

The Film Properties of Waterborne Polyurethane Modified by Epoxidized Soybean Oil and Styrene

Heqing Fu, Lina Wang, Wanting Lai, and Hui Zhang

School of Chemistry and Chemical Engineering, South China University of Technology, Guangdong Guangzhou, China

The waterborne polyurethane (WPU) modified by epoxidized soybean oil (ESO) and styrene (St) (WPU-ESO-St) was synthesized by free-radical emulsion polymerization using styrene (St) as a monomer, and azodiisobutyronitrile (AIBN) as initiator. The research on the mechanical properties of the film showed that with the increasing of the $[NCO]/[OH]$ ratio, the contents of ESO, DAAM and the St, the tensile strength increased, and elongation at break decreased. The surface morphology of the film was characterized by atomic force microscopy (AFM). The glass transition temperature (T_g) of the film was characterized by differential scanning calorimetry (DSC) analysis.

Keywords epoxidized soybean oil, glass transition temperature, mechanical properties, styrene, surface morphology, waterborne polyurethane

INTRODUCTION

Solvent polyurethane was restricted because of its emission of volatile organic compound (VOC). Waterborne polyurethane (WPU) overcame the shortcomings of solvent polyurethanes, such as poisonous, flammable, bad smell, and environmental pollution. Therefore, much research has been done on waterborne polyurethane due to industrial demand [1–27].

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Address correspondence to Heqing Fu, School of Chemistry and Chemical Engineering, South China University of Technology, Guangdong Guangzhou 510640, China. E-mail: fuhq@scut.edu.cn

However, the performance of a single waterborne polyurethane was not good, because of poor wettability on the nonpolar substrate, low bonding strength, low initial tack, slow drying rate, poor water and alkali resistance, high cost, and so on. Therefore, waterborne polyurethane must be modified. The water and heat resistance of the styrene are good, and epoxidized soybean oil (ESO) is a lower-cost, non-toxic, heat- and solvent-resistant renewable resource.

In order to obtain a high-performance waterborne polyurethane, the polyurethane was modified by epoxidized soybean oil and styrene. There have been many reports about the modification of polyurethane. However, there has not been a report about the film properties of waterborne polyurethane modified by epoxidized soybean oil and styrene at the same time.

EXPERIMENTAL

Materials

Toluence diisocyanate (TDI) (supplied by Bayer); 1,4 butanediol (BDO) (supplied by Guangzhou Petrochemical Factory); dimethylolpropionic acid (DMPA) (supplied by Perstop); epoxidized soybean oil (ESO, supplied by Dongfeng Chemical Co., Ltd); polypropylene glycol (N220, $M_w = 2000$) (supplied by Aldrich); n-methyl pyrrolidone (NMP) supplied by Shanghai Chemical Agent Factory); acetone (supplied by Guangzhou Fine Chemical Factory); triethylamine (TEA) and ethylene diamine (EDA) (supplied by Shanghai Fine Chemical Factory); styrene (St) a (supplied by Shanghai Fine Chemical Factory); 2,2'-Azobisisobutyronitrile (AIBN) (supplied by Guangzhou Fine Chemical Factory); deionized water was made by our laboratory.

Synthesis of Waterborne WPU-ESO Dispersions

A 1000 mL four-necked flask equipped with a mechanical stirrer, thermometer, and condenser was placed in a constant-temperature water bath. The TDI and N220 were added to a flask. The reaction was carried out at 85°C under nitrogen atmosphere. When the amount of residual NCO groups reached the desired value (it was obtained by n-dibutylamine titration), the BDO, ESO, and DMPA were added into the flask while the temperature was at 80°C. The reaction proceeded until the residual NCO groups reached the desired value. The prepolymer was cooled to 40°C, and was neutralized by TEA. Then it was dispersed by water at a high rate (the rate was from 2000 to 6000 rpm). Afterwards, the chain extender EDA was added to react with unreacted NCO groups. Finally, the WPU-ESO hybrid dispersions were made.

Synthesis of WPU-ESO-St Hybrid Dispersions

WPU-ESO hybrid dispersions acting as seed emulsions were introduced into a 1000 mL four-necked flask equipped with a mechanical stirrer, thermometer, and condenser and placed in a constant-temperature water bath. Then St monomer and AIBN initiator were added dropwise to the flask. The reaction continued for 5 h, then hybrid dispersions were cooled to room temperature, and the WPU-ESO-St hybrid dispersions were made.

