

Morphology and Mechanical Properties of Urethane Acrylate Resin Networks

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ABSTRACT: A series of urethane acrylate resins (UARs) having various amounts of hard segment were synthesized from poly(oxypropylene) diols (PPOs) with different molecular weights and characterized. The relationship between the morphologies and mechanical properties of these UAR (UARX-Y-Z, in which X means the molecular weight of PPO, Y means the content of hard segment, and Z means the content of comonomer) networks was investigated in detail. It was found that the morphology of the UARX-Y-Z network was related to the contents of hard segment and the comonomer (methyl methacrylate—MMA) as well as the molecular weight of PPOs. The UAR1000-0-34 network synthesized from PPO210 ($M_n = 1000$) is a homogeneous system due to the good compatibility between the PPO210 and the MMA segment. The UAR1000-0-60 network exhibits the morphology of partial microphase separation resulting from increasing the length of the MMA segment, so as to decrease the miscibility between the soft and hard segment. For the UAR1000-30-34 network having a higher content of the hard segment, the hard segments tend to form domains with the limited short-range and long-range order, leading to the formation of the microcrystallites, and therefore it shows higher tensile strength and elastic modulus. For UAR400-0-34 network with lower molecular weight PPO204 ($M_n = 400$), a high glass transition temperature and some microcrystallites were observed. Such a network exhibits the best mechanical properties over all UAR networks studied. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1532–1537, 2000

Key words: urethane acrylate resin; poly(oxypropylene); polymer network; morphology; mechanical property

INTRODUCTION

Urethane acrylate resins (UARs) have been extensively investigated in the past two decades as photocurable coatings useful for protecting some material surfaces such as papers, woods, fibers, and plastics. The photocurable copolymerization

of UAR with different initiation systems and the relationships between the morphologies and physical properties for these UAR networks were studied and reviewed in detail.^{1–4} In a previous paper, the copolymerization kinetics of UARs having various contents of hard segment and different soft segments synthesized from different molecular weights of poly(oxypropylene) diols (PPOs) with 2,2'-azobis-isobutyronitrile (AIBN) as initiator was monitored by means of Fourier transform IR (FTIR), and it was indicated that the network formation for these UARs could be related to the viscosity and the development of

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morphology during the copolymerization process.⁵ In this paper, the relationship between the morphologies and mechanical properties of such UAR networks is reported.

EXPERIMENTAL

Materials

Difunctional poly(oxypropylene) polyols (PPO204, PPO210, and PPO220; hydroxyl number: 235, 95, and 55 mg KOH/g, respectively) were supplied by Gao Qiao No.3 Chemical Plant. Toluene diisocyanate (2,4-TDI) was provided by Shanghai No.1 Reagent Plant. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers.

The diols were dried at 100°C under vacuum for 12 h, then treated with 4A molecular sieves for over one week before use. Methyl methacrylate (MMA) was dried with MgSO₄ for several days after washing through Na₂CO₃ solution, then distilled under vacuum. AIBN was filtered and recrystallized from hot ethanol and dried under vacuum at room temperature. The free radical initiator (AIBN) for UAR was used at 1.96% (by wt) of UAR.

Synthesis and characterization of UAR

UAR was first prepared by reacting PPO204, PPO210, or PPO220 (molecular weight: 400, 1000, and 2000, respectively) with 2,4-TDI (molar ratio of TDI and diol was at 2) at the temperature below 40°C. When the content of the —NCO group in the reaction system dropped to the half amount, which was measured according to ASTM D1638-74, the reaction temperature was raised up to 55°C and hydroxyethyl methacrylate (HEMA) containing a small amount of dibutyltin dilaurate (0.2 wt %) was added in drops to the reaction system (the molar ratio of HEMA and the remaining —NCO groups was at 1). When the concentration of —NCO groups in the reaction mixture was below 0.2 wt %, the urethane acrylate oligomer (UAO) was obtained.

If 1,4-butane diol (BDO) was added in drops to the reaction medium before adding HEMA, the UAOs having various amounts of hard segment were prepared. All procedures for synthesis of UAO have been monitored by using FTIR and have been described in elsewhere.⁵ MMA as comonomer was then introduced into the UAO to

prepare UAR. Since the structure of these UARs are different, for simplicity they are expressed as UARX-Y-Z, in which X means molecular weight of polyol, Y means the weight content of hard segment, and Z means the weight content of comonomer (MMA) in the system.

The number average molecular weight of UAO was measured by using the bromine addition method according to GB12005.3-89 and by using a Waters GPC-244 or KNAUER-11.00 Vapor Pressure Osmometer (VPO). Thus, the number average functionality (f) of these UAOs synthesized can be calculated ($f = 2M_{\text{VPO or GPC}}/M_{\text{c=c}}$). The structure of UAO was further investigated by means of ¹H NMR Bruker WP-100SY.

