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Effect of ionic group on the behaviour of polyurethaneurea emulsion*

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A novel linear polyurethaneurea emulsion was synthesized from poly(propylene oxide) diol, toluene diisocyanate, dimethylol propionic acid, 2-methyl-1,3-propane diol and ethylenediamine. The effect of the fraction of and the distribution of ionic group on the properties of polyurethaneurea emulsion was investigated by infrared spectroscopy (i.r.), differential scanning calorimetry (d.s.c.), transmission electron microscopy (TEM), a rotary viscometer, etc. In polyurethaneurea investigated, hydrogen-bonds existed not only in the hard segment but also in the soft segment. With increasing the fraction of ionic groups, microphase separation was enhanced and the polyurethaneurea emulsion viscosity increased. In addition, the synthetic method has a profound effect on the distribution of ionic groups, and the emulsion having well-distributed ionic groups is more stable in storage. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyurethaneurea; ionic group; 2-methyl-1,3-propane diol)

INTRODUCTION

Polyurethane is extensively hydrogen-bonded owing to the existence of a variety of polar groups and higher electronegative atoms such as N and O. In polyether polyurethane, the -NH group of the urethane linkage in the hard segment is the donor, ether oxygen in the soft segment and carbonyl group in the hard segment are the hydrogen-bonded acceptors[1]. If -NH groups are hydrogen-bonded with -O- in the soft segment, microphase mixing is favoured; however, if they are hydrogen-bonded with carbonyl groups in the hard segment, microphase separation is favoured. Microphase separation has a profound influence on the mechanical properties of polyurethane.

Introduction of ionic group into the polyurethane would be expected to alter intermolecular bonding and morphology. In general, ionic groups are introduced by using a chain extender containing carboxylic[2], a sulfonate[3] or a tertiary amine group[4,5]. These ionic groups in the hard segment would strengthen the interaction between the hard segments. In spite of the fact that many previous investigations have reported on the microphase structure in conventional polyurethane[6–10], little attention was paid to the effect of ionic group, such as its concentration and its distribution, on polyurethane emulsion.

In this study, a series of stable linear polyurethaneurea emulsions were synthesized, and the effect of ionic group on the behaviour of hydrogen-bond and the properties of polyurethaneurea emulsion was determined by infrared spectroscopy, differential scanning calorimetry, transmission electroscopy, a rotary viscometer, and so on.

EXPERIMENTAL

Materials

Poly(propylene oxide) diol (PPOD, Tienjin Petroleum Chemical Factory) with a molecular weight of 2000, which has secondary hydroxyl groups as terminal groups, was dehydrated under vacuum at 100°C for 4 h before use. Toluene diisocyanate (TDI, Shanghai Chemicals Co. 2, 4/2, 6 isomer = 80/20) and 2-methyl-1,3-propane diol (MPDO, MP diol, ARCO Co.) were distilled under reduced pressure. Dimethylol propionic acid (DMPA, Tokyo Chemicals Co.) was dried in vacuum at 80°C for 4 h. Dimethylformamide (DMF), triethylamine (TEA), ethylenediamine (EDA), and acetone were dried over 40 nm molecular sieves for 1 week.

Synthesis

PPOD was heated to 80°C under nitrogen atmosphere, followed by adding dropwise TDI into PPOD, and the reaction continued until NCO value approaching a theoretic value by using the standard dibutylamine method titration. The NCO-terminated prepolymer was obtained, and cooled to 60°C. DMPA and MPDO (dissolved in DMF) were added dropwise into NCO-terminated prepolymer, the reaction was carried out at 60°C for 6 h, then cooled to 40°C, and neutralized with TEA (dissolved in acetone) for 1 h, then EDA was added and stirred for an additional hour, then deionized water was added slowly, and stirred vigorously for 30 min. The acetone added during the reaction was distilled under reduced pressure, and a stable anionic polyurethaneurea emulsion (APU) was obtained. The appearance of APU

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varied from a transparent solution to a milky white emulsion with a solids content of about 30%.

Infrared spectroscopy

I.r. studies were carried out on a Nicolet 20SX FTIR spectrophotometer. The prepolymer solutions during the reaction were casted directly on KBr windows and dried under an i.r. lamp for 15 min, then analysed. The number of scans per spectrum was 32.