Preparation of WPU-ESO-St Films

The WPU-ESO-St films were prepared by placing about 50 mL WPU-ESO-St hybrid dispersions in a PTFE mold and allowing it to dry at room temperature for a week. Then they were annealed in an oven at 50°C for 4 h followed by heating at 80°C for a day. Finally, the WPU-ESO-St films were obtained.

CHARACTERIZATION

Mechanical Property Analysis

Tensile strength and the elongation at break of the WPU-ESO-St films were measured at room temperature with the instron tension meter Model 3367. A crosshead speed of 50 mm/min was used throughout these investigations to determine the ultimate tensile strength and the elongation at break.

Morphology Analysis

The morphology of WPU-ESO-St films was investigated by means of atomic force microscopy (AFM). AFM image was obtained as follows. A NanoScope multimode AFM (CSPM3000, BenYuan Nano Apparatus Ltd., China) was used, and AFM scans were performed in tapping mode with untreated silicon cantilevers under ambient conditions. The scan speed was at 1.0 Hz for all images.

Differential Scanning Calorimetry (DSC) Analysis

The glass transition temperature of the samples was characterized with a STA449C DSC instrument. The heating rate was at 10°C/10 min. The first heating run was carried out to remove the thermal history of the samples. From the second run, the glass transition temperature (T_g) was obtained.

RESULTS AND DISCUSSION

Mechanical Property Analysis

Effect of [NCO]/[OH] Ratio on the Mechanical Properties

Figure 1 shows the effect of [NCO]/[OH] ratio on the tensile strength and elongation at break of WPU-ESO-St films. With the increasing of the [NCO]/[OH] ratio, the tensile strength increased, and elongation at break decreased. This could be explained that with the increasing of [NCO]/[OH] ratio, the content of the hard segments increased. The content of the hard segments affected the mechanical characteristic of WPU-ESO-St films. The higher the content of the hard segments, the hardness of WPU-ESO-St films increased more, and the flexibility of the WPU-ESO-SB film decreased more. On the other hand, with the increasing of the [NCO]/[OH] ratio, the crosslink density increased. Higher crosslink density would result in higher hardness. Therefore, the tensile strength increased, and elongation at break decreased.

Effect of ESO Content on the Mechanical Properties

Figure 2 shows the effect of the ESO content on the tensile strength and elongation at break of WPU-ESO-St films. From Figure 2 it can be seen that with the increasing of the ESO content, the tensile strength increased, and elongation at break decreased.

There were three to four epoxy groups in the epoxidized soybean oil (ESO) molecule. With the ESO content increasing, the epoxy group ring opened and

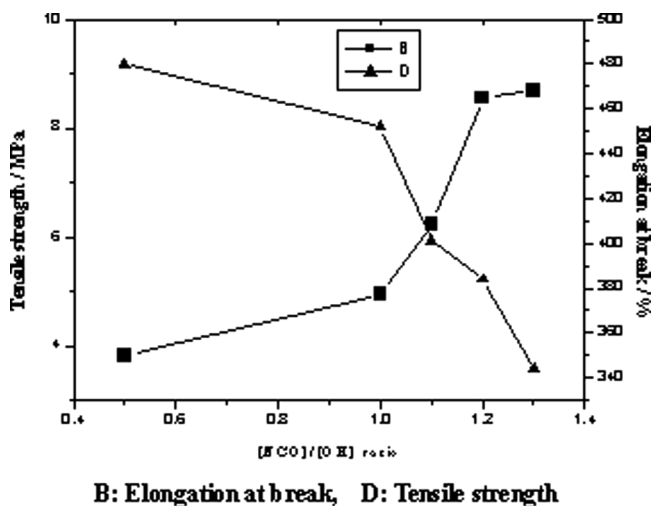
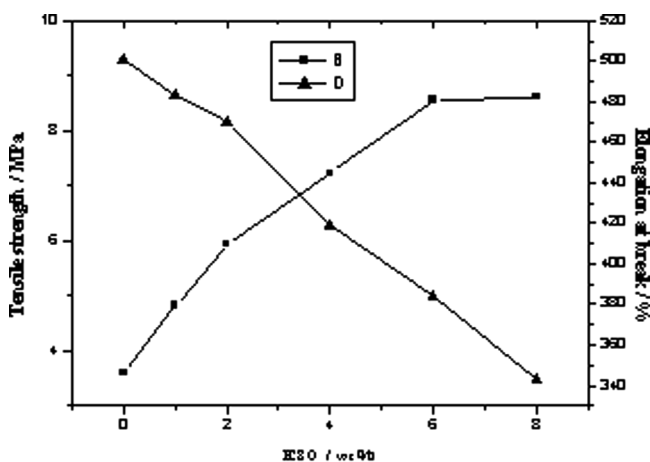


