Preparation and Properties of Acrylic Melamine Hard Coating

Go Nishino, Hideki Sugimoto, Eiji Nakanishi

Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

ABSTRACT: Melamine resin polymers exhibit high transmittance, high pencil hardness, and high refractive index. However, high temperatures and long reaction times are required to obtain the desired condensation products. In this study, acrylic-modified melamine resins were synthesized that were cured by irradiation with ultraviolet (UV) light. The synthesized acrylic-modified melamine resins could be cured rapidly due to the radical reaction of the acrylic groups and retained high transparency and high refractive index as features of the melamine resin polymers. The polymerized film by UV curing had low shrinkage and high refractive index. Compared with general multifunctional moiety-type acrylic monomers such as pentaerythritol triacrylate and dipentaerythritol hexaacrylate, the acrylic-modified melamine resins had the same degree of hardness. In addition, flexibility, a feature of the urethane moiety, was imparted to the polymer by the reaction of residual hydroxyl groups with isocyanate. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 307–315, 2012

Key words: acrylic-modified melamine; hardness; transparency; radical polymerization; thin films

INTRODUCTION

Plastics are used in widespread applications, including consumer electronics, furniture, cars, and miscellaneous daily goods. However, they are damaged easily because of their low surface hardness. Therefore, hard coating is widely used in the surface treatment to improve easily damaged plastics.[1–6]

In particular, transparent hard-coated materials are needed in touch-type electronic equipment such as touch panels, cellular phones, notebook computers, digital cameras, optical disks, lenses, membrane switches, small game machines, and PDAs to protect the design of the base materials.

Acrylic resins have high transparency and can improve the surface hardness of plastics by coating as thin films.[3,4] Moreover, they can be cured at low temperature in a short time by irradiation.[7]

However, general acrylic resins have a large volume constriction rate when curing, are not flexible, and are fragile, cracking easily. In addition, it is difficult to use general acrylic resins for the surface treatment coating of lenses, antireflective hard coats, and optical multilayer films, because the refractive index is not high enough.

On the other hand, melamine (1,3,5-triazine-2,4,6-triamine) condensation polymer, produced by treatment of melamine with an acid catalyst after addition of the methylol groups with formaldehyde, possesses high crosslink density.[8,9] Melamine condensation polymer has high transparency, excellent hardness, high refractive index, heat resistance, and possesses waterproof, tracking resistance, and antifouling properties. Therefore, it is applied to melamine facing plates, melamine facing tableware, various painting materials, and heatproof electrical parts. Although the hardness is excellent, it is fragile and requires a long production time at high temperature. If we can develop a rapid cure of acrylic resins while maintaining the desired features of the melamine resins, we can apply this resin to the surface modification of thin films with high heat shrinkage, high refractive index lenses, and antirefractive layers of films and shorten the production time of the product compared with the melamine resins previously described.

The method of processing the hard coat onto the surface of molded products such as cellular phones, notebook computers, and car interior materials includes not only the direct coating but also the insert-molding, that is, plastic injection molding while simultaneously inserting a thin film. Surface treatment by insert-molding has advantages over the direct coating method, such as the improvement of the production speed and yield, and a reduction in costs. In general, the film is heated from 110 to 160°C and pressurized in the insert-molding. Therefore, the elongation percentage is high during this temperature span and a material with high hardness at room temperature is expected. If flexibility at 110–160°C

