Microporous polyurethane–acrylamide film cured by electron beam irradiation*

Masayuki Ando, Takakazu Goto, Mitsuru Tsuchiya
Central Research Institute, Dai Nippon Printing Co. Ltd, Ichigayakaga-cho, Shinjuku-ku, Tokyo 162-01, Japan

and Toshiyuki Uryu
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

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The morphology and aggregation structure of electron beam (EB)-cured microporous polyurethane–acrylamide film was investigated. The urethane–acrylamide prepolymer was synthesized by the reaction of poly(butylene adipate)diol, 4,4'-diphenylmethane diisocyanate, and *N*-(hydroxymethyl)acrylamide. It was found from scanning electron microscopy that the urethane-acrylamide film, which was prepared by using a methyl ethyl ketone and dimethylformamide (3:1 v/v) mixture as casting solvent, had a microporous structure with pore size of several micrometres, and that the morphology was fixed by EB irradiation. The pore volume of the EB-cured microporous film was determined to be about 460 $mm^3 g^{-1}$ by mercury porosimetry. The micropores were not destroyed even after immersing in solvent, possibly because the cured film had high crystallinity and dense crosslinking. Moreover, it was found by X-ray photoelectron spectroscopy that terminal portions of urethane–acrylamide were localized at the film surface.

(Keywords: electron beam solid-state polymerization; polyurethane–acrylamide; microporous film; crystallinity; crosslinking; surface structure)

INTRODUCTION

A urethane–acrylate is one of the most useful radiation-curable prepolymers which produces polymeric materials with versatile structures and properties by means of radiation polymerization[1–4]. Using a low energy electron beam (EB) as a radiation source, we have performed studies on the relationships between the structure and properties of the films obtained by EB solid-state polymerization of urethane–acrylates[5–10].

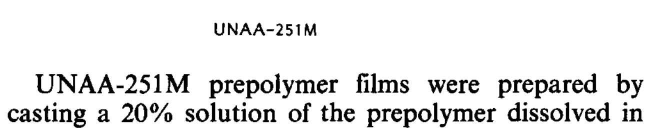
Further investigation of EB-cured films, when an EB-curable prepolymer was changed from urethane–acrylate to urethane–acrylamide and the casting solvent from pure methyl ethyl ketone (MEK) to a mixture of MEK and *N*,*N*-dimethylformamide (DMF), showed that a microporous morphology was found in the prepolymer and EB-cured film. There are few reports on crosslinked materials with micropores[11–14]. Such formation of micropores is of interest from the viewpoints of the control and fixation of the superstructure which polymers induce[15–21]. In addition, such a microporous film is expected to provide a functional membrane.

In this study, we wish to report synthesis and morphology of EB-cured microporous polyurethane–acrylamide films and to characterize them by means of scanning electron microscopy (SEM), mercury porosimetry, the BET method, X-ray diffractometry, differential scanning calorimetry (d.s.c.), and X-ray photoelectron spectroscopy (X.p.s).

EXPERIMENTAL

Materials

Urethane–acrylamide prepolymer (UNAA-251M) was synthesized by a two-step reaction[5]. After 40.0 g (1 eq.) of poly(butylene adipate)diol (PBAD; number average molecular weight, $\bar{M}_n$, about 2500; Nippon Polyurethane Ind. Co. Ltd) were allowed to react with 8.4 g (2 eq.) of 4,4'-diphenylmethane diisocyanate (MDI), 3.4 g (2.1 eq.) of *N*-(hydroxymethyl)acrylamide (*N*-HMAAm) were added to the isocyanate-capped intermediate.



UNAA-251M

UNAA-251M prepolymer films were prepared by casting a 20% solution of the prepolymer dissolved in a MEK-DMF (3:1 v/v) mixture on polyethylene terephthalate (PET) film at 25°C and 65% of relative humidity, followed by evaporating the solvents. Polymer