Figure 1: Effect of (NCO)/(OH) ratio on the tensile strength and elongation at break of WPU-ESO-St films.



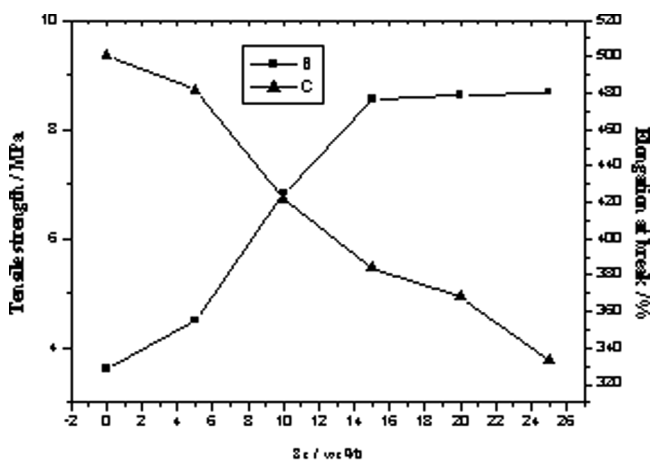
B: Elongation at break, D: Tensile strength

Figure 2: Effect of ESO content on the tensile strength and elongation at break of WPU-ESO-St films.

cross-linked with polyurethane. Therefore the tensile strength increased, and elongation at break decreased.

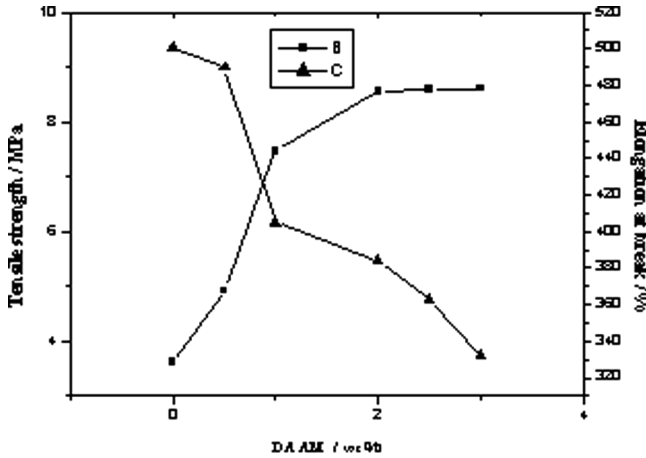
Effect of St Content on the Mechanical Properties

Figure 3 is the effect of St content on the tensile strength and elongation at break of WPU-ESO-St films. From Figure 3 it can be seen that with



B: Elongation at break, D: Tensile strength

Figure 3: Effect of St content on the tensile strength and elongation at break of WPU-ESO-St films.



B: Elongation at break, D: Tensile strength

Figure 4: Effect of DAAM content on the tensile strength and elongation at break of WPU-ESO-St films.

the increasing of the ESO content, the tensile strength increased, and elongation at break decreased. This was because the St was the hard monomer, and it had high glass transition temperature. When it was polymerized with polyurethane, the hardness of the WPU-ESO-St films increased, which resulted in the tensile strength increasing and elongation at break decreasing.

Effect of DAAM Content on the Mechanical Properties

Figure 4 is the effect of DAAM content on the tensile strength and elongation at break of WPU-ESO-St films. From Figure 4 it can be seen that with the increasing of the DAAM content, the tensile strength increased, and elongation at break decreased. The reason was that the DAAM was a cross-linking agent; with the increasing of DAAM content, there was more DAAM cross-linking with polyurethane, and the degree of cross-linking increased, which resulted in the tensile strength increasing, and elongation at break decreasing.