Correspondence to: G. Nishino (chn15003@stn.nitech.ac.jp).
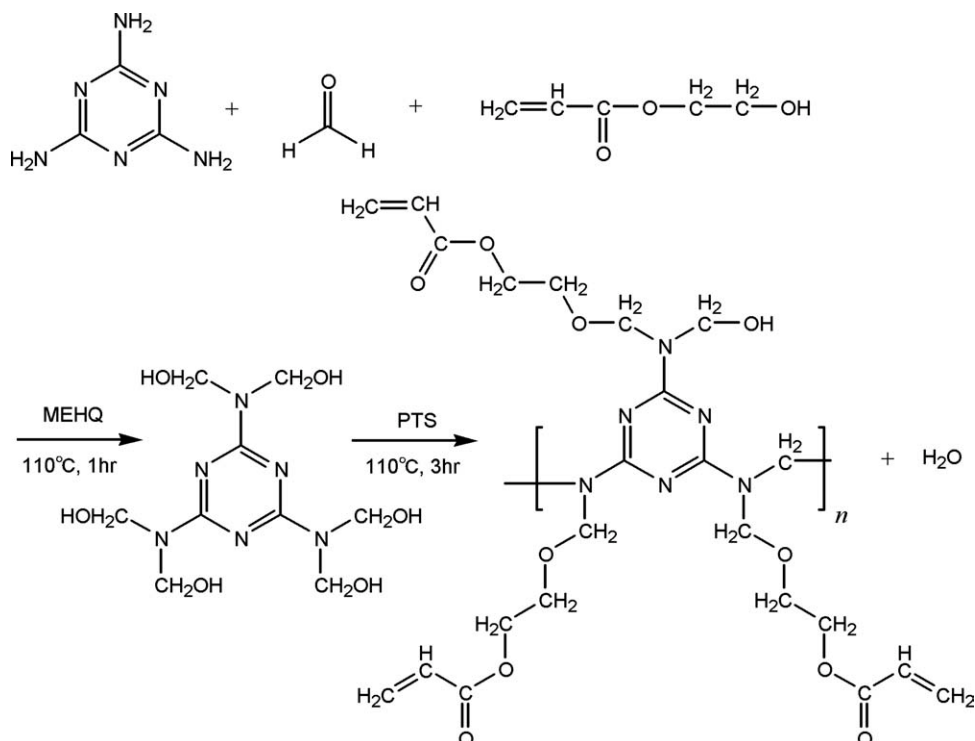
Scheme 1 Synthetic route of AM.

can be imparted to the melamine and acrylic resin, it is possible to manufacture the molded product by performing film insert-molding.

In this study, we synthesized acrylic melamine (AM) via condensation of 2-hydroxyethyl acrylate (HOA) and methylol melamine. In addition, we synthesized urethane-modified AM (UrAM) via the combination of the isocyanate functional moiety to the residual hydroxyl groups of AM. Our goal is the development of a material with high transparency, high hardness, and high refractive index and that possesses excellent molding capabilities.

EXPERIMENTAL

Materials

Melamine was provided by Nissan Chemical. Paraformaldehyde (purity 92%) was provided by Mitsubishi Gas Chemical. HOA was provided by Kyoeisha Chemical. *Para*-toluenesulfonic acid (PTS), used as the catalyst for the condensation reaction, was provided by Meiyu Sangyo, and 4-methoxyphenol (MEHQ; Kishida Chemicals) was used as the polymerization inhibitor. Trimeric isocyanurate (TPA-100) was provided by Asahi Kasei Chemicals. Dibutyltin dilaurate was used as the catalyst for the urethane reaction and was provided by Tokyo Kasei Kogyo. 1-Hydroxy-1-cyclohexylphenyl ketone (Irgacure 184; BASF, Japan) was used as a photoinitiator. 2-Butanone (MEK) (Kishida Chemicals) was used as a solvent.

Synthesis of AM

A typical synthesis of AM is shown in Scheme 1. First step, melamine was reacted with paraformaldehyde in a 1:6 molar ratio with 6 mol of HOA and an appropriate quantity of MEHQ at 110°C for 1 h with stirring. Second step, a given amount of PTS was added, and the reaction was maintained at 110°C. The product (AM6) was obtained by dehydrating for about 3 h. The condensation reaction was confirmed by the appearance of an IR peak attributed to the ether bond (at 1100 cm^{-1}; Fig. 1).

The molar ratio of HOA to melamine was changed to 4 mol (AM4), 5 mol (AM5), 7 mol (AM7), and 8 mol (AM8), and the same synthetic procedure was followed.
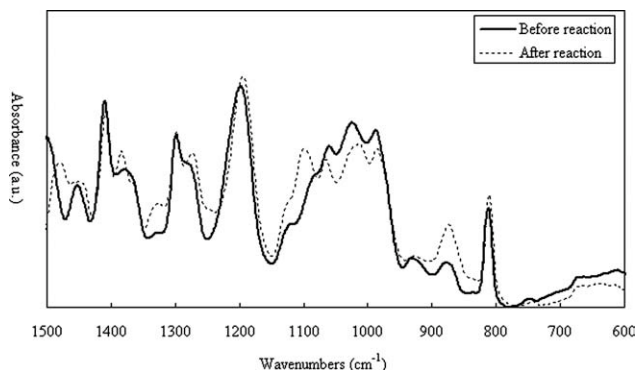

