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Effects of the antioxidant CA ratio on the properties of UV-curable waterborne polyurethane for application in damping coating

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Abstract. A series of UV-curable waterborne polyurethane with antioxidant CA (CWPU) were prepared successfully by FT-IR. The influence of CA on different properties of the CWPU emulsions and films was investigated using DLS, and DMA. The results indicated that with the increase of CA, the latex particle size increased. Meanwhile, all the films had the loss factor ≥ 0.3 spanning a temperature range of approximately 95°C, with a maximum value increased from 0.64 to 1.09, respectively. The CWPU films could be used as a coating for damping applications.

1. Introduction

The issue of noise and vibration pollution has raised remarkable attention during these years. Viscoelastic polymers are suitable for attenuating vibrations and sounds resulting from their broad glass-transition regions. Therefore, viscoelastic polymers are diffusely applied in areas like the construction industry, high-speed trains, and transportation. Above the glass transition temperature (T_g), the segments of whole polymer bones can be in ample motion. The loss factor ($\tan\delta$) of efficient damping materials must bridge a broad temperature range of at least 60°C which is higher than 0.3 to meet the need for damping vibrations [1-3]. Polyurethane (PU) is a kind of vital viscoelastic polymers with a unique chemical structure which can undergo glass transition over a huge temperature range by adjusting the ratio of soft and hard segments in PU chains. The increasing awareness of environmental and health stimulates that waterborne polyurethane (WPU) is a generic substitute to traditional polyurethane due to its benefits of energy saving, rapid processing, non-flammable, non-toxic, and non-pollution, etc. WPU also have some drawbacks, including a narrower temperature range, poor water and weather resistance. Moreover, the type and content of raw materials restrict its properties and applications [4]. However, these problems can be solved by small molecule filling, crosslinking modification, polymer blending, and so on.

Previous studies showed that polyurethane/small molecule systems could significantly perform the damping property for internal friction between the macromolecule and small molecules in the blends, which transforms a large amount of mechanical energy. Hindered phenols are phenolic compounds with a tert-butyl group ortho to the phenolic hydroxyl group which is widely used antioxidant for



rubber and plastics. Wu et al [5, 6] first discovered that the addition of hindered phenol to the polyurethane could significantly improve the damping properties of the polyurethane, resulting in a hindered phenol/polyurethane hybrid damping material.

In this study, the antioxidant CA was chosen as a chain extender, and a series of CWFPU with different antioxidant CA content were prepared. The properties of the CWFPU emulsions and films were investigated by Fourier transform infrared (FT-IR) spectroscopy, dynamic light scattering (DLS), and dynamic mechanical analysis (DMA). The effects of the CA concentration on the emulsion properties and damping properties were studied.

2. Experimental

2.1. Materials

Polytertramethylene ether glycol (PTMG, $M_n = 1000$ g/mol) was purchased from Bayer Co. Ltd (Germany) and dehydrated under reduced pressure at 120 °C for 2 h. Isophoronediiisocyanate (IPDI) was supplied by Wanhua Polyurethane Co., LTD. (Yantai, China). 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (DMPA) were dried under vacuum at 100 °C. N,N-diethylethanamine (TEA), Hydroxyethyl acrylate (HEA) and Ethyl acetate (EA) used after dehydration from molecular sieve 4 Å were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. [dibutyl(dodecanoyloxy)stannyl] dodecanoate (DBTDL), and 1,1,3-tris(2-Methyl-4-hydroxy-5-tert-butylphenyl)butane (Antioxidant CA) was applied as received supplied by Sinopharm Chemical Reagent CO., LTD.