Differential scanning calorimeter

A Du-Pont 1090 thermal analyser was used to examine the thermal properties of the emulsion-cast films over the temperature range of −120 to 200°C. The heating rate was 20°C min^{-1} and the sample size was 10 mg or so. Film is prepared by casting emulsion on a polytetrafluoroethylene plate, followed by drying at 80°C for 8 h. The transparent film obtained, then dried in vacuum for 4 h.

Transmission electron microscopy

The particle size of APU emulsion was observed with a JEM-100CX transmission electron microscope, which operated at 100 kV. The APU emulsion was coated on copper grids of 300 or 400 mesh, and stained with OsO_4 for 1 week.

Molecular weight measurement

Molecular weights of APU were determined by a German Knauer Liquid Chromatograph. The eluent was DMAc, and refractive index detector was used with polystyrene calibration.

Viscosity measurement

A NDJ-79 rotary viscometer was used to measure the rotational viscosity of APU emulsion (solids content 20%) at 25°C.

High temperature stability

APU emulsion with 20% solids content were heated at 60°C for 48 h, then observed whether coagulation happened.

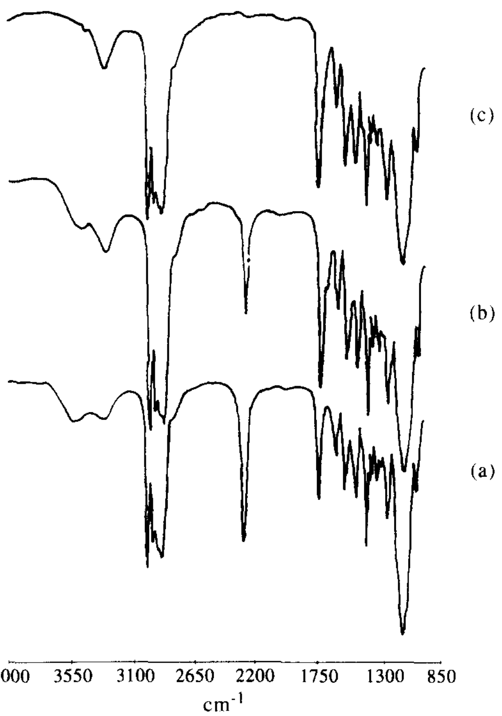

Figure 1 I.r. spectrum of APU prepolymer at room temperature: (a) prepolymer of PPOD and TDI; (b) prepolymer of DMPA and prepolymer (a); (c) polyurethaneurea

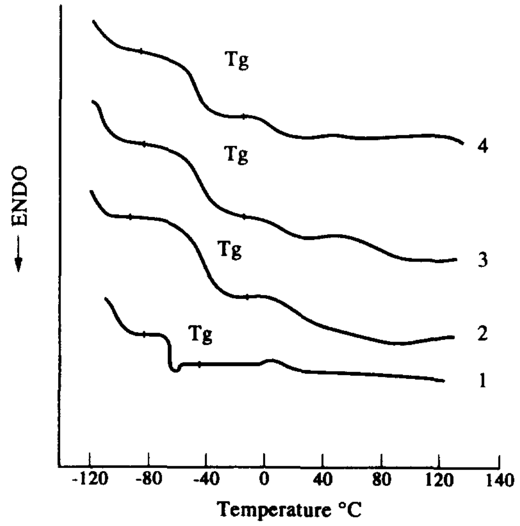

Figure 2 D.s.c. curves for PPOD and APU films: 1—PPOD; 2—APU-42; 3—APU-40; 4—APU-1

