Preparation of the Non-isocyanate Polyurethane Coatings

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Abstract

Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the polyamine and cyclic carbonate terminated polyester. Cyclic carbonate terminated polyester was synthesized from the reaction of the carbon dioxide and epoxidized polyester which was prepared from the polyester polyol with the epichlorohydrin under the catalyst. The properties of the epoxidized and cyclic carbonate terminated polyester were characterized by Brookfield viscometer, NMR and FT-IR. The cyclic carbonate terminated polyester could react with polyamine to give nonisocyanate polyurethane networks.

Introduction

Polyurethanes have been an important class of resins for organic coatings because they have toughness, excellent wear and tear properties [1]. And polyurethanes are usually synthesized through the polycondensation reaction between a diisocyanate and diol [2]. This is less desirable because the diisocyanate is highly hazardous, and the phosgene which is the raw material of isocyanate is instable and toxic. It was know that the carbamate group can be synthesized by the reaction of the primary amine with cyclic carbonate [3]. This provides a useful way to obtain nonisocyanate polyurethanes.

Linear nonisocyanate polyurethanes can be obtained by the reaction of bifunctional five-membered aliphatic cyclic carbonates with diamines[4,5]. Optically active poly(hydroxyurethane)s with M_n of 11,000-24,000 were prepared by the reaction of L-Lysine with bifunctional five-membered cyclic carbonate[6] . A series of polyurethanes with M_n of 6,000-9,000 and relatively low PDI around of 1.5 were obtained by the polyaddition of phenoxycarbonyloxymethyl ethylene carbonate with diamines[7]. Polyhydroxyurethane can also be prepared in high yields by the reaction of the bis(cyclic carbonates) with diamines in aqueous media[8]. A network of nonisocyanate polyurethanes can be obtained when multifunctional cyclic carbonate oligomers are used in the reaction with multifunctional primary amines [9].

The poly(cyclic carbonate)s were usually prepared by the reaction of poly(epoxide)s under CO_2 in the presence of catalyst[5]. Most of poly(epoxide)s for nonisocyanate polyurethane synthesis reported are low molecule monomers[4-8]. Recently, epoxidized soybean oil oligomer has been reported as a starting material to prepare nonisocyanate polyurethanes [10]. Polyester is a widely used polyol reagent to prepare polyurethanes by reaction with polyisocyanates. Here, our interest is the preparation of nonisocyanate polyurethanes. In best of our knowledge there is no report of the synthesis of nonisocyanate polyurethanes by using epoxidized polyester oligomer as starting material. In this paper, hydroxyl terminated polyester was first prepared, then epoxidized polyester was prepared from the hydroxyl terminated polyester with the epichlorohydrin under the catalysts, and lastly, cyclic carbonate

terminated polyester was synthesized from the reaction of epoxidized polyester and the carbon dioxide. The hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyesters were characterized by FTIR and NMR. Non-isocyanate polyurethane coatings were prepared by the thermo-curing of the cyclic carbonate terminated polyester and polyamine.

Experimental

Materials: Adipic Acid (AA), *p*-xylene, 1,6 hexane diol (HD), trimethylolpropane (TMP), dibutyl tin oxide (DBTO), zinc perchlorate hexahydrate, tetrabutylammonium bromide (TBAB), epichlorohydrin (>99%), isophorone diamine (>98%), sodium hydroxide(>97%), acetone, and dichloromethane, all Aldrich products were used as received.