2.2. Preparation of UV-curable waterborne polyurethanes containing Antioxidant CA (CWPU)

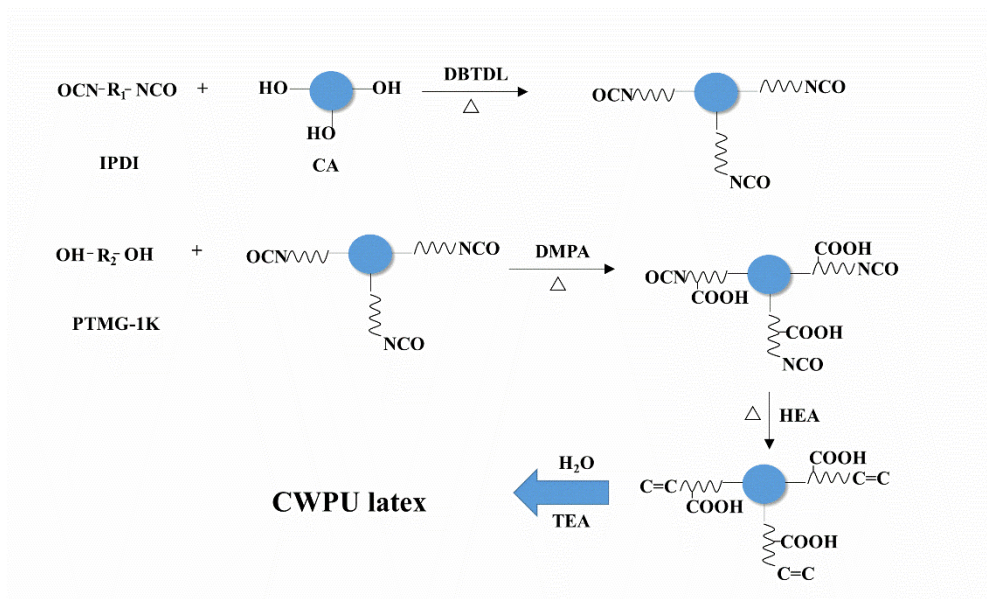
The synthetic process of CWPU emulsion is illustrated in Scheme.1. IPDI and Antioxidant CA were put into the reaction flask equipped with the catalyst (DBTDL) under a mechanical stirrer, thermometer and N₂ atmosphere. The reaction was heated for 2 h under stirring at 85°C. PTMG and DMPA were then added into the reactor for another 3 h. After that, HEA with a stoichiometric amount was added dropwise at 70°C for 2 h. TEA (TEA/DMPA = 1/1, mol) was introduced into the mixture at 35°C and kept for 30 min. Finally, the polyurethane solution was cooled down to the room temperature and dispersed into deionized water high with agitation speed for 1 h. The white-blue CWPU emulsion was prepared and the solid content was governed to 30%. The basic recipes are shown in Table 1.

2.3. Preparation of the CWPU films

The preparation of the CWPU films are followed by the process that firstly mixed the emulsions with 4 wt.% photoinitiator Irgacure1173 based on the ionomer onto a cleaned Teflon disc, secondly dried at ambient temperature four days and then at 60°C for 4 h for annealing, and finally, cured under a curing lamp at room temperature. The obtained films of about 0.5 mm were stored in a desiccator before measurements.

2.4. Characterization

The spectra of Fourier transform infrared (FT-IR) were obtained on a Nicolet 560 infrared spectrometer to identify the CWPU films structure. Each film was recorded in the range of 4000-500 cm⁻¹ at a resolution of 4 cm⁻¹, with the average of 32 scans. Their particle sizes and distributions were tested by nanoparticle size analyzer (Nano-ZS, Malvern Ltd., UK). The dynamic mechanical analysis (DMA) of the CWPU films were measured with a DMA 242 C analyser (NETZSCH Instruments, Germany) under a heating rate 5°C min⁻¹ from -100~150°C at 1 Hz. All the films were measured under tension mode.



Scheme 1. Scheme illustration for preparation of CWPU emulsion.

Table 1. The basic recipes and emulsion properties of CWPUs.

Samples	CA(wt%)	IPDI(w,g)	PTMG(w,g)	DMPA(wt%)	Particle size(nm)	PdI
CWPU1	6.50	17.50	15.00	5.00	40.91	0.203
CWPU2	10.50	17.50	15.00	5.00	60.99	0.054
CWPU3	14.50	17.50	15.00	5.00	72.80	0.093