Preparation of UAR Network

UAR and AIBN were thoroughly mixed with a mechanical agitator at a rate of 1200 rpm for about 3 min under nitrogen atmosphere, and the mixture was cast into a glass mold covered with cellophane film. It was then cured at 80°C for 2 h, and 120°C for 5 h.

Morphology Characterization and Mechanical Property Measurement

Differential scanning calorimetry (DSC) was measured with a DuPont Instrument 1090 Thermal Analyzer at a heating rate of 20°/min. Wide-angle x-ray diffraction (WAXD) measurement was carried out with Rigaku D/max-γ B Instrument. The UAR network sample was cut by using an ultramicrotome (LKB-5, Swiss). This cut specimen was at about 50 nm thickness and was stained with RuO₄. Then, the section of such a specimen was coated with carbon vapor and was observed by using transition electron microscopy (TEM; JEOLTEM-1200EXII). Tensile strength of these UAR networks was measured according to GB1040-79 at 25°C, by using a Shimadza AG-2000A testing machine, and the impact strength was tested according to GB1043-79 at 25°C by means of a Charpy impact instrument.

RESULTS AND DISCUSSION

Characterization of UAO

Table I shows that the number average functionality for the UAOs synthesized are all less than 2.3. This means that there are two double bonds existing at the end of most UAO macromolecular

Table I Some Physical Parameters for UAO

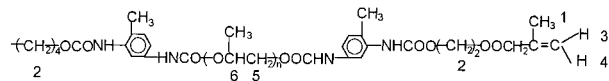
Type of UAOs	Molecular Weight of PPO	Amount of Hard Segment (% by wt)	Concentration of Double Bond ($\times 10^3$ mol/g)	$M_{c=}$ ^a	M_{GPC}	f^c
UAO-400-0	400	0	3.901	1270	1360 ^b	2.14
UAO-1000-0	1000	0	3.360	1930	2150 ^b	2.28
UAO-2000-0	2000	0	3.085	2690	2880 ^b	2.14
UAO-1000-21	1000	21	2.936	3260	3420	2.10
UAO-1000-24	1000	24	2.793	4250	4290	2.02
UAO-1000-30	1000	30	2.637	6349	6540	2.06

^a Calculated from concentration of double bond measured by using bromine standard method.

^b Measurement by using VPO.

^c The number average functionality (f) is expressed as $f = 2M_{GPC \text{ or VPO}}/M_{c=}$.

chains. However, for better investigating the relationship between the morphology and mechanical property of UAR networks, the structure of UAO should be examined further. Figure 1 presents a ¹H-NMR spectrum for the UAO formula having a hard segment (UAO-1000-24) as follows:



It is clear that the peaks can be ascribed to the different kinds of protons, i.e., δ :1.13 (H_{-1H} , s, 3H), 4.28 (H_{-2H} , m, 2H), 5.58 (H_{-3H} , m, 1H), 6.14 (H_{-4H} , w, 1H), 1.68 (H_{-5H} , w, H), 3.60 (H_{-6H} , m, 1H), and the protons on phenyl skeletal at $\delta = 7.3$, somewhat similar to those reported by Rajalinam etc.⁶ Thus, the well-defined UAOs were synthesized and characterized.

Morphologies of UAR Networks

Figure 2 shows the DSC scan plots for some polyol, UAO, and UAR networks. The DSC scan

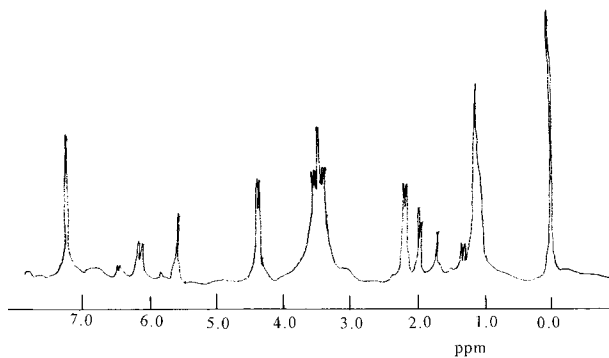


Figure 1 ¹H-NMR spectrum of UAO-1000-24.

results are listed in Table II. The DSC curve of UAO-1000 synthesized from PPO210 ($M_n = 1000$) only exhibits one T_g , which is much higher than that of PPO210 and must result from the good miscibility between the PPO segment and the urethane group tipped by the HEMA unit. Only one T_g for the UAR1000-0-34 network is also observed, indicating that the UAR1000-0-34 network is a homogeneous system at the composition of 66/34 (UAO-1000/MMA, by wt). However, the DSC curve for the UAR1000-0-60 network containing more MMA (60%, by wt) exhibits two T_g s, and they dramatically shift into higher and lower temperatures, respectively, compared with those for pure poly(methyl methacrylate) (PMMA) ($T_g = 111^\circ\text{C}$)⁷ and UAO-1000, due to partial mi-