Synthesis of hydroxyl terminated polyester (H-PE)

Adpic acid (AA) (146.14g, 1 mol), 1,6 hexane diol (HD) (118.18 g, 1mol) and Trimethylolpropane (TMP) (67.09 g, 0.5mol) were taken in a 500 ml four-neck round bottom flask which was equipped with a mechanical stirrer, a gas inlet, a temperature controller, a Dean-Stark trap and a condenser. The reaction proceeded under argon to minimize oxidative degradation. To accelerate the reaction, 0.4 wt % of DBTO, a transesterification catalyst, was used. Then, 3 wt % of *p*-xylene was also added into the reaction mixture to remove water from the resin as azeotropic mixture. The reaction temperature was carefully controlled using a temperature controller and a thermocouple in order to minimize evaporation of diol. The temperature of the mixture was increased from 20-150 ^{0}C at a rate of 4.3 ^{0}C/min, and then from 150-210 ^{0}C at a rate of 0.25 ^{0}C/min. The final temperature was held until the resin had an acid number measured by titration less than or equal to 10 mg KOH/g resin. The hydroxyl number of polyesters (297 mg KOH/g resin) was determined by ASTM method (ASTM D 1957-86).

Synthesis of epoxidized polyester (E-PE)

Epichlorohydrin (17.135g) was added carefully while stirring the hydroxyl terminated polyester H-PE (50 g) and zinc perchlorate hexahydrate (1.5 g) mixture at 80 ^{0}C. After 20 hours reaction, the temperature was cooled down to 60 ^{0}C and 300 mL acetone was added. Then, 23.15 g of NaOH (32% aqueous solution) was added drop wise. Stirring was continued for 5 hours. Filtered while hot and the solvent were removed under reduced pressure to yield epoxidized polyester (E-PE).

Synthesis of cyclic carbonate polyester (CC-PE)

Epoxidized polyester (E-PE) (20g) and the catalyst tetrabutylammonium bromide (TBAB) (0.654 g) were placed in a 50 mL reactor, stirred, and heated. The reaction was carried out at 110 ^{0}C for 12 hours to yield cyclic carbonate polyester (CC-PE). The conversion of epoxy to carbonate was monitored by IR spectroscopy.

Polyurethane preparation

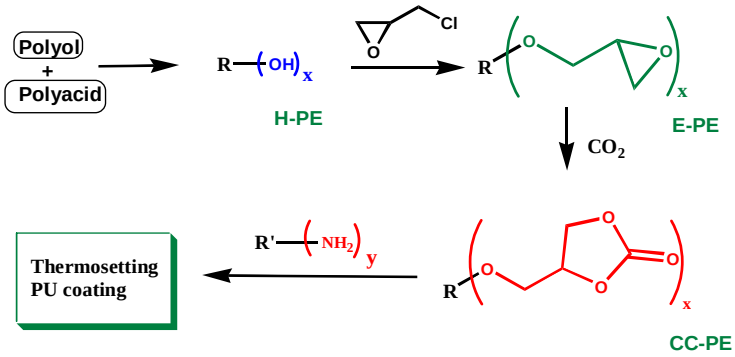
0.25 g of cyclic carbonate polyester (CC-PE) was placed in a 2 mL vial followed by isophorone diamine and acetone and mixed thoroughly. The viscous solution was poured into a mold and heated at 70 ^{0}C for 24 h.

Characterizations

The FT-IR spectra of the hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyester were measured in a Nicolet 380 FTIR spectrophotometer. The results were analyzed using OMNIC software. The NMR spectrum of the hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyester were taken in a Varian Mercury 300 MHz spectrophotometer.

Results

Scheme **1** gives the overall synthetic approach by using hydroxyl terminated polyester as starting materials to prepare nonisocyanate polyurethane. Epoxidized polyester (E-PE) was obtained in the reaction of the hydroxyl terminated polyester (H-PE) with epichlorohydrin by using zinc perchlorate hexahydrate as catalyst. FTIR results in Figure **1.b** show the new peaks at 909 and 854 cm^{-1} formation which correspond the epoxy group. ^{1}H NMR in Figure **2.b** and ^{13}C NMR in Figure **3.b** also show the epoxy group formation. Cyclic carbonate polyester (CC-PE) was prepared from the epoxidized polyester (E-PE) and carbon dioxide. FTIR results in Figure **1.c** show the new peak at 1802 cm^{-1} formation which correspond cyclic carbonate, and the peaks at 909 and 854 cm^{-1} disappearance which correspond the epoxy group. ^{1}H NMR in Figure **2.c** and ^{13}C NMR in Figure **3.c** also shows the cyclic carbonate group formation and epoxy group disappearance. H-PE has a Brookfield viscosity of 5800 mPas, the E-PE has a Brookfield viscosity of 1100 mPas, and the CC-PE has a Brookfield viscosity of 9400 mPas.



