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Preparation of a Novel Prepolymer of Polyurethane Acrylate

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Abstract. A new prepolymer of polyurethane acrylate (PUA) was synthesized from cyclohexanone-formaldehyde resin (CFR) with high hydroxyl value, toluene diisocyanate (TDI) and 2-hydroxyethyl methacrylate (HEMA) by using dibutyltion dilaurate as catalyst via two steps. The result from Fourier transform infrared spectrum (FT-IR) showed that methacrylate group was introduced into the terminal of CFR by using TDI as bridge and curable PUA was obtained. Then, the PUA was cured by using azodiisobutyronitrile as catalyst at 110-130^{o}C for 2h. The resulting product has excellent solvent resistance.

Introduction

A low molecular weight non-conventional cyclohexanone-formaldehyde resin (CFR) shows unique compatibility with a great number of polymers. It is soluble in most organic solvents such as aromatic hydrocarbons, ketones, esters, alcohols, etc. It is usually used as additives to modify the properties of high molecular weight film formers [1-4]. But it has some disadvantages such as the poor thermal stability, yellowing resistance and the deep color, which limits its application in coating to a certain degree. If used in coating or adhesive system, it couldn't cross-link with main resins and form network structure, so the obtained coating often owned low resistance toward chemical, gasoline or solvent [5]. Some works on modifying CFR have been performed [6-9]. Polyurethane acrylate (PUA) is an important curable prepolymer, and may be prepared from a di-(or poly-) isocyanate, a polyol, and an acrylate with hydroxyl groups [10, 11]. PUA can be cured under UV irradiation or heating and a polymer with three-dimensional network structure will form. The polymer usually provides excellent physical and mechanical properties, such as adhesion on substrates, flexibility and impact strength [12, 13]. However, little work has been performed to prepare PUA based on CFR. Having reactive methylol group, CFR can easily react with isocyanate [14-16]. Therefore, development of a new PUA based on CFR would be of scientific and industrials importance.

In this paper, a new prepolymer of PUA was synthesized from CFR with high hydroxyl value. The structure of the obtained prepolymer was characterized by FT-IR spectrum. Then, the prepolymer was cured under heating and the solvent resistance of the product was measured.

Experimental

Materials. Cyclohexanone-formaldehyde resin (CFR) was provided by Yueyang Intech Synthetic Materials Co. Ltd. Bromo-phenol blue, azodiisobutyronitrile, hydrochloric acid, 5A molecular sieve, methanol and the other materials were of analytical grade and obtained from the Kermel Reagent Co., Tianji, China. Toluene diisocyanate (TDI) and hydroquinone was used without any further purification. Hydroxyethyl methacrylate (HEMA), dibutyltin dilaurate (DBTDL), butyl acetate, acetone, toluene, dibutyl amine, and tetrahydrofuran were used after drying over 5-A molecular sieves.

Instruments. FT-IR were recorded on a Thermo Nicolet Avatar 370 FT-IR Spectrometer, within a spectral range of 400-4000cm^{-1}.Samples for FT-IR analysis were prepared by drying dispersions directly on KBr pellet.

Determination of the content of the free isocyanate group. Determination of the content of -NCO group in reaction mixture was performed according to reference [10], Firstly, superfluous dibutyl amine reacted with the free isocyanate group, then the residual dibutyl amine was titrated by using HCl, and bromo-phenol blue was chosen as the indicator.

Synthesis of polyurethane acrylate (PUA). PUA was synthesized via a two-step procedure (Fig.1). Firstly, 22g of CFR (-OH value 280mg KOH/g, acetic anhydride method), 60g butyl acetate, 17.4g TDI and 1% DBTDL (based on the mass of the CFR) were mixed in a four-necked flask equipped with a nitrogen inlet, a mechanical stirrer, a temperature sensor and a drying tube. The mixture was stirred at 30°C until its -NCO value was reached to half of the initial value, and an intermediate product, CFR-TDI was acquired. Secondly, 13g of HEMA and 1g of hydroquinol as inhibitor were added to the above-obtained mixture, the reaction proceeded at 50°C until the -NCO value was less than 0.1%. Finally, 100ml of methanol was added into the mixture, a precipitation was formed. After the solvent was removed, the precipitation was washed with deionized water for three times, then filtrated under negative pressure and dried at 50°C.