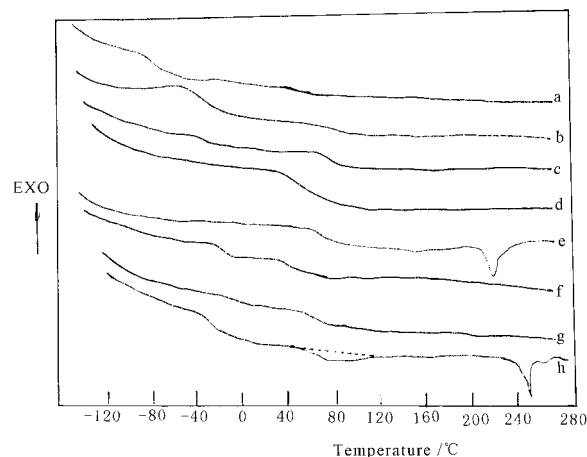


Figure 2 DSC plots for PPO, UAO-1000, and UAR networks. (a) PPO210, (b) UAO-1000, (c) UAR1000-0-60 network, (d) UAR1000-0-34 network, (e) UAR400-0-34 network, (f) UAR2000-0-34 network, (g) UAR1000-24-34 network, and (h) UAR1000-30-34 network.

Table II The Glass Transition Temperatures for PPO210, UAO-1000, and UAR Networks

Type of Samples	T_g (°C)	
	T_{g1}	T_{g2}
PPO210	-69	
UAO-1000	-32	
UAR1000-0-34 network		48
UAR1000-0-60 network	-23	73
UAR1000-24-34 network		61
UAR1000-30-34 network	-18 ^a	
UAR400-0-34 network		77 ^b
UAR2000-0-34 network	-11	32

^a Two endothermic peaks at 80°C (T_a) and 253°C (T_b), respectively.

^b One endothermic peak at 221°C (T_b).

crophase separation of the UAR1000-0-60 network. It is evident that such a partial microphase separation behavior could be induced in the case that there exists longer MMA segments between the two crosslinkage points in the UAR1000-0-60 network.⁸ Damyanidu et al.⁷ have pointed out that the compatibility between PMMA and the poly(ether-urethane) network made from poly(ether polyol) is poor. Thus, the improvement of compatibility in such a network may be attributed to the HEMA unit, which links the urethane group and PMMA segment leading to partial microphase separation.

The DSC curve for the UAR1000-24-34 network having hard segments (24 wt %) exhibits only one T_g , as shown in Figure 2 and Table 2. Thus, it still is a homogeneous system. However, the UAR1000-30-34 network containing more hard segments (30%, by wt) displays one T_g and two endothermic peaks on its DSC plot. It is well recognized that for poly(ether-urethane) the hydrogen atoms existing in urethane groups form hydrogen bonds very easily with the carbonyl of another urethane group as well as the ether oxygen atom of the polyether segment.^{9,10} In this case, the T_g for soft segment of polyether can rise up and the hard segment can tend to aggregate to form domains with the limited short-range order, long-range order or even with microcrystallites.¹¹⁻¹³ Figure 3(a) presents the TEM photo of the UAR1000-30-34 network. It is clear that the hard segments aggregate each other to form domains whose diameter is less than 100 nm. The interface of these domains is not clear, indicating

that there is some compatibility between the phases. Furthermore, there are some black stripes existing in such domains, which therefore could be attributed to the microcrystallites. This experimental behavior was further observed by means of WAXD, as shown in Figure 4. It shows that there are two small peaks at 18.7° and 21.0° (the equivalent diffraction spaces are at 4.78 and 4.51, respectively), indicating the microcrystallites. Thus, the relative crystalline degree is calculated by using a technique of peak separation and integration with using a computer and found to be at around 23% for such a system.

The DSC scans for UARs synthesized from PPOs having different molecular weights were also measured, as shown in Figure 2 and Table II.