Scheme 1. Nonisocyanate polyurethane preparation procedure

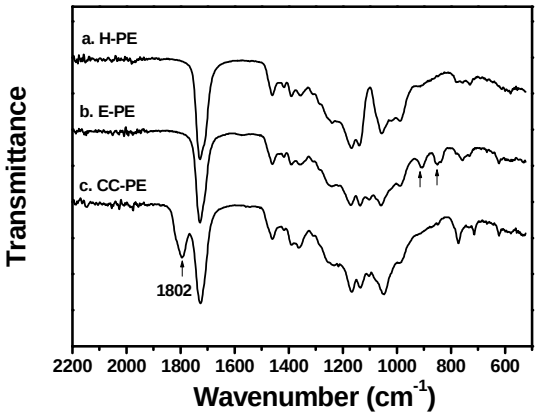


Figure 1. FTIR spectra of hyrdroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE)

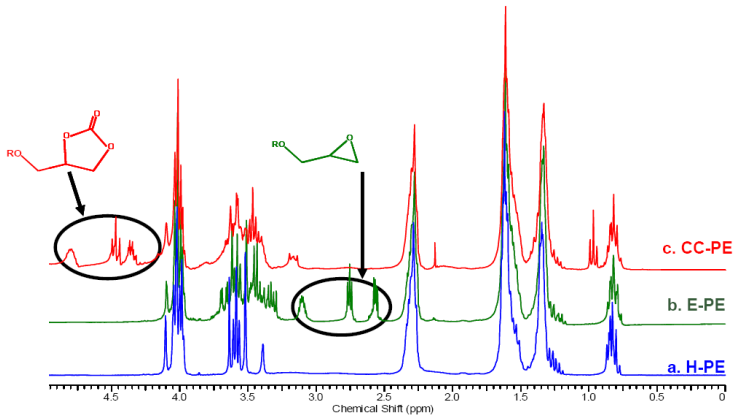


Figure 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of hyrdroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE).

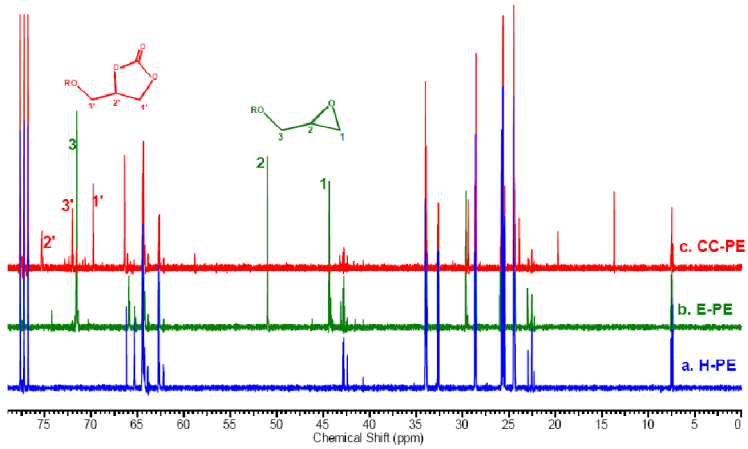


Figure 3. ^{13}C NMR spectra (300 MHz, $CDCl_3$) of hyrdroxyl terminated polyester (H-PE), epoxidized polyester (E-PE) and cyclic carbonate polyester (CC-PE).

The CC-PE formation with time was monitored by using IR spectroscopy by focusing on the appearance of a new peak at 1805 cm^{-1} due to the carbonyl of the cyclic carbonate moieties. As shown in Figure **4**, the peak intensity in 1805 cm^{-1} keep increase with the reaction time.