Differential Scanning Calorimetry (DSC) Analysis

Figure 5 shows the DSC spectra of WPU film without modification. Figure 6 shows the DSC spectra of WPU-ESO-St films. The polyurethane molecule is composed of soft segments and hard segments. There is a microphase

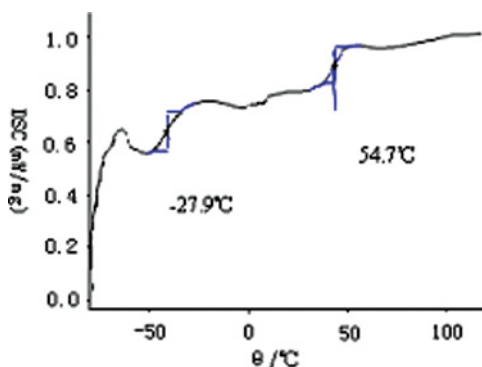


Figure 5: DSC curve of WPU film without modification.

separation in the polyurethane molecule. The degree of microphase separation and the glass transition temperature of soft segments and hard segments were determined by the DSC spectra.

From Figure 5 it can be seen that the glass transition temperature (T_g) of soft segments was -27.9°C and the glass transition temperature (T_g) of hard segments was 54.7°C .

From Figure 6 it can be seen that the glass transition temperature (T_g) of soft segments was -11.4°C and the glass transition temperature (T_g) of hard segments was 59.7°C . From Figure 5 and Figure 6 it can be observed that the difference between the glass transition temperature (T_g) of soft segments and hard segments in the WPU without modification was larger than that of the WPU-ESO-St films. When the WPU was modified by epoxidized soybean oil and styrene, the cross linkage was formed, which led to the degree of microphase separation in the WPU-ESO-St that was smaller than that of WPU without modification.

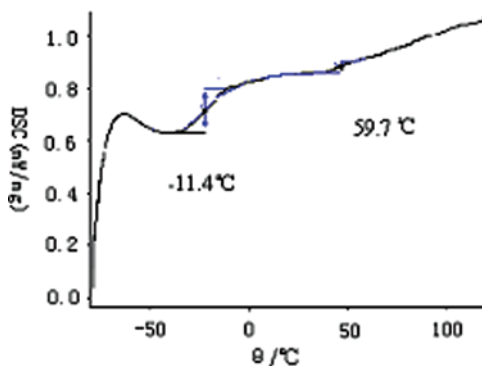


Figure 6: DSC curves of WPU-ESO-St films.

Atomic Force Microscope (AFM) Analysis

The surface morphology of the film was characterized by the Atomic Force Microscope (AFM). Figure 7 is the AFM image of WPU surface morphology. Figure 8 is the AFM image of WPU-ESO-St surface morphology.

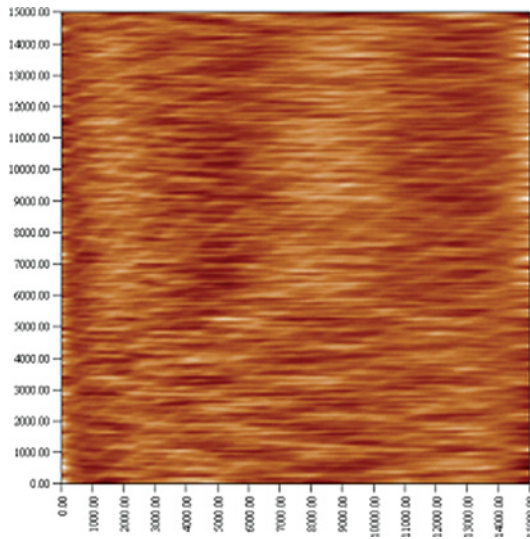


Figure 7: The AFM image image of WPU-ESO-St surface morphology.