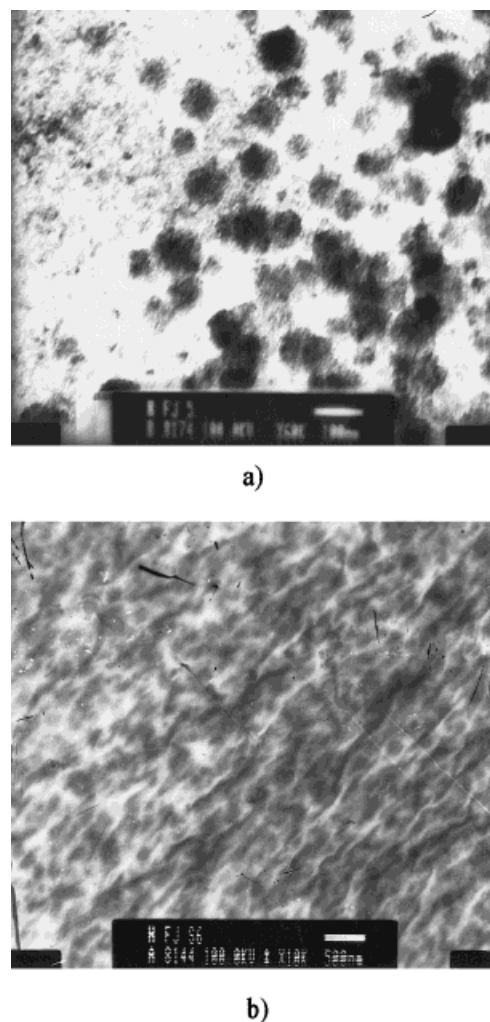


Figure 3 TEM photographs of some UAR networks. (a) UAR1000-30-34 network and (b) UAR400-0-34 network.

For the UAR2000-0-34 network having a longer soft segment, two T_g s are observed on the DSC plot, which must result from increasing the molecular weight of PPO in this network, giving rise to partial microphase separation. Furthermore, it is interesting to find that the DSC curve for the UAR400-0-34 network made from low molecular weight PPO204 ($M_n = 400$) displays one T_g as well as an endothermic peak at 221°C. Since the T_g observed is as high as at 77°C, it should be related to the MMA segments containing some polyether segments in this network. However, the endothermic peak at 221°C may be attributed to the "hard segment" composed of the PPO204/HEMA/urethane group, which seems to arrange in order, as shown in Figure 3b. Figure 4 also shows two weak diffraction peaks at 18.6° and 21.1°C, respectively for this system, indicating that there exists some microcrystallites, in agreement with the observations from DSC and TEM, but its relative crystalline degree is found to be at only 10.5%, which is less than that for the UAR1000-30-34 network. In this case, it means that the ordering structure of the so-called hard segment should be poorer than that of real hard segment composed of the BDO/urethane group for such networks.

Mechanical Properties

Mechanical properties of UAR networks synthesized from PPOs with different molecular weights and having various amounts of hard segment all are listed in Table III. The experimental data show that the UAR400-0-34 network exhibits the highest elastic modulus and tensile strength as well as the

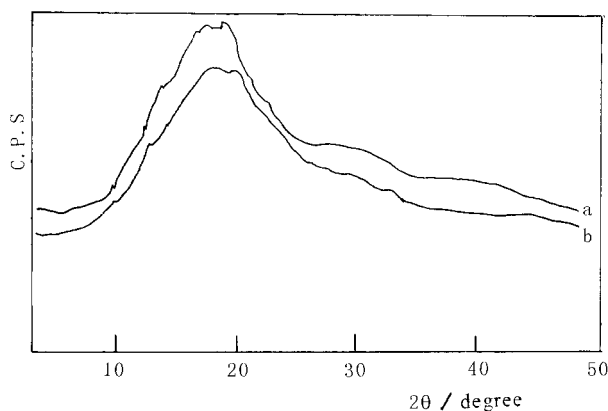


Figure 4 WAXS profiles of some UAR networks. (a) UAR1000-30-34 network and (b) UAR400-0-34 network.

Table III Mechanical Properties for Different UAR Networks

Type of UARs	Elastic Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
UAR400-0-34 ^a	983.0	36.8	8.6
UAR1000-0-34	15.9	9.7	163.0
UAR2000-0-34	4.8	6.2	290.0
UAR1000-21-34	25.8	16.7	184.0
UAR1000-24-34	211.4	18.2	120.0
UAR1000-30-34	315.5	22.4	75.0

^a Impact strength is equal to 30.4 KJ/m². UAR1000-0-34 and UAR2000-0-34 networks are too soft to measure the impact strength.

lowest elongation at break over all the UAR networks synthesized. Furthermore, it also reveals higher impact strength. As mentioned above, for the UAR400-0-34 network, there exists more hard segment structure resulting in microcrystallite and higher T_g , so it not only has excellent rigidity, but also has the better toughness. For UAR1000-30-34 networks, the elastic modulus and tensile strength increase with increasing the content of hard segment in these systems appreciably. It is clear that the hard segment really reinforces the UAR network whose mechanical properties are better than those of polyurethane (PU) containing 41% (by wt) of hard segment and even better than those of interpenetrating polymer networks of PU and vinyl ester resin.¹³ The rigidity of the UAR2000-0-34 network is not good enough. It must result from the longer polyether segments existing in the network leading to this material with quite high elasticity.

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