Rapid and Sensitive Determination of the Conversion of UV-cured Acrylic Ester Resins by Pyrolysis-Gas Chromatography in the Presence of an Organic Alkali

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The double-bond conversion of UV-cured resins prepared from pentaerythritol triacrylate (PETA) was determined by pyrolysis-gas chromatography in the presence of an organic alkali, tetramethylammonium hydroxide (TMAH). The pyrogram of the uncured prepolymer compound, consisting of PETA and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, contained specific products reflecting the original acrylate structure, such as methyl acrylate (MA) and methyl ethers of pentaerythritol. Meanwhile, in pyrograms of the UV-cured PETA, the yields of MA considerably decreased. The double-bond conversions of the cured resins, irradiated with various UV dosages, were calculated based on the relative yields of MA among specific products in the pyrograms. The conversions determined by this approach were analyzed by comparing them with those estimated by Fourier-transform infrared spectroscopy.

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Introduction

Photopolymerization induced by ultraviolet (UV) light has been recognized as being the key technology in various industrial fields because of its distinct advantages, such as low energy requirements, solvent-free systems, and image-forming ability. Nowadays, UV-curing technology has been introduced into advanced applications, such as electronic devices, optical and electro-optical materials, liquid crystal displays (LCD) and stereo-lithography as well as conventional ones, such as paints, inks, and printing plates.¹⁻³ Although several types of UV-curable resins including cationic and thiol-ene systems have been developed, acrylate-based monomers and oligomers are most widely utilized because of their chemical versatility.

Analytical techniques used to determine the degree of cure of photo-cured resins are critical because they affect various properties of the resins, such as the mechanical strength, chemical and heat resistance, and electronic behavior. The most widely utilized method for this purpose is Fourier-transform infrared spectroscopy (FT-IR).⁴ Generally, the conversion of a UV-cured resin can be determined by monitoring the decrease in specific absorptions based on acryloyl groups in the IR spectrum. However, in some applications, such as pigmented coatings and adhesives for lamination, the degree of the cure is difficult to be determined by this approach because of interference by the IR absorption of other components located close to the characteristic peaks of interest.

Meanwhile, pyrolysis-gas chromatography (Py-GC) is a useful method for determining the conversion of intractable polymers, such as cured epoxy resins.⁵ In this case, the degree

of cure can be monitored from the yield of the characteristic pyrolysis products with epoxide groups. Furthermore, Py-GC in the presence of an organic alkali, such as tetramethylammonium hydroxide (TMAH), has been advantageous for acquiring valuable information on the chemical structures of intractable polymeric materials containing polar components.⁶ Recently, the authors successfully applied this technique to the compositional analysis of multi-component UV-cured acrylate resins,⁷ a detailed characterization of the network structure in cross-linked poly(ethylene glycol) diacrylate⁸ and an evaluation of the molecular weight of original bisphenol A type epoxy acrylate prepolymers in UV-cured resins.⁹ In these cases, methyl acrylate (MA) was formed from remaining acryloyl groups through the simultaneous pyrolysis and methylation that occurred at ester linkages of the acrylates. Moreover, the yields of MA in the pyrogram of the UV-cured resins considerably decreased as a result of cross-linking formation. In this work, the double-bond conversion of acryloyl groups in UV-cured resins prepared from pentaerythritol triacrylate was determined based on the peak intensity of MA observed by the reactive Py-GC in the presence of TMAH. The results obtained by this approach were considered in comparison with those estimated by FT-IR measurements.