Figure 1 IR spectra of AM6.
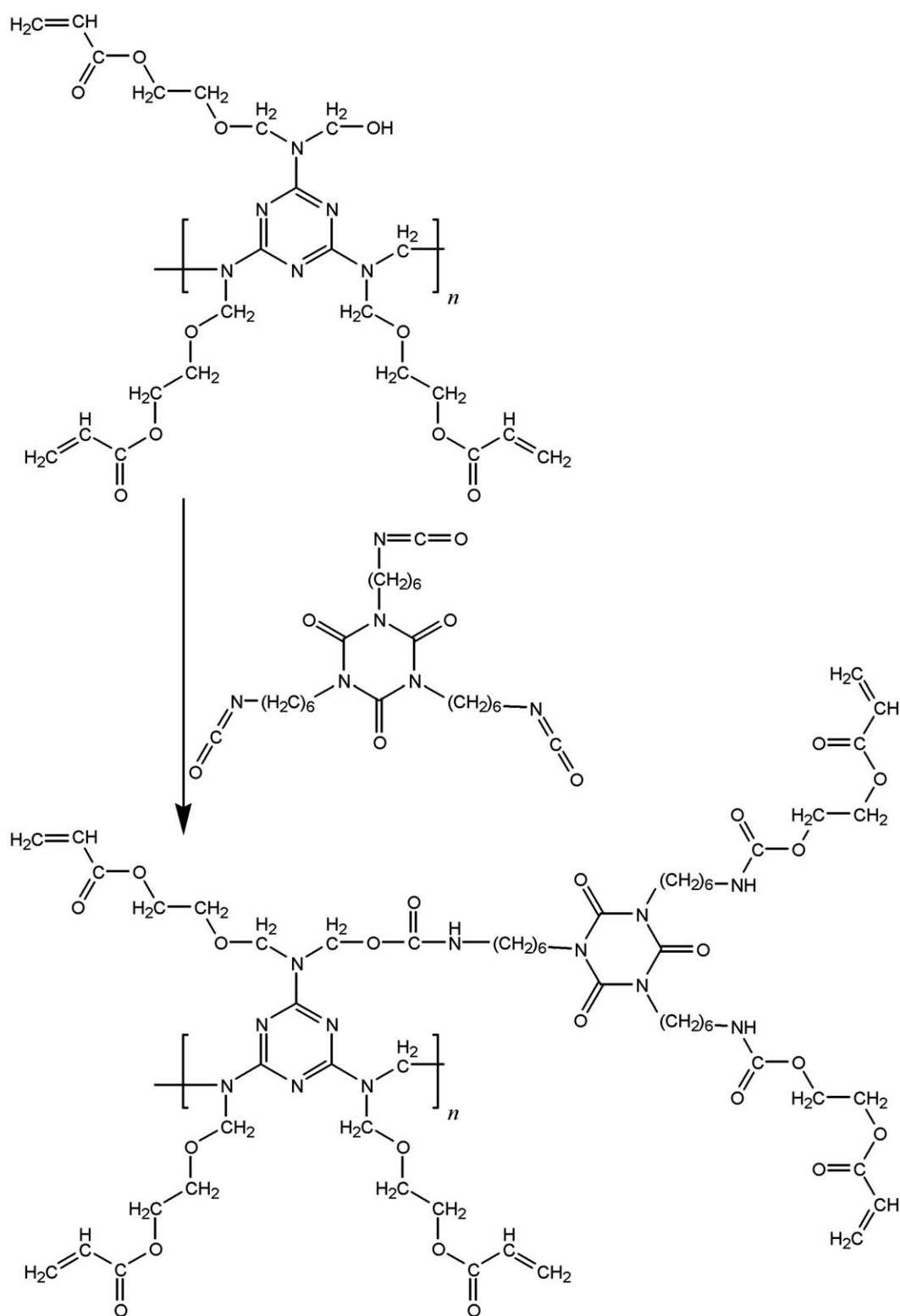
Scheme 2 Synthetic route of UrAM.

Synthesis of UrAM

A typical synthesis is shown in Scheme 2. AM6 (5.00 g) was reacted with trimeric isocyanurate (TPA-100, 1.82 g) and dibutyltin dilaurate (0.03 g) in 2-buta-none (MEK) at 40°C with stirring. The product (UrAM6) was obtained in 1 h. The urethane reaction was confirmed by the disappearance of the peak attributed to the —NCO moiety (at 2280 cm^{-1}) in the IR spectrum (Fig. 2).
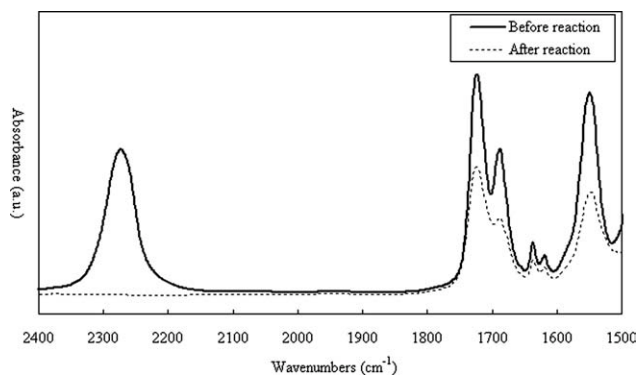
Figure 2 IR spectra of UrAM6.