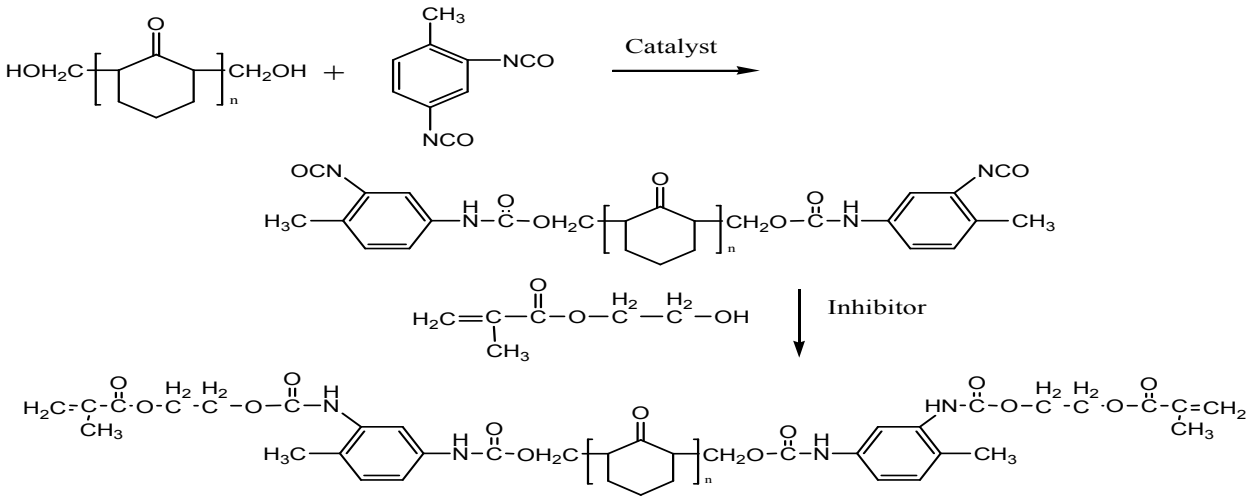

Fig.1 Schematic illustration of the procedure involved in preparation of polyurethane acrylate

Thermocuring experiment. PUA was dissolved in small amount of tetrahydrofuran, followed by adding azodiisobutyronitrile (1% of the mass of the PUA) as initiator. The obtained mixture was stirred well for 10-15min. After the solvent was evaporated, the mixture was cured by heating at 110-130°C for 2h in an air circulated oven, then cooled to room temperature in the desiccator. Thus, a thermo-cured polymer (TCP) was acquired.

Test of the solvent resistance. The solubility of various samples was investigated as follows: 20 mg of solid sample and 2mL of solvent were mixed in a test tube and shaken at room temperature. If dissolution occurred in 5min, it was considered to be soluble. If dissolution was not completed at room temperature or under heating, it was considered to be slightly soluble. If the dissolution did not occur at room temperature or under heating, it was considered to be insoluble.

Results and discussion

Effect of reaction time on the content of –NCO group in reaction mixture. Effect of reaction time on the content of –NCO group was shown in the Fig.2. The content of –NCO group decreased with the increasing of time. After CFR reacted with TDI for 2h at 30°C, the content of –NCO group was 4.36%, approximately to half of the initial value of 8.36%. Then, HEMA was added and reacted with the rest –NCO group. After the reaction had lasted for another 3h, the content of –NCO group decreased to 0.1%. The reaction was keep for another 0.5h so that the content of free –NCO group was less than 0.1%. Therefore, the reaction time for preparation of PUA was chosen to be 2h in the first step and 3.5h in the second step.

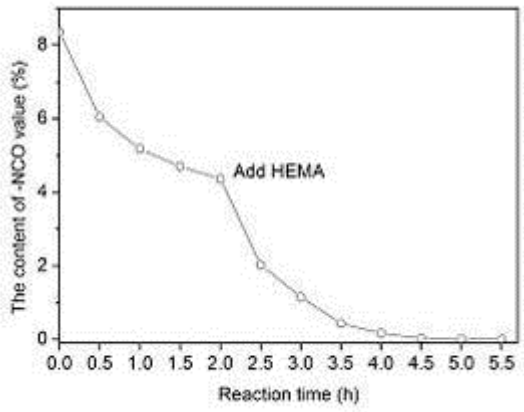

Fig.2 Effect of reaction time on the content of –NCO group

FT-IR analysis of various samples. The FT-IR spectra of various samples were shown in Fig.3. The broad absorption band near 3391cm^{-1} in Curve 1 of Fig.3 was ascribed to the stretching vibration of -OH group in CFR (1), and the intensity of this peak greatly decreased in Curve 2, 3, 4 of Fig.3, which indicated that most of -OH group in CFR had reacted with TDI while CFR-TDI (2), PUA (3) or TCP (4) formed. The peak at 2261cm^{-1} in Curve 2 of Fig.3 was assigned to the asymmetric stretching vibration of -NCO group, suggesting that one -NCO group in TDI had reacted with -OH group in CFR and another -NCO group in TDI had been introduced into CFR-TDI (2). The disappearance of the peak at 2261cm^{-1} in Curve 3, 4 of Fig.3 indicated that -NCO group had reacted completely with -OH group of HEMA while PUA(3) or TCP(4) formed. The peak at 812cm^{-1} in Curve 3 of Fig.3 was ascribed to the deforming vibration of C-H bond in C=CH_2 group, and indicated that methacrylate group had been successfully introduced into the structure of PUA (3). The disappearance of the peak at 812cm^{-1} in Curve 4 of Fig.3 proved that PUA had thermocured. A new peak at 3129cm^{-1} in Curve 2, 3, 4 of Fig.3 was assigned to the stretching vibration of -NH group that provided by the reaction between –NCO group in TDI and –OH group in CFR or HEMA.