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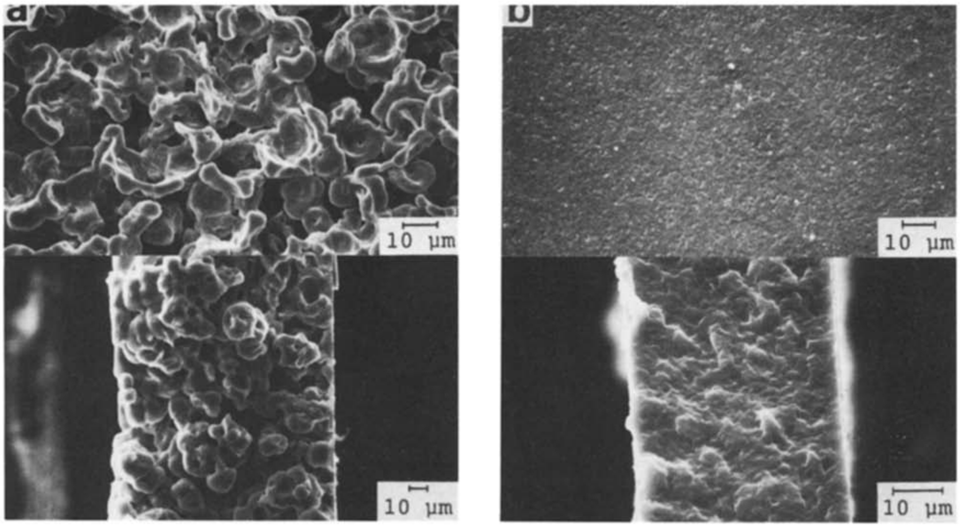

Figure 1 Surface (above) and section (below) SEM photographs of the casting films of UNAA-251M. Casting solvent: (a) MEK/DMF = 3/1 (v/v); (b) MEK

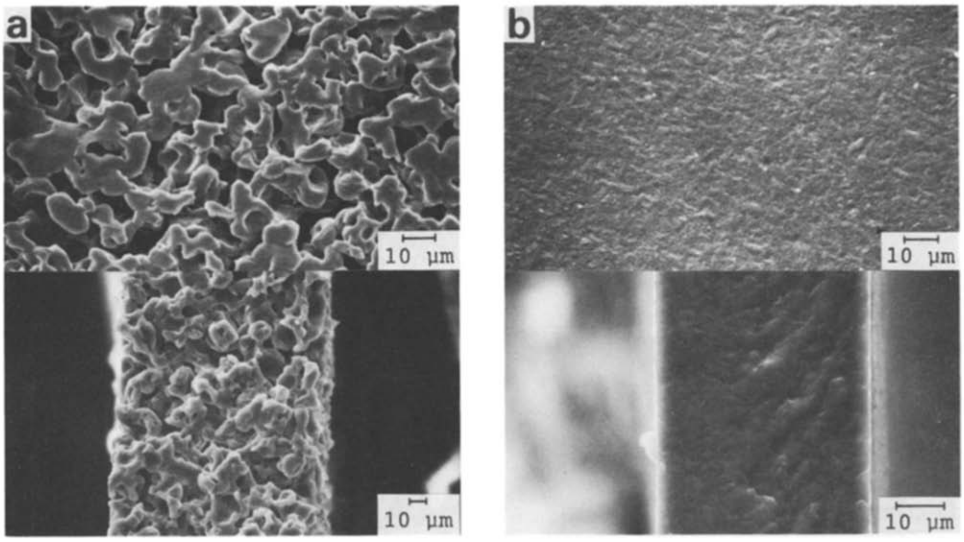

Figure 2 Surface (above) and section (below) SEM photographs of the EB-cured films obtained through extraction with THF after exposing the casting films of UNAA-251M to EB. Irradiation dose: 10 Mrad. Casting solvent: (a) MEK/DMF = 3/1 (v/v); (b) MEK

solution in pure MEK was also cast. It was finally dried under vacuum at room temperature.

Electron beam (EB) irradiation

EB irradiation was performed with an electro-curtain type accelerator (Energy Science Inc.) equipped with a linear filament under a nitrogen atmosphere. The irradiation dose was in the range 0.5–10 Mrad using 0.5–10 mA at an accelerated voltage of 175 kV.

Characterization methods

The morphology of film surfaces and sections was observed using an Akashi SEM (model ALPHA-30W).

Pore volume was determined by using a Carolo Erba Model 2000 porosimeter. The measurement range was from 7.6 to 1.5×10^{-2} m in radius. Surface area, according to the BET method, was obtained from the adsorption measurements with nitrogen by using a Kinoshita KR-2000 surface area measuring instrument.