In addition, UrAM5, UrAM7, and UrAM8 were obtained by the use of AM5, AM7, and AM8 instead of AM6 according to the same procedure.

Synthesis of urethane-modified acrylic resin (Ur-AM)

Urethane-modified acrylic resin without the melamine ring was synthesized as a comparison material. HOA (3.48 g) was reacted with TPA-100 (5.04 g) and dibutyltin dilaurate (0.04 g) in MEK at 40°C with stirring. The product (TPA100-HEA) was obtained in 1 h. The end point of the urethane reaction was confirmed by the disappearance of the peak attributed to the —NCO moiety (at 2280 cm^{-1}) in the IR spectrum.

Preparation of hard-coated PET specimens by photopolymerization

The photoinitiator (Irgacure 184, 0.3 wt %) was added to AM5-8, UrAM5-8, and TPA100-HEA, then the mixtures were each spread on 100 μm of PET film to 4 μm thickness. Ultraviolet light (UV; Fusion UV systems, H bulb, 240 W/cm, 200 mJ/cm^2) was used to irradiate the system to induce polymerization. In addition, dipentaerythritol hexaacrylate (DPHA, Nippon Kayaku) and pentaerythritol triacrylate (PET-30, Nippon Kayaku) were cured by the same procedure.

Measurements

The synthesized AMs were characterized by ^{1}H NMR (Bruker AVANCE 200-MHz NMR spectrometer) and FTIR (Nicolet AVATAR320S spectrophotometer) measurements. Chemical shifts in the ^{1}H NMR spectra are reported as δ values (ppm) relative to tetramethylsilane as an internal standard. Chloroform-*d* was used as the solvent. FTIR spectra were measured in the 4000–400 cm^{-1} region by the liquid film method with a Zn-Se crystal cell. To measure the molecular weight of AM and UrAM, gel permeation

TABLE I
Synthetic Results of AM Series

	M_n	Residual HOA (wt %)	Number of functional groups[a]	Density of acryloyl (wt %)[b]
AM5	1,990	25.1	3.3	39.3
AM6	2,386	26.4	3.9	41.7
AM7	2,204	36.8	3.8	43.7
AM8	2,347	41.8	3.9	45.3
DPHA	594	–	6.0	71.7
PET-30	298	–	3.0	71.4

[a] Number of acryloyl groups to monomer unit.
[b] Weight of acryloyl group/molecular weight.

