카르복실화된 폴리카프로락톤디올을 가진 수분산 폴리우레탄의 제조와 특성(II)

- 카르복실화된 소프트 세그멘트 조성과 평균 분자량의 영향

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Preparation and Properties of Waterborne Polyurethane Anionomers based on Carboxylated Polycaprolactonediol

- Effects of the Carboxylated soft-segment composition and Average molecular weight

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1. Introduction

Polyurethanes are used for a wide range of commercial applications such as adhesives or coatings for various substrates including textile fablics, plastic, wood, glass fibers and metals. The types of polyurethane ionomers have been reported according to the ionic charges on the polymer main chain, i.e. , anionomers[1], cationomers[2], and zwittericonomers[3]. Ionization causes improved toughness, tear strength, and abrasion resistance. The presence of the ionic species in Pu ionomers has a considerable effect on the physical properties, and it is reasonable to suppose that the interactions between ions and their counterions are responsible for these effects. One of the most important characteristic of many polyurethane ionomer is their ability to disperse or dissolve in water if a sufficient amount of ionic moiety is incorporated[4].

In this study, the carboxylate group was introduced into the PCL soft segment and based on this , a new family of polyurethane ionomers was perpared. The microstructure and properties of these ionomers were studied by different techniques.

2. Experimental

2.1 Materials

Materials are described in Table I. Dimethylol propionic acid(DMPA, Aldrich), Polycaprolactone(PCL, Aldrich) was dried at 1 ~ 2 mmHg and 100℃ for at least 5 hours before use. 4,4'-Diphenylmethane diisocynate(MDI, Aldrich), ε-Caprolactone(CL, Fluka), Ethylene diamine(EDA, Aldrich), Triethylamine(TEA, KASEI), Acetone, N-methyl-2 pyrrolidone(NMP, Aldrich), stannous octoate(Fluka) and Dibutyl-tin-dilaurate(DBTDL, Aldrich) were used without further purification.

2.2 Synthesis

Synthesis of Carboxyl polycaprolactone(CPCL)

The reaction proceeded under nitrogen protection in a four - necked round-bottom flask equipped with a reflux condenser, a gas inlet, a stirrer and a thermo-sensor. Caprolactone was mixed with the stoichiometric amount of dimethylol propionic acid (and stannous octoate catalyst). After reaction at 80℃ for 24 hours, the products were vacuum distilled to remove the unreacted CL. Then washed with water to remove the unreacted DMPA(and stannous octoate). The products were dried in a vacuum oven at 80℃ for a week. The oligomers were characterized by titration and DSC measurement. The results are shown in Table II.

Synthesis of the waterborne Polyurethane-urea

The distilled Carboxylated Polycaprolactonediol(CPCL) and 4,4'-Diphenylmethane diisocyanate(MDI) were heated to 50℃ with stirring to homogenize. Acetone(10 wt%) and DBTDL (150ppm)catalyst were then added to the mixture and reacted at 80℃ under nitrogen atmosphere until the theoretical NCO content was reached as determined by the di-n-butylamine titratior method. The NCO-terminated prepolymer was neutralized by triethylamine(TEA) at below 50℃ for 30min. Then was chain extended by adding chain extender with water by dropping for 1hour at below 40℃. The dispersion was stirred for 1hour.

Waterborne Polyurethane-urea of Ca. 35wt% solids was obtained upon removal of actone by rotary vacuum pump. Polyurethane-urea films were cast from emulsion on a Teflon plate and dried at 70℃ for 12hours. The remaining moisture was removed at 60℃ 20mmHg for 3 days.

2.3 Characterization

Particle size analysis was done using light-scattering equipment (Autosizer, Melvern IIC). A few drops of the dispersion were diluted in deionized water before the measurement.

FT IR spectra were collected using a Nicolet impact 400D at resolution of 4 cm^{-1}, and 32 scans were signal-averaged at room temperature.

The thermal behavior of samples was examined by using a DSC 220C (Seiko) at a heating rate of 10℃/min under a nitrogen atmosphere.