RESULTS AND DISCUSSION

Effect of ionic group on the behaviour of hydrogen-bond during the reaction

Figure 1 shows the i.r. spectrum of the samples, which were analysed just after the prepolymerization of PPOD and TDI (a), introduction of ionic group (b) and chain-extension with EDA (c), respectively. Before the introduction of ionic group, urethane carbonyl groups are non-hydrogen-bonded (peak located at 1731 cm^{-1})[11], and more free -NH groups (peak located at 3449 cm^{-1}) exist than hydrogen-bonded -NH groups (peak located at 3295 cm^{-1}) with -O- in the soft segment[12]. When ionic groups were introduced, urethane carbonyl groups are completely hydrogen-bonded (peak located at 1724 cm^{-1}). Meanwhile, the peak area of hydrogen-bonded -NH group at 3295 cm^{-1} increases, and the peak area of free -NH groups at 3449 cm^{-1} decreases. After the chain extension, -NCO absorption at 2273 cm^{-1} disappears and -NH groups are almost completely hydrogen-bonded, which shows a small shoulder at 3450 cm^{-1}. No allophanate absorption band at 1708–1653 cm^{-1} has been observed, this might be due to its concentration below the detection of i.r. measurements[9]. From these i.r. analyses, it is concluded that -NH groups are hydrogen-bonded not only with carbonyl groups in the hard segment, which has an absorption band at 1724 cm^{-1}, but also with -O- in the soft segment, which has an absorption band at 3295 cm^{-1}. Moreover, the carboxyl group is more polarized than a carbonyl group, thus exhibiting a stronger hydrogen-bonded ability.

Effect of ionic group fraction on the property of APU

In d.s.c. analysis, the width of transition zone provides a qualitative measure of phase homogeneity, and the

Table 1 D.s.c. data for PPOD and APU with different ionic fraction

Sample[a]	Ionic fraction (molar ratio[b] %)	MPDO fraction (molar ratio %)	M_n $\times 10^4$	T_g (°C)	T_{onset} (°C)	T_{end} (°C)	Zone width (°C)
PPOD	0	0		−67.4	−70.5	−66.3	4.2
APU-42	11.2	3.6	3.7	−46.6	−58.3	−34.5	23.8
APU-40	18.6	0	4.0	−47.2	−57.3	−38.0	19.3
APU-1	20.2	0	2.7	−50.7	−59.5	−40.5	19.0

[a] The hard segment content of all samples is 19.5% (wt) except PPOD
[b] The molar ratio is the ratio to the polyurethaneurea as a whole

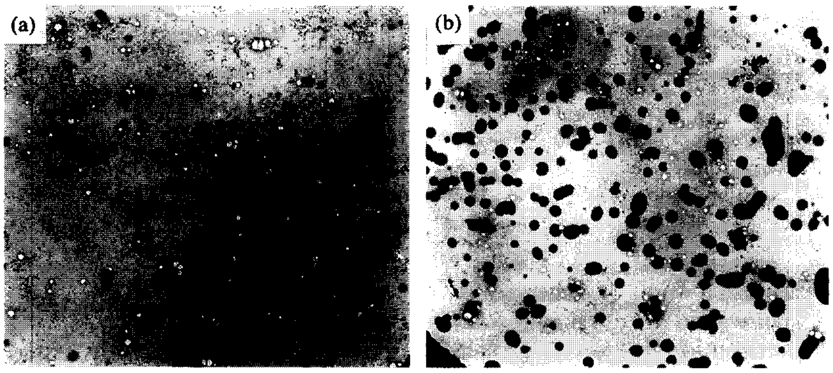

Figure 3 TEM micrographs of APU emulsions with different ionic fraction (x 1000): (a) APU-41 (ionic fraction: 14.8%); (b) APU-44 (ionic fraction: 8.9%)

variation in the magnitude of T_g indicates the degree of microphase separation[1]. *Figure 2* shows the d.s.c. curves for PPOD and the various APU with different ionic fraction. From these T_g data (see *Table 1*), it is found that the T_g of all APU is higher than that of PPOD. According to the result of i.r. analysis, a strong hydrogen-bond between the hard segment and the soft segment exists, small amounts of hard segment dissolved in the domain rich in soft segment, resulting in an elevation in the soft-segment glass transition temperature. In addition, a decrease in T_g and narrowing the width of transition zone are observed as the fraction increases although the molecular weights of APU are different. This suggests that increasing ionic fraction improves the microphase separation. With an increase in ionic group, the interaction between the hard segments, such as hydrogen-bond and Coulombic interaction, increases, thus less hard segment dissolved in the domain rich in soft segment and microphase separation is enhanced; in consequence, the T_g of APU approaches the T_g of PPOD.

In order to study the effect of ionic fraction on the behaviour of APU emulsion, APU emulsion was investigated by TEM and a rotary viscometer.