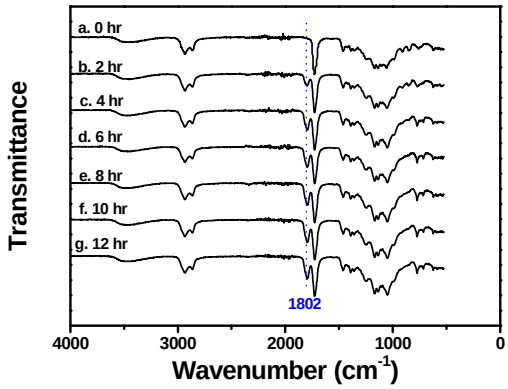


Figure 4. FTIR spectra of CC-PE formation with time

The polyurethane was prepared by the reaction of cyclic carbonate polyester (CC-PE) with isophorone diamine at 70 ^{0}C. The nonisocyanate polyurethane formation with time was monitored by focusing on the disappearance of cyclic carbonate peak at 1805 cm^{-1}. Figure **5** shows the polyurethane formation with time when the mole ratio of isophorone diamine (IPDA) to CC-PE is fixed (the mole ratio of amine to cyclic carbonate is 1.25). It shows that most of the cyclic carbonate was disappeared after 24 hours reaction. Figure **6** shows the polyurethane formation with different amine to cyclic carbonate ratio when curing time is fixed. It shows that when the amine to cyclic carbonate mole ratio is 1.25, most of the cyclic carbonate was disappeared after 24 hours reaction.

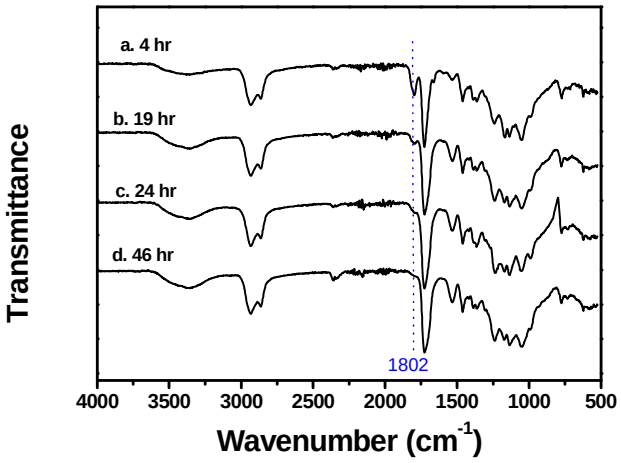


Figure 5. FTIR spectra of non-isocyanate polyurethane formation with time by using CC-PE cured with IPDA under 70^{o}C (NH_2/CC=1.25).

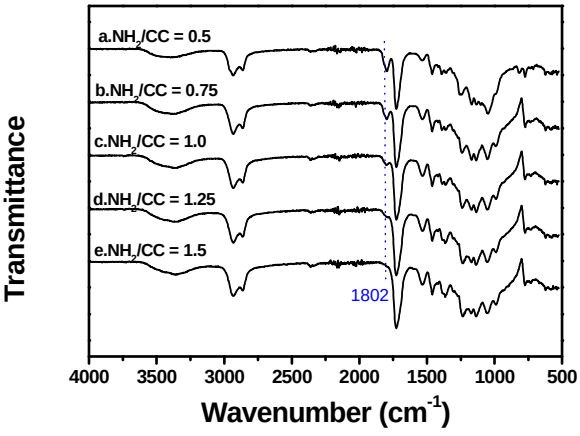


Figure 6. FTIR spectra of non-isocyanate polyurethane formation at different amine to cyclic carbonate ratio by using CC-PE cured with IPDA under 70^{o}C.

Summary

In summary, the hydroxyl terminated, epoxidized, and cyclic carbonate terminated polyesters were synthesized and characterized by NMR. The cyclic carbonate terminated polyester formation with time was monitored by using IR spectroscopy. Nonisocyanate polyurethane coatings were prepared by the thermo-curing of the cyclic carbonate terminated polyester and polyamine.

Reference

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