chromatography (GPC; TOSOH, HLC-8220) was used. Gas chromatography (GC; Hitachi High-Tech, G-3500) was used to estimate the amount of remaining HOA in AM and UrAM by calculating the peak area ratio to the internal standard that was mixed HOA with ethylene glycol monobutyl ether by same contents. Total light transmittance was evaluated by a HAZE-GARD II (Toyoseiki) with the method of JIS K7361-1, and haze was evaluated based on JIS K7136-1 with the same equipment. Refractive indices were measured by multiwavelength Abbe refractometers (Atago DR-M2) at 589(D) nm. Cure shrinkage was recorded as the average warpage of four corners in a 10 cm^2 of curing film. To evaluate the surface hardness of the coating film, pencil hardness (Toyoseiki, Pencil scratch hardness tester, Model No. P) was measured with the method of JIS K5600-5-4 at room temperature. Scratch resistance was measured by a flat-type abrasion tester (Toyoseiki) by using steel wool (Japan steel wool, #0000) as follows: a load of 500 g was placed on a 1-cm^2, 10 round trips of 13 cm were performed, and the number of scratches was measured. To evaluate the moldability, the degrees
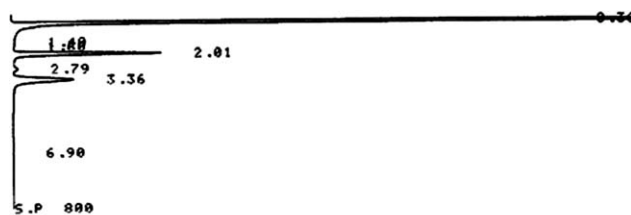
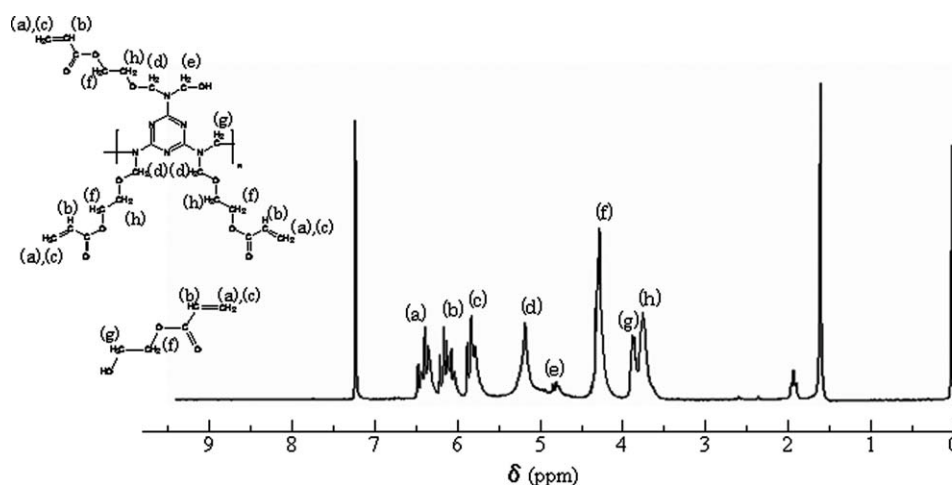| No.	RE (min)	CONC (%)	BC
1	0.36	1797906	88.581
2	1.40	278	0.014
3	1.60	315	0.016
4	2.01	131815	6.494
5	2.79	4849	0.239
6	3.36	93885	4.626
7	6.90	637	0.031
TOTAL		2029685	100

Figure 3 GC spectrum of AM6.

Figure 4 NMR spectrum of AM6.

of elongation and flexibility were measured. Degree of elongation was measured by a tensile tester (Instron, Model No. 5582) at 130°C. Flexibility was measured by a cylindrical Mandrel bending tester (BYK Gardner, No. 5710) by the method of JIS K5600-5-1. Dynamic mechanical analysis (DMA) measurements on the polymer were carried out using a SII nanotechnology model DMS6100 viscoelastometer from 40 to 180°C at 1 Hz, at a heating rate of 2°C/min. The test pieces were cut into 50 mm × 50 mm × 0.1 mm sizes after adding the Irgacure 184 (0.3 wt %) to the resins and curing by UV light.

RESULTS AND DISCUSSION

Characterization of AM

AM4 was not soluble in general organic solvents, because the condensation of the melamine was too advanced. The AM5-8 polymers were soluble in solvents such as chloroform and THF. Table I and Figures 3 and 4 show the results and data from the GPC, GC, and NMR measurements. The amount of remaining HOA was calculated from the peak of HOA detected at 3.36 min by the GC measurement. Using this value, the amount of HOA that reacted with melamine was calculated, and the unit numbers of functional groups were determined. It was

found that three to four molecules of HOA combined with melamine and the two residual methylol groups of melamine contributed to the condensation with the next melamine ring.

The number of acryloyl groups of AM6 increased to 3.9, whereas that of AM5 was 3.3. However, increased molar ratios of HOA as in AM7 and AM8 (number of acryloyl groups, 3.8–3.9) did not increase the number of functional groups. This is because the condensation reaction with HOA and the condensation reaction of the melamine progress simultaneously; therefore, about four functional moieties on average are thought to be involved for one melamine. If one melamine has three HOA functional moieties, the molecular weight of this monomer unit becomes 555. Therefore, about four on average is used to determine the extent of polymerization in the calculation of the number average molecular weight of 2300 based on the GPC measurement.

Next, we focused our attention on the optical characteristics of the UV-irradiated polymers (Table II and Fig. 5). All polymers exhibited excellent optical

TABLE II
Optical Characteristics of AM Series

	Tt (%)	Hz (%)	Refractive index n_D
AM5	91	0.4	1.57
AM6	91	0.4	1.56
AM7	91	0.4	1.56
AM8	91	0.4	1.56
DPHA	91	0.4	1.53
PET-30	91	0.4	1.53
PET Film	91	0.7	–

Figure 5 Film photographs of AM6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Physical Characteristics of AM Series