Thermal analysis of aqueous dispersion of polyurethane was carried out using TGA(TA instruments) over the range 30 °C to 600 °C at a heating rate of 20 °C/min. Sample was taken from aqueous dispersion of polyurethane film.

Tensile properties were measured at room temperature using Untied Data System(Instrong, SSTM-1) tensometer following the ASTM D-638 specfication. A crosshead speed of 20mm/min was used throughout these investigations to determine the ultimate tensile strength and elongation at break for all the samples. The values quoted are the average of four or five tests.

3. Results and Discussion

Waterborne polyurethane anionomers were prepared by polyaddition reaction using 4,4′-Diphenylmethane diisocynate(MDI), Carboxylated polycaprolactonediol (CPCL) and ethylene diamine as a chain extender, followed by neutralization of pendant COOH group was introduced into the PCL soft segment. IR-Peak of this composition are shown in Figure 1. DSC data of dried CPCL and PCL were shown in Table II. It could clearly be observed that Tm of CPCL increased with increasing molecular weight. Tm and ΔH of CPCL were lower than those of PCL. It is because of this that the carboxylate disturbs the close packing of the CL and reduces the cohesions

4. References

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Sample	MDI Mol (weight)	CPCL Mol (weight)	DMPA weight in CPCL	DMPA Mol (weight)	EDA Mol (weight)	TEA Mol (weight)	COOH (%)	Solids (%)
CPu-8 (Mn 800)	3.1 (15.510g)	1(16g)	0.4534 (6.621g)		2 (2.4072g)	0.4534 (0.9176g)	1.2	35%
CPu-13 (Mn 1300)	3.1 (15.510g)	1(26g)	0.4923 (11.718g)		2 (2.4072g)	0.4923 (0.9963g)	1.01	35%
CPu-20 (Mn 2000)	3.1 (15.510g)	1(40g)	0.5095 (18.767g)		2 (2.4072g)	0.5095 (1.0311g)	0.79	35%
Pu-20 (Mn 2000)	3.1 (15.510g)	1(40g)		1(2.6826g)	1 (1.2036g)	1 (2.0238g)	1.52	35%

Table I. Formulation details for the WPu synthesis

Sample	Mn(Theroy)	Tm(℃)	⊿H (J/gdeg)
CPu-8	800	28.8	19.1
CPu-13	1300	30.0	21.5
CPu-20	2000	31.1	22.4
Pu-20	2000	47.9	90.9

Table II. PCL and the Synthesized CPCL

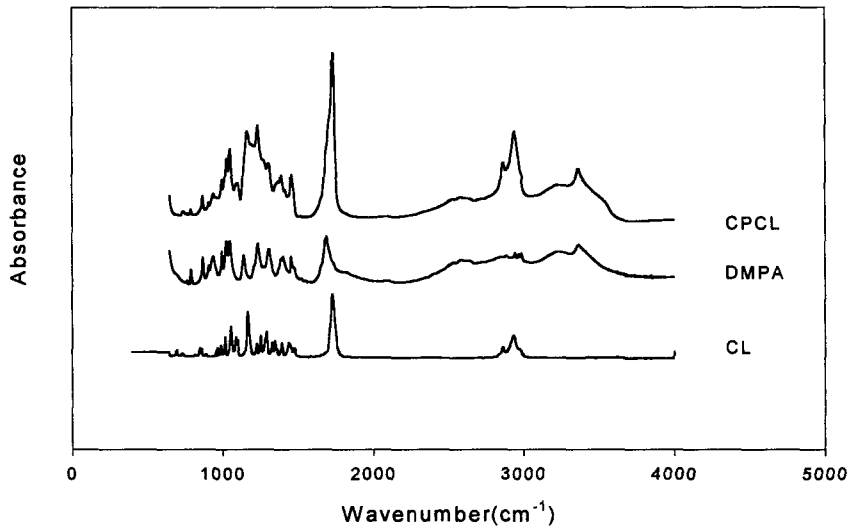

Figure 1. IR-Peak of Caprolactone(CL), Dimethylol propionic acid(DMPA) and Carboxylated polycaprolactone(DPCL)