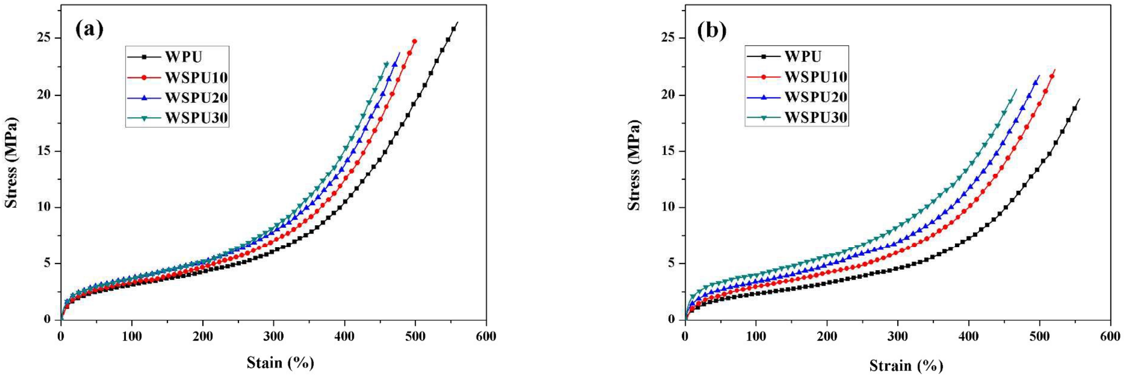


Fig.6 Stress–strain curves for WPU and WSPU films with different soaking time in deionized water. a) No soaking, b) 96 h.

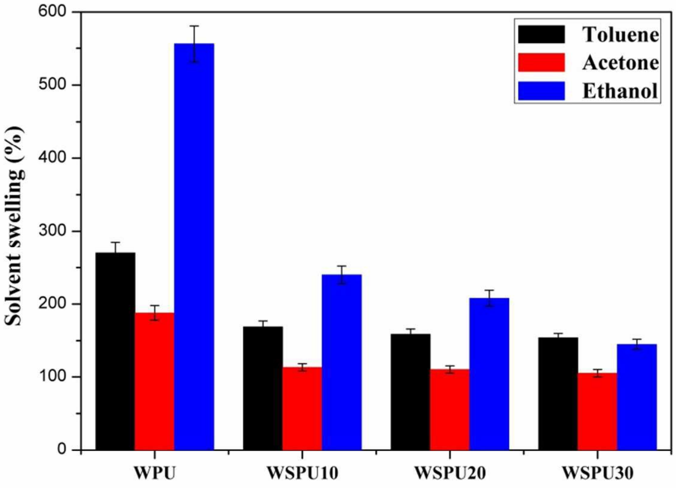


Fig. 7 The solvent swelling of WPU and WSPU films in toluene, acetone and ethanol respectively

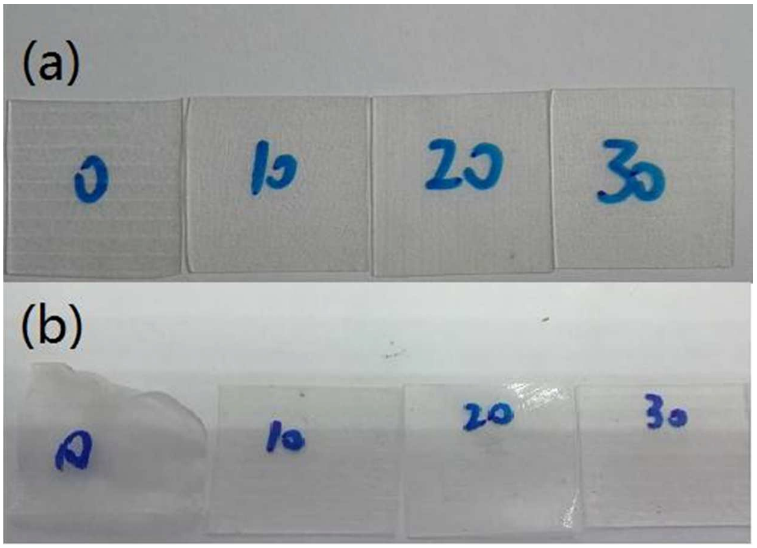


Fig. 8 Surface appearance of WPU and WSPU films before (a) and after (b) immersed for 24h in toluene solvent. 0) WPU, 10) WSPU10, 20) WSPU20, 30) WSPU30