	Pencil hardness	Scratch resistance (piece)	Flexibility (R)	Elongation at 130°C (%)	Curl (mm)	T_g from tan δ (°C)
AM5	2H	0	1.5	14	0	123
AM6	2H	0	2.5	4	3	91
AM7	2H	0	3.0	7	4	103
AM8	2H	0	2.5	7	5	113
DPHA	2H	0	10.0	1	16	–
PET-30	2H	0	6.0	2	10	–
PET Film	B	Many	–	–	0	–

properties. The polymers were colorless and had transparent total light transmittance (Tt) of 91% and haze (Hz) of 0.4%. The refractive indices of these polymers were 1.56–1.57 and had a high value compared with about 1.53 of DPHA (Nippon Kayaku) and pentaerythritol triacrylate (PET-30, Nippon Kayaku). The high refractive index originates from the triazine ring of the melamine. Because the refractive indices are higher than the usual acrylic resin, applications to a high refractive index layer of antireflective film, surface treatment of base materials with high refractive indices, surface treatment of optical lens, LED sealants, and materials for liquid crystal displays can be expected.

The surface properties of the cured film are shown in Table III and Figure 6. The pencil hardness of AM was 2H, equal with DPHA and PET-30, and the scratch resistance was also equal. In general, it is thought that as the number of functional groups and density of the acryloyl groups become higher, hardness becomes higher, too. However, AM series only had three to four functional groups and about 40 wt % densities of acryloyl groups, yet had the same hardness as DPHA with six functional groups and PET-30 with three functional groups and a density of acryloyl groups of 70 wt %. This is a feature of

the condensation of melamine. In addition, a small value was indicated in curl measurements compared with DPHA and PET-30. In general, as the number of functional groups and density of acryloyl groups become higher, curing shrinkage becomes higher, too. AM has three to four functional groups and about 40 wt % density of acryloyl groups as previously mentioned. The density of acryloyl groups of AM was lower than DPHA and PET-30. This is because many functional groups do not contribute directly to the radical reaction. Flexibility is similarly thought to be excellent because the crosslink density is low. The degree of elongation at 130°C was higher than DPHA and PET-30. Analytical results by DMA are shown in Figure 7. It was thought that flexibility at 130°C was excellent because the synthetic AM inhibited the rigidity of the acryloyl groups and had a glass transition temperature (T_g) of 90–130°C.
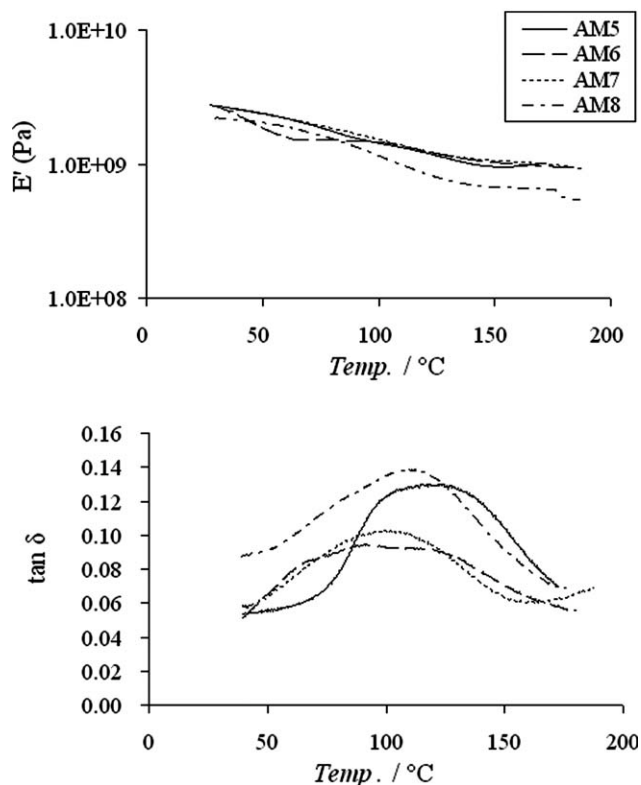

Figure 6 Film photographs of AM6 after scratch resistance test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 7 E' and tan δ of AM series.

TABLE IV
Synthetic Results of UrAM Series

	M_n	Residual HOA (wt %)	Density of acryloyl (wt %)[a]	Density of urethane (wt %)[b]
UrAM5	1,815	7.8	28.8	6.8
UrAM6	1,937	9.8	30.6	6.8
UrAM7	1,713	11.6	32.1	6.8
UrAM8	1,738	12.8	33.2	6.8
TPA100-HEA	852	6.9	25.0	15.1
DPHA	594	–	71.7	0.0
PET-30	298	–	71.4	0.0

[a] Weight of acryloyl groups/molecular weight.
[b] Weight of isocyanate group/molecular weight.