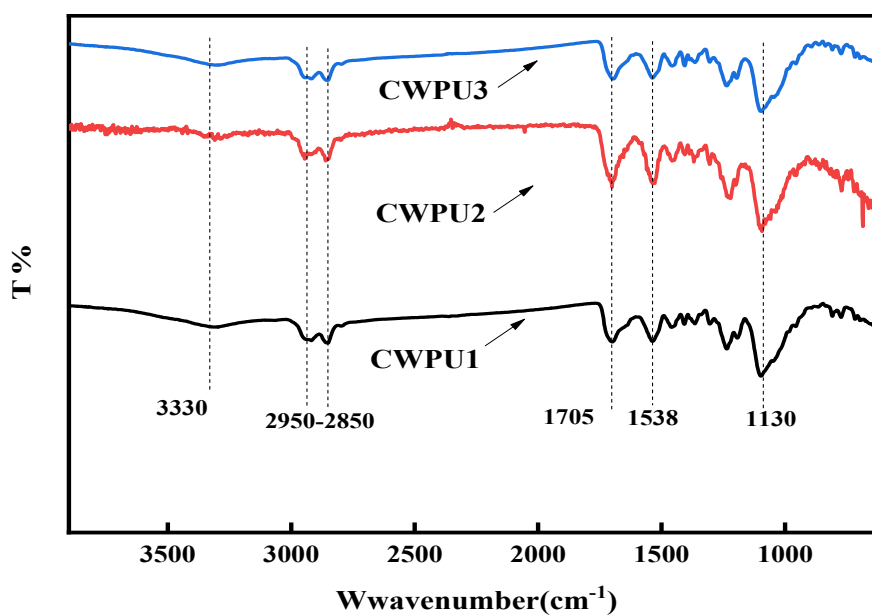


Figure 1. FTIR spectra of CWPU films.

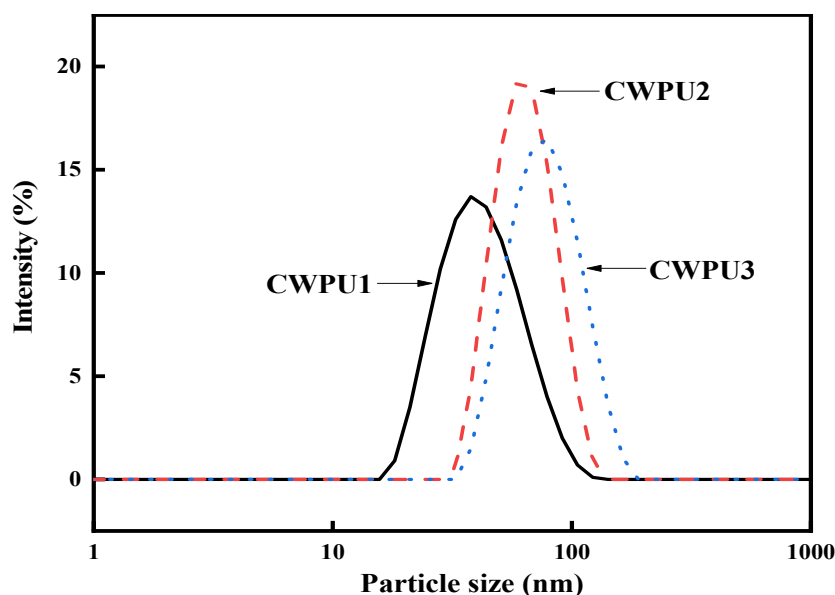
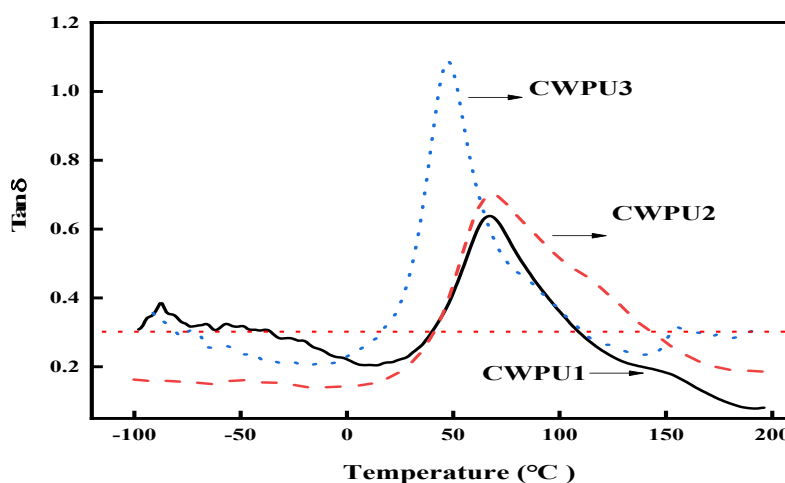


Figure 2. Particle size distribution of CWPU emulsion.

Figure 3. DMA analysis of the UV-WFPU films: loss factor ($\tan \delta$) vs. temperature.