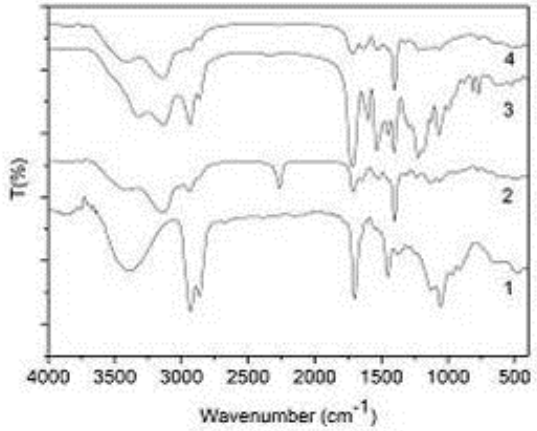

Fig.3 FT-IR spectra of CFR (1), CFR-TDI (2), PUA (3) and TCP (4)

Table 1 The solvent resistance of various samples in common solvents

Solvent	CFR	PUA	TCP
Ethanol	s	s	i
Butyl acetate	s	s	i
Tetrahydrofuran	s	s	i
Cyclohexanone	s	s	i
Petroleum ether	sl	i	i
Toluene	i	i	i

(s: soluble; sl: slightly soluble; i: insoluble)

The solvent resistance of various samples. The solubility of various samples was showed in Table 1. The CFR and PUA could be dissolved in some common solvents, but the TCP didn't be dissolved in the same solvents, which indicated that the PUA had cross-linked and formed a three-dimensional network structure during the theromcuring process. The obtained polymer, TCP, had excellent solvent resistance.

Conclusions

The PUA was synthesized from CFR, toluene diisocyanate and hydroxyethyl methacrylate by using dibutyltin dilaurate as catalyst via a two-step method. FT-IR analysis shows that -OH group in CFR and hydroxyethyl methacrylate can react with –NCO group in TDI, and a new prepolymer of PUA was obtained. The PUA could be thermocured easily and the resulting product had excellent solvent resistance.

Acknowledgements

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References

[1] Y. Zhang; X. Zeng; P. Li: Moden Chemical Industry.Vol.26 (2006), p.35.

[2] H. Ren; Q. Zhang; X. Chen: Polymer. Vol.48 (2007), p.887.

[3] V. Athawale; A. Chamankar: J. Am. Oil Chem. Soc. Vol.75 (1998), p.887.

[4] N. Kizilcan; A. Akar: Angew. Makromol. Chem. Vol.266 (1999), p.1.

[5] P. Gloeckner; B. Burian; P. Denkinger: U.S. Patent 7, 812, 109. (2010).

[6] E. Ates; N. Kizilcan: Pigment & Resin Technology. Vol.40 (2011), p.29.

[7] E. Sezer; N. Kizilcan; K. Coban: Int. J. Elechem, Vol.2011 (2011), p.1.

[8] N. Kizilcan; B. Hocaoglu; B. Ustamehmetoglu: Pigment & Resin Technology, Vol.40 (2011), p.143.

[9] H. Patel; M. Naji: Int J Plast Technol, Vol.14 (2010), p.17.

[10] A. Anila; C. Huang; W. Shi: Colloid Polym Sci. Vol.283 (2004), p.200.

[11] Y. He; M. Zhou; B. Wu: Prog. Org. Coat. Vol.67 (2010), p.264.

[12] H. Lee; C.Wang: Journal of Polymer Research. Vol.12 (2005), p.271.

[13] J. Ledrl; J. Saiter; J. Grenet: J. Therm. Anal. Calorim. Vol.58 (1999), p13.

[14] N. Uyanik; N. Kizilcan, A. Akar: J. Appl. Polym. Sci. Vol.67 (1998), p.643.

[15] N.Kizilcan; A. Akar: J. Appl. Polym. Sci. Vol.70 (1998), p.655.

[16] N.Kizilcan; A.Akar: Macromol. Symp. Vol.122 (1997), p.349.