Characterization of urethane-modified acrylic resin (UrAM)

UrAM5-8 polymers were soluble in solvents such as chloroform and THF. The results of the GPC and GC measurements are shown in Table IV and Figure 8. Compared to AM5-8, the density of the acryloyl groups decreased and the urethane groups increased because of the urethane modification. A HOA peak at 3.36 min was detected in the GC measurements. The remaining HOA was decreased by reaction with TPA-100. Based on these results, the number average molecular weight (M_n) did not change drastically compared with AM. This is because the urethane reaction occurred not only with the methylol groups of AM but also with the remaining HOA.

The optical properties are shown in Table V and Figure 9.

UrAM possessed properties similar to AM in the transparency and the refractive index. The refractive index was higher than TPA100-HEA, DPHA, and PET-30 that did not contain melamine.
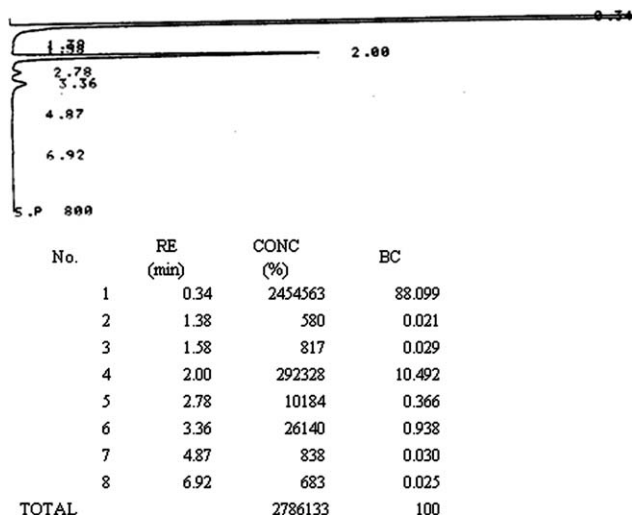
TABLE V
Optical Characteristics of UrAM Series

	Tt (%)	Hz (%)	Refractive index n_D
UrAM5	91	0.4	1.55
UrAM6	91	0.5	1.55
UrAM7	91	0.4	1.54
UrAM8	91	0.4	1.54
TPA100-HEA	91	0.4	1.52
DPHA	91	0.4	1.53
PET-30	91	0.4	1.53
PET Film	91	0.7	–

The physical properties of the polymers that were irradiated with UV light are shown in Table VI and Figure 10. Although it was predicted that the surface hardness would decrease by decreasing the density of the melamine and acryloyl groups, UrAM6-8 had the same pencil hardness and scratch resistance compared with DPHA and PET-30. The surface hardness was maintained even though the acryloyl group density decreased to about 30 wt %. This is because the crosslink density was not decreased by reaction of the remaining hydroxyl groups or methylol groups of AM with TPA-100. On the other hand, the UrAM5-polymerized film was lower in hardness than UrAM6-8. Its pencil hardness was *H*, and scratch was confirmed in scratch resistance tests. This is because the acryloyl group density of UrAM5, 28.8 wt %, was lower than the others. A density of acryloyl group =30 wt % is desirable. Of more interest is an improvement of the elongation percentage. The elongation percentage of the UrAM polymers increased by about 20% by urethane modification compared with the AM series.

T_g is confirmed to be 120–140°C by DMA measurements, and a decrease of storage modulus (E') is

No.	RE (min)	CONC (%)	BC
1	0.34	2454563	88.099
2	1.38	580	0.021
3	1.58	817	0.029
4	2.00	292328	10.492
5	2.78	10184	0.366
6	3.36	26140	0.938
7	4.87	838	0.030
8	6.92	683	0.025
TOTAL		2786133	100

Figure 8 GC spectrum of UrAM6.

Figure 9 Film photographs of UrAM6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Physical Characteristics of UrAM Series

	Pencil hardness	Scratch resistance (piece)	Flexibility (R)	Elongation at 130°C (%)	Curl (mm)	T_g from tan δ (°C)
UrAM5	H	4	1.0	31	0	125
UrAM6	2H	0	1.0	17	1	131
UrAM7	2H	0	1.0	22	1	135
UrAM8	2H	0	1.0	18	1	122
TPA100-HEA	HB	Many	1.0	21	0	95
DPHA	2H	0	10.0	1	16	–
PET-30	2H	0	6.0	2	10	–
PET Film	B	Many	–	–	0	–

shown in this temperature range (Fig. 11). T_g and a decrease of E' also appeared in AM. However, there was only about $0.5E + 1$ (Pa) decrease for AM, whereas UrAM decreased about $1E + 1$ (Pa). This result indicates that the mobility of the UrAM polymers is higher than that of AM. The degree of freedom became higher in the heating region because urethane linkages have high-molecular cohesion and hydrogen bonding. In a similar manner, TPA100-HEA, with a low density of acryloyl groups and urethane linkages, has high elongation percentage and flexibility. However, it does not have triazine rings. Therefore, it has low pencil hardness and scratch resistance.