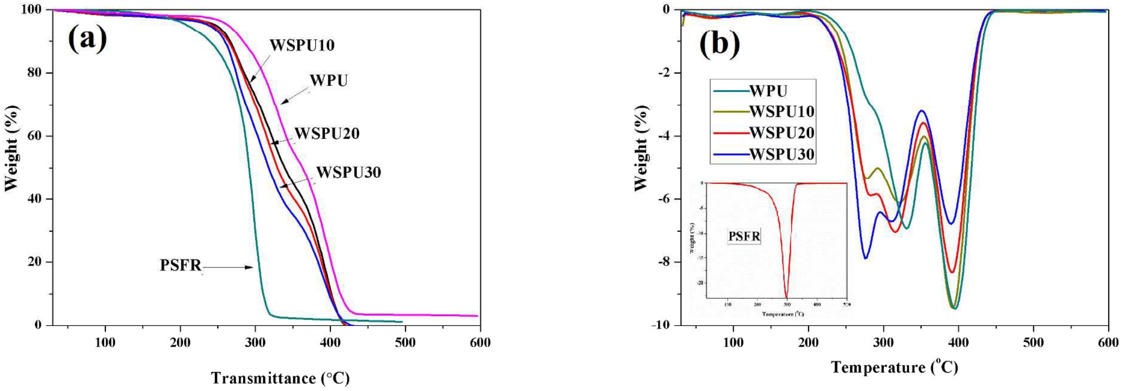


Fig. 9 TGA and DTG curves of PSF, WPU, and WSPU films

Table 1 Molecular weight and DMA data of WPU and different WSPU films

Sample	Monomer composition (weight ratio)	GPC			DMA (^{o}C)
		M_n	M_w	PDI	Tg
WPU	PSF:PTMG =0:100	22740	34337	1.51	45.34
WSPU10	PSF:PTMG =10:90	21291	33639	1.58	48.56
WSPU20	PSF:PTMG =20:80	21168	31540	1.49	50.99
WSPU30	PSF:PTMG =30:70	20855	30448	1.46	52.06

Table 2 Water absorption (a) and solvent swelling (b) of WPU and WSPU films

(a)

Soaking time (h)	Water absorption (%)			
	WPU	WSPU10	WSPU20	WSPU30
24	4.7	2.7	2.5	3.3
48	5.0	3.2	3.0	3.7
72	6.0	3.5	3.2	3.9

96	6.2	3.8	3.4	4.2

(b)

	Solvent swelling (%)			
Solvent	WPU	WSPU10	WSPU20	WSPU30
Toluene	270	169	159	154
Acetone	188	113	110	105
Ethanol	556	240	208	145

Table 3 Tensile properties of WPU and WSPU films with different soaking time. a) Tensile Strength, b) Elongation at break

(a)

	Tensile Strength (MPa)					
Soaking Time (h)	0	24	48	72	96	Retention (%)
WPU	26.5	25.1	24.6	22.2	19.7	74.3
WSPU10	24.7	23.5	22.9	22.7	22.3	90.1
WSPU20	23.7	23.2	22.8	22.6	21.8	91.7
WSPU30	22.9	22.3	21.5	20.9	20.5	89.5

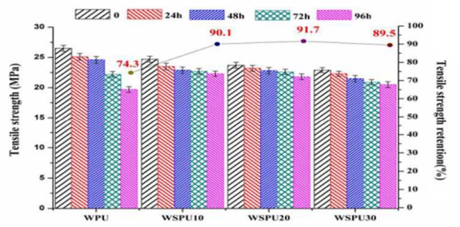
(b)

	Elongation at break (%)				
Soaking Time (h)	0	24	48	72	96
WPU	560	577	583	585	556
WSPU10	499	512	530	557	521
WSPU20	478	502	515	535	499
WSPU30	460	481	492	502	467

Table 4 TGA data of WPU and WSPU film samples

PUD	Monomer composition	T_5 (^{o}C)	T_{10} (^{o}C)	T_{50} (^{o}C)
WPU	PSF:PTMG =0:100	264.6	282.9	362.9
WSPU10	PSF:PTMG =10:90	247.4	264.9	338.6
WSPU20	PSF:PTMG =20:80	242.6	262.6	328.8
WSPU30	PSF:PTMG =30:70	237.6	257.6	317.5
PSF	-	209.8	237.6	291.1

Enhancement of water and organic solvent resistances of waterborne polyurethane film by incorporating liquid polysulfide



Excellent water and organic solvent resistances could be obtained by incorporating liquid polysulfide in waterborne polyurethane film.