Crystallinity of the films was examined by X-ray diffractometry and d.s.c. The X-ray diffraction intensity profiles were obtained using a Geigerflex (Rigaku Denki Co. Ltd.) with nickel-filtered CuKα radiation[5]. The d.s.c. thermograms were obtained using a Perkin-Elmer DSC-II. The samples were placed in the d.s.c. at 30°C and then cooled to 0°C, and then the measurement was carried out from 0 to 100°C at a heating rate of 20 deg min^{-1} under a nitrogen stream.

The mechanical strength of the films was estimated using a Tensilon (model UTM-III-100, Toyo Baldwin Co. Ltd)[5].

The structure of the film surface was evaluated from the chemical composition analysed by X.p.s. The X.p.s. spectra were obtained using a V. G. Scientific ESCA LAB-MK-II with a MgKα X-ray source. The X-ray gun was operated at 12 kV and 20 mA. For determination of binding energy, the highest resolution spectrum was obtained with a 20 eV pass energy, and the energy resolution was 0.1 eV. The take-off angle, which is

Table 1 Crystallinity of various films of UNAA-251M

Casting solvent	Dose (Mrad)	Gel fraction (%)	X-ray dffractometry		D.s.c.
			Degree of crystallinity (%)	Crystallite size (Å)	Heat of fusion, ΔH (cal g^{-1})
MEK/DMF (3/1 v/v)	0	0	42.0	338	16.0
	10	83.3	32.5	162	10.1
MEK	0	0	40.1	130	13.8
	10	86.4	28.0	111	9.0

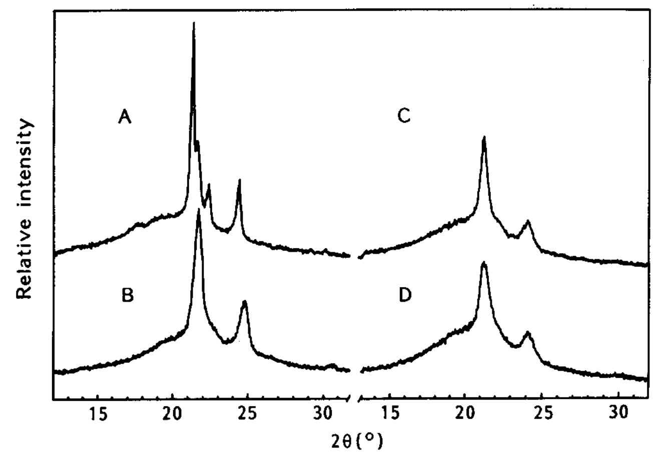

Figure 3 X-ray diffraction intensity profiles for the casting films of UNAA-251M (A, B) and their EB-cured films obtained through extraction with THF (C, D). Irradiation dose: 10 Mrad. Casting solvent: (A, C) MEK/DMF = 3/1 (v/v); (B, D) MEK

designated as the angle between the normal to the sample surface and electron collection optics, was fixed at 15°. The chemical composition (mole fraction) was calculated using the relative yield factors according to Jorgensen *et al.*[22]. For comparison, elemental analysis of UNAA-251M was carried out by using a Yanagimoto CHN Corder MT-3 (Yanagimoto Seisakusho Co. Ltd).

RESULTS AND DISCUSSION

Morphology

Prepolymer films for EB irradiation were prepared by casting from MEK/DMF = 3/1 (v/v) and MEK solutions of UNAA-251M in order to investigate the effects of casting solvent on the structure of the EB-cured films. After drying, these surfaces and sections were observed by using an SEM (*Figure 1*). The film (*Figure 1a*) cast from the MEK/DMF = 3/1 (v/v) solution exhibited a microporous morphology with pore sizes of several micrometres. Sectional photographs of the film showed that the micropores exist throughout the film. On the contrary, the casting film (*Figure 1b*) from the MEK solution of UNAA-251M had no pore and showed the characteristic of uniform solid film. Such microporous prepolymer film was readily polymerized by EB irradiation to reach 83% of the gel fraction at 10 Mrad. The gel fraction was comparable to the gel fraction of the uniform film.