Figure 3 shows TEM micrographs of two APU emulsions with different ionic fraction. It can be seen that the particle size of emulsion decreases with increasing ionic fraction. This is ascribed to the hydrophilicity of APU. In the APU emulsion, ionic groups are located on the surface of droplets owing to the difference of hydrophilicity between ionic centre and hydrophobic segment. Furthermore, the surface tension of droplets depends on the number of ionic groups on the specific surface of droplets. As ionic fraction increases, the number of ionic groups located on the specific surface of droplets increases, and the surface tension decreases, thus APU disperses in a small size.

The results of rotary viscosity measurement are listed in *Table 2*. APU emulsions have a more or less extensive boundary layer, where the water content increases in the outward direction[4]. As ionic fraction increases, this effect becomes more significant, so the turbidity decreases and almost clear solutions are obtained. Meanwhile, as ionic fraction increases, the viscosity increases owing to an elevation in the effective hydrodynamic volume with decreasing the particle size[2].

Effect of ionic group distribution on the APU emulsion

According to Seymour and Cooper[1], the endotherm region observed in the d.s.c. for polyurethane may all be ascribed to morphological effect, and different degree of short-range order may exist simultaneously due to the distribution in hard segment length. Two APU emulsions with the different distribution of hard segment

Table 2 Effect of ionic fraction on rotary viscosity of APU emulsion

Samples	APU-40	APU-41	APU-42	APU-68
Ionic fraction (molar ratio %)	18.6	14.8	11.2	9.3
MPDO fraction (molar ratio %)	0	0	3.6	5.5
Viscosity (MPa s)	22.5	5.6	2.0	2.7
Appearance	Transparent	Translucent	Milky white	Milky white

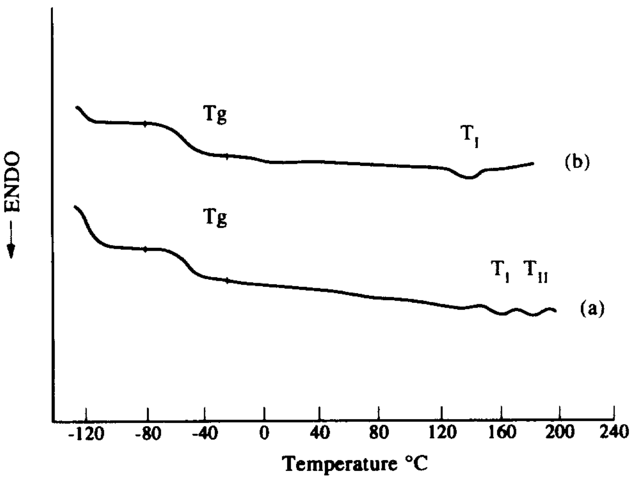

Figure 4 D.s.c. curves for APU with different distribution of ionic groups: (a) APU-66 (one-stage method); (b) APU-44 (two-stage method)

length, that is, the different distribution of ionic groups were synthesized. APU synthesized through two-stage method has a narrow distribution in hard segment length[13] and the ionic groups are well-distributed; However, APU synthesized through one-stage method has a wide distribution because the differences of relative activity of OH groups exist among PPOD and lower molecular weight chain-extenders such as MPDO and DMPA. At the initial stage of reaction with isocyanate, a chain-extender with active OH group is more competitive than PPOD, so longer hard segments form. With a decrease in the concentration of a chain-extender, hard segment length becomes shorter,the ionic groups are not well-distributed as a result of the wide distribution of hard segment length. *Figure 4* shows d.s.c. curves for APU with different ionic distribution. APU-44 synthesized through two-stage method has one endotherm at 145°C, and APU-66 synthesized through one-stage method has two endotherms at 162 and 185°C. Clusters of shorter hard segments give rise to the lower temperature endotherm, while the longer hard segments disorder at higher temperature. In this regard, APU-66 has a wider distribution in hard segment length and a longer hard segment length.

In addition, the stability of these two APU emulsions was investigated by heating at 60°C for 48 h. It was found that APU-66 coagulated, and APU-44 was still stable. This observation suggests that APU emulsion synthesized through two-stage method has a good stability as a result of a well-distribution of ionic group.

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