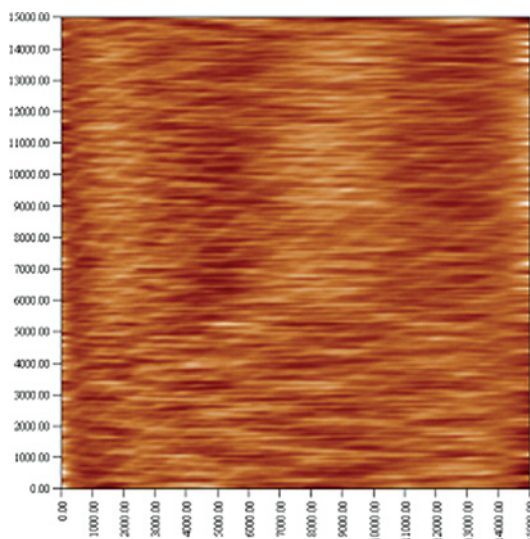


Figure 8: The AFM image image of WPU-ESO-St surface morphology.

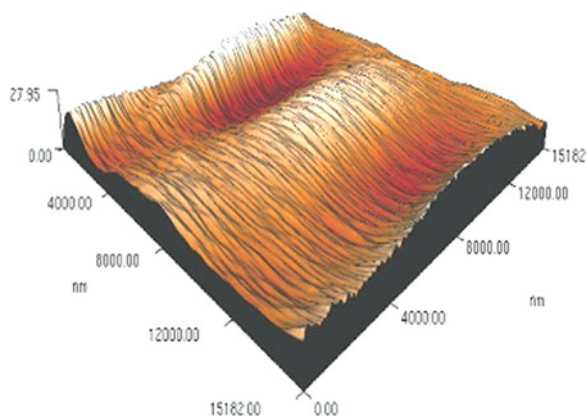


Figure 9: The 3-D AFM image of WPU film without modification.

From Figures 7 and 8 it can be observed that the surface morphology of WPU film was smooth, and the surface morphology of WPU-ESO-St films was reticular. After the WPU was modified by epoxidized soybean oil and styrene, the cross linkage was formed; therefore the surface morphology of WPU-ESO-St films was reticular.

In order to clearly see the surface morphology of the film, the film was characterized by 3-D AFM. Figure 9 is the 3-D AFM image of WPU film without modification. From Figure 9 it can be seen that the surface topography of WPU film was flat continuous.

Figure 10 is the 3-D AFM image of WPU-ESO-St films. From Figure 10 it can be seen that the surface topography of the WPU-ESO-St films surface consisted of bright and dark areas, i.e., it showed the sea-island structure. It was assumed that the dark areas were the styrene-rich phase, and bright areas were the polyurethane-rich phase. Thus, the WPU-ESO-St had a two-phase

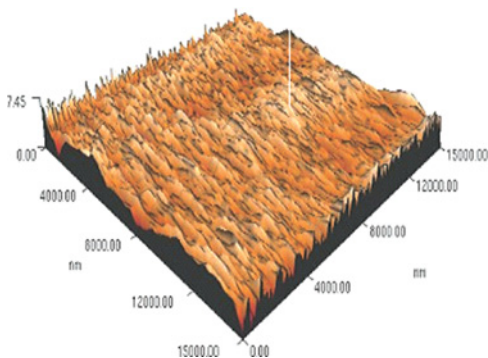


Figure 10: The 3-D AFM image of WPU-ESO-St films.

structure, and the styrene-rich phase was continuously distributed in the polyurethane-rich phase.

CONCLUSION

The mechanical properties and other properties of the WPU-ESO-St films were characterized by DSC, AFM, and tension meter. Effects of [NCO]/[OH] ratio, the contents of ESO, DAAM, and the St on the mechanical properties were studied. The research on the mechanical properties showed that with the increasing of the [NCO]/[OH] ratio, the contents of ESO, DAAM, and the St, the tensile strength increased, and elongation at break decreased. The morphology of WPU-ESO-St films was investigated by means of AFM. The AFM image showed that the surface morphology of WPU film was smooth, and the surface morphology of WPU-ESO-St films was reticular. The 3-D AFM image showed that the surface topography of WPU film was flat continuous, and the surface topography of WPU-ESO-St films was a continuous distribution of hills and valleys; the surface consisted of bright and dark areas, i.e., it showed the sea-island structure. DSC analysis showed that the difference between T_g of soft segments and hard segments in the WPU without modification was larger than that of the WPU-ESO-St.

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