As shown in *Figure 2*, this microporous morphology was fixed by EB irradiation. Although SEM observations of the two types of crosslinked films shown in *Figure 2* were performed after tetrahydrofuran (THF) extraction of the soluble components from as-irradiated films, the microporous morphology of the prepolymer scarcely changed. A decrease in unevenness of the surface and slight shrinkage of the film were seen. Thus, using EB-reactive prepolymer, the morphology formed during vaporization of the mixture solvent can be fixed by being accompanied by high crosslinking. So far, various attempts to fix the morphology of polymers have been performed[18–21], but there has been no report that EB solid-state polymerization of a radiation-reactive prepolymer has been carried out for the fixation of morphology.

Pore volume and surface area of the EB-cured micro-

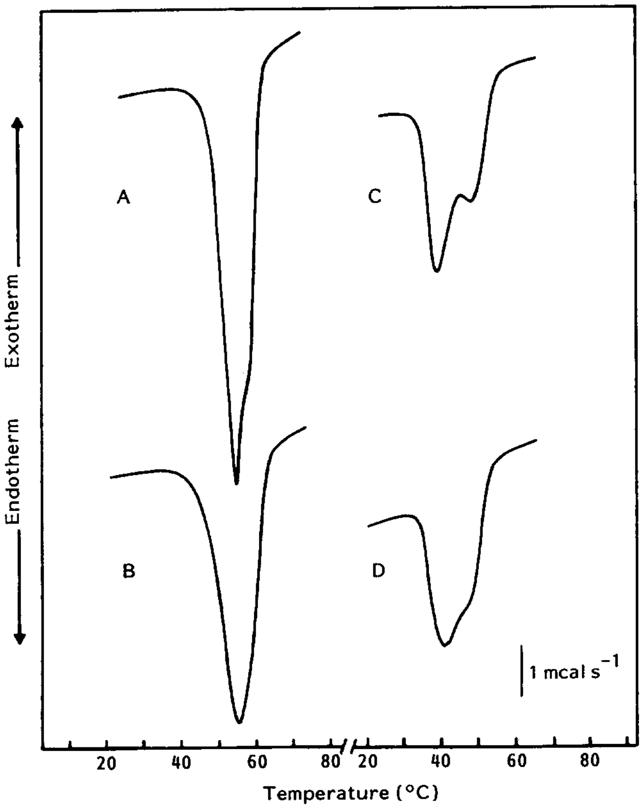

Figure 4 D.s.c. thermograms for the casting films of 251M (A, B) and their EB-cured films obtained through extraction with THF (C, D). Irradiation dose: 10 Mrad. Casting solvent: (A, C) MEK/DMF = 3/1 (v/v); (B, D) MEK