CONCLUSIONS

In this study, a novel AM that combined melamine with HOA and a UrAM that combined AM with isocyanate were synthesized. The synthetic AM featured high transparency, high refractive index, high

hardness, and low shrinkage. AM possessed both features of the melamine and acrylic groups. Previously, long reaction times were needed in products containing melamine. However, these materials could be cured rapidly by exposure to UV radiation. Therefore, it is possible to expect not only process improvement but also applications of the coating on base materials of low heat resistance or high heat shrinkage. The UrAM had elongation character at 130°C in addition to high transparency, high refractive index, and high hardness. These materials can be applied to the surface treatment of plastic molding by using the film insert-molding method. The melamine-containing polymers had high hardness compared with past acrylic acid ester or urethane
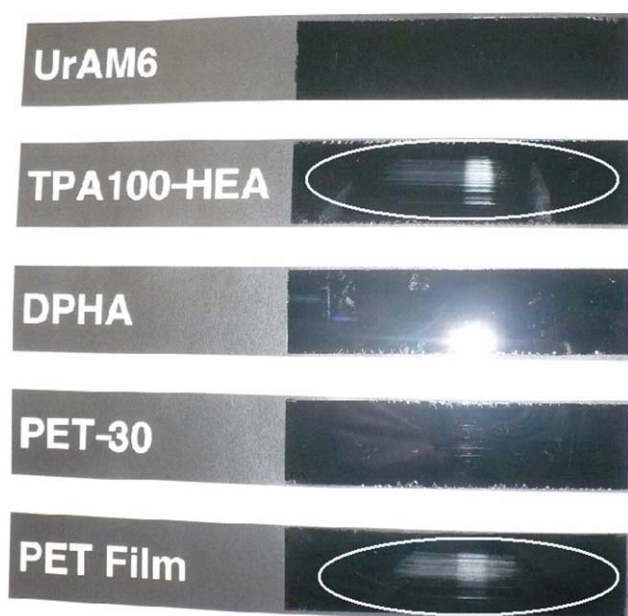

Figure 10 Film photographs of UrAM6 after scratch resistance test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
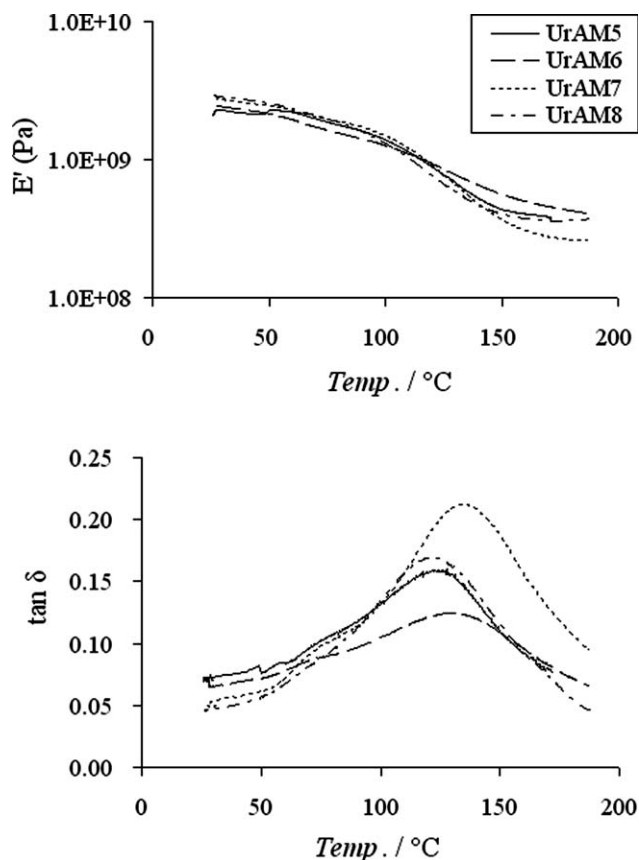

Figure 11 E' and tan δ of UrAM series.

acrylates. Thus, this method produces materials that are excellent not only for their moldability but also for the prevention of surface damage.

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