3. Results and discussion

3.1. FT-IR analysis

The structure of the CWPU films was using by FT-IR analysis. CWPU1-3 films had quite similar FT-IR spectra. These results are shown in Figure 1 that the absorption bands of N-H and C-H ($-\text{CH}_2-$ or $-\text{CH}_3-$) were at 3300 and $2950\text{--}2850\text{ cm}^{-1}$, respectively. There was the disappearance of free NCO groups of absorption peaks between 2205 and 2270 cm^{-1} , suggesting the end of reaction completely. The adsorption intensities of peaks around 1530 , 1730 , and 1100 cm^{-1} respectively attributed to the stretching vibrations for N-H (δ N-H), C=O, and C-O-C groups respectively; which reported that the PU preparation was consistent with the predicated process.

3.2. DLS analysis

Figure 2 and Table 1 show the particle size and distribution index (PDI) of CWPU emulsion with different CA contents. As the content of CA increased from 6.50% to 14.50% , the mean diameter of particle size increased from 49.91 nm to 72.80 nm with a monomodal peak distribution, correspondingly.

As shown, the particle size of the CWPU emulsions obviously increased with increasing CA content. For the waterborne polyurethane system, the latex particles size is mainly governed by the content of hydrophilic groups (DMPA), and little hydrophilic group content often resulted in larger latex particles size. Moreover, particles size was enlarged due to the intensification of CA content, crosslinking degree and molecular weight.

3.3. DMA analysis

For judging the damping capacity (dissipation vibration energy) of the material, the loss factor ($\tan\delta$) is a vital index to measure [7]. For actual damping properties, $\tan\delta$ of the damping material must be higher than 0.3 over a temperature range of at least 60°C.

Dynamic mechanical analysis (DMA) was tested to research the effect of CA content on glass transition temperature (T_g). Figure 3 shows the $\tan\delta$ curves revealed that the loss factor in the glassy plateau region increased when the increment of CA content, indicating that the resilience of CWPU films was enhanced. As shown in Table 2, all the samples show an excellent temperature range at which $\tan\delta$ was ≥ 0.3 was approximately 95°C. Moreover, with increasing CA content increased from 6.50 to 14.50, the maximum $\tan\delta$ of the films increased from 0.64 to 1.09 and T_g decreased from 66.4°C to 47.8°C for good compatibility between the soft and hard section. The better the compatibility, the poorer is the alignment of the phases. As the CA content expands, the interaction between the PU and CA networks makes harder in the motion of the molecular chains. In the current study, CWPU2 had the broadest temperature range, implying that it could transform mechanical energy into heat energy at an applied force efficiently. Due to the interactions hydrogen bonding during the main chain and antioxidant CA resulting in molecular chain movement, the maximum $\tan\delta$ is improved greatly by increasing of CA content.

Table 2. Characteristic DMA of UV-WFPU films.

Samples	T_g (°C)	Tan δ peak value	Temperature range (°C) $\tan \delta \geq 0.3$
CWPU1	66.4	0.64	59.6(-97.8-38.2) 71.6(39.2 -110.8)
CWPU2	68.8	0.70	103.2(40.2-143.4)
CWPU3	47.8	1.09	95.6 (15.8-111.4)

4. Conclusion

In summary, we reported the influence of the antioxidant CA content on different properties of CWPU emulsions and films in detail. The chemical structure of CWPU measured by FT-IR was indicated the accomplishment of the reaction. Via particle size analysis of emulsions, it was found that preparation of a series of CWPU emulsions with narrow particle sizes and a controllable PDI was introduced CA from 6.50 to 14.50%. DMA indicated that the antioxidant CA could be rapidly enhanced the damping properties of the CWPU films. Moreover, this research may provide the facile method for damping coating have the potential to the industry sector.

References

- [1] Song M, Hourston D J and Schafer F U 2001 *J. Appl. Polym. Sci* **81** 2439-42
- [2] Huang G S, Li Q and Jiang L X 2002 *J. Appl. Polym. Sci* **85** 545-51
- [3] Trakulsujaritchok T and Hourston D J 2006 *Eur. Polym. J* **42** 2968-76
- [4] Deng Y J, Zhou C, Zhang M Y and Zhang H X 2018 *Prog. Org. Coat* **122** 239-47
- [5] Wu C F 2001 *J. Appl. Polym. Sci* **80** 2468-73
- [6] Wu C F, Yamagishi T A, Nakamoto Y, Ishida S I, Kubota S and Nitta K H 2000 *J. Polym. Sci. Pol. Phys* **38** 1496-503
- [7] Urayama K, Miki T, Takigawa T and Kohjiya S 2004 *Chem. Mater* **16** 173-8