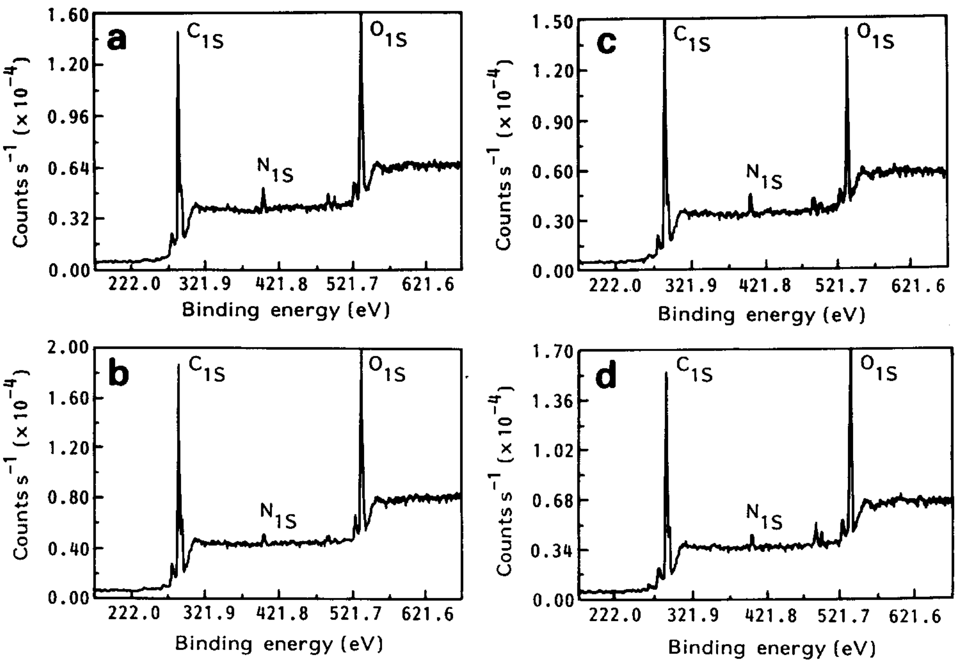

Figure 5 X.p.s. spectra for the casting films of UNAA-251M (A, B) and their EB-cured films obtained through extraction with THF (C, D). Irradiation dose: 10 Mrad. Casting solvent: (A, C) MEK/DMF = 3/1 (v/v); (B, D) MEK

Table 2 Surface characterization by X.p.s. for various films of UNAA-251M

			X.p.s.[a]	
Casting solvent	Dose (Mrad)	Gel fraction (%)	N_{1s}/C_{1s} ($\times 10^2$)	O_{1s}/C_{1s} ($\times 10^2$)
MEK/DMF = 3/1 (v/v)	0	0	8.4	37.0
	10	83.3	5.3	35.0
MEK	0	0	4.0	38.0
	10	86.4	3.7	38.1

[a] Chemical composition as an atomic ratio

Chemical composition as an atomic ratio determined by elemental analysis for UNAA-251M: N/C ($\times 10^2$) = 4.3; O/C ($\times 10^2$) = 34.7

porous film was determined to be 459 mm^3 g^{-1} and 12.3 m^2 g^{-1}, respectively. These large values imply that the film has a large porosity throughout.

Crystallinity

Since UNAA-251M prepolymer is semicrystalline, it is assumed that the two different morphologies were caused by variation in aggregation structure of polymer chains. Thus, to obtain information on such crystalline structure, the crystallinity of each film was estimated by X-ray diffractometry and d.s.c. The representative X-ray diffraction intensity profile of each film is shown in *Figure 3*. The degree of crystallinity and crystallite size were calculated from the diffraction peaks, as summarized in *Table 1*. It is confirmed that the diffraction peaks are derived exclusively from PBAD moieties.

The microporous film had a higher degree of crystallinity and larger crystallite size than the uniform film both before and after EB irradiation. There was a remarkable difference in the crystallite size. It was revealed that the microporous morphology is formed by constriction and reordering (crystallization) of polymer chains which are caused during successive vaporization of a mixed solvent. Such a morphology was fixed by EB irradiation though there was also a slight reduction in crystallinity[5,15]. The decrease in crystallinity is possibly due to the crosslinking induced by EB also in crystalline regions. Analysis of a first-order endothermic peak in d.s.c. thermograms supported these assumptions (*Figure 4* and *Table 1*).

It is expected that the EB-cured microporous film should have good mechanical strength due to the high crystallinity and crosslinking density. Mechanical strength was examined in terms of tensile testing. The EB-cured microporous film had a strength of about 45 kg cm^{-2} in spite of possessing numerous micropores, being half that of an EB-cured uniform film.

Surface structure

Surface structure of the microporous film was examined by X.p.s. to obtain information on the aggregation structure of polyurethane materials[16]. The X.p.s. spectra are shown in *Figure 5*. The peaks arising from N_{1s} were larger in the microporous films than in the uniform films, independent of the curing state.

To elucidate the concentration of nitrogen atoms at the surface, the chemical composition of N_{1s}/C_{1s} as an atomic ratio was estimated from these spectra together with the chemical composition N/C of UNAA-251M estimated by elemental analysis (*Table 2*). The N_{1s}/C_{1s} values of the uniform prepolymer and its EB-cured films are consistent with the N/C values obtained by elemental analysis, including the film obtained from the MEK solution. On the other hand, the N_{1s}/C_{1s} value of the surface of microporous prepolymer film was twice as large as that of the uniform film, and that of the cured microporous film was 1.2 times as large as that of the latter. This implies that terminal amide groups of the prepolymer are concentrated on the film surface.

In conclusion, successive solvent vaporization produced microporous film with amide groups concentrated on the surface. Such a structure was fixed by EB irradiation to give a microporous film with fairly high mechanical strength.

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