Experimental

Materials

Pentaerythritol triacrylate (PETA) was obtained from Kyoeisha Chemical Co., Ltd. The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (benzil dimethyl ketal; BDMK), purchased from Wako Pure Chemical Industries Ltd., was used without further purification. Figure 1 shows a typical formation pathway of the UV-cured PETA using BDMK as a

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Fig. 1 Formation pathway of UV-cured PETA.

photoinitiator. By absorbing UV light, BDMK decomposes through α -splitting to give a benzoyl radical and a dimethoxybenzyl radical. The latter forms methyl benzoate and a methyl radical through further decomposition. Among these radicals obtained from BDMK, the benzoyl radical is considered to predominately initiate photopolymerization, although the other radicals may contribute to the initiation to some extent.¹⁰

The procedure for preparing UV-cured samples for Py-GC measurements is basically the same as those described in our previous papers.^{7,8} A UV-curable material was prepared by dissolving BDMK into PETA at 70°C (PETA:BDMK = 100:3). The prepolymer solution was applied to a glass plate to give about a 10 μm thick film using a bar applicator.¹¹ Then, UV-curing was carried out in air by passing the applied film on a glass plate through UV-curing equipment consisting of a conveyor, a medium-pressure mercury lamp (80 W/cm and total output 2 kW) mounted in a dichroic mirror, and an infrared cut-off filter. The dosage for a single pass was determined to be 35 mJ/cm^2 by a UV-integrator (EYE Graphics UVPF-36, wavelength range = 300–390 nm). The irradiation was repeated until prescribed dosages of between 35 and 630 mJ/cm^2 . Meanwhile, UV-cured samples for FT-IR measurements were prepared by almost the same procedure, except that the prepolymer solution was applied to a potassium bromide plate.

Reactive Py-GC measuring conditions

The equipment and procedure for reactive Py-GC measurements are almost the same as those described in our previous papers.⁷⁻⁹ A vertical microfurnace-type pyrolyzer (Frontier Laboratory PY2020D) was directly attached to the inlet of a gas chromatograph (Shimadzu GC 2010) equipped with a metal capillary column (Frontier Laboratory Ultra ALLOY PY-2, 30 m $\times$ 0.25 mm i.d., coated with a 0.5 μm film of cross-linked polydimethylsiloxane) and a flame ionization detector (FID).

A methanol solution (25 wt%) of TMAH $[(\text{CH}_3)_4\text{NOH}]$ (supplied by Aldrich) was used as the reagent for reactive

Fig. 2 Pyrograms of (a) uncured PETA containing BDMK and (b) UV-cured PETA observed at 375°C in the presence of TMAH.

pyrolysis. About 100 μg of the milled UV-cured sample was placed in a platinum sample cup together with 4 μl of the TMAH solution. The sample cup was positioned at the top of the pyrolyzer near room temperature, and then dropped into the continuously heated center. Although almost similar pyrograms were observed at pyrolysis temperatures of 350, 375, 400 and 425°C, the optimum pyrolysis temperature was empirically chosen to be 375°C to obtain the highest yield of methyl derivatives while minimizing the contribution of random thermal cleavage of the polymer chain. A flow rate of 50 ml/min helium carrier gas was used to rapidly sweep the pyrolysis products from the pyrolyzer to the separation column. The carrier gas flow was then reduced to 0.8 ml/min at the inlet of the capillary column by means of a splitter. The column temperature was initially set at 30°C for 5 min to separate low boiling-point pyrolyzates, and then elevated up to 320°C at a rate of 10°C/min. Identification of the peaks on the pyrograms was performed by using a Py-GC/MS system (Shimadzu QP-5050A), to which the same type of microfurnace pyrolyzer was directly attached. In the Py-GC/MS system, not only an electron ionization, but also a chemical one with isobutane as the reagent gas were used for a reliable confirmation of the molecular weight.

FT-IR measuring conditions

An FT-IR measurement was carried out by using an FT-IR spectrometer (JEOL JIR-6500). FT-IR spectra were taken in the region of 4000–400 cm^{-1} at a resolution of 4 cm^{-1} . All measurements were performed at 20°C under a dried air atmosphere. Double-bond conversions were calculated from the absorbance at 1635 cm^{-1} based on acryloyl groups.

Table 1 Pyrolysis products formed from the prepolymer compound and its cured resin

Peak code ^a	Chemical structure	Effective carbon number ^b
MA		1.8
MB		6.75
DB		7
P ₁		4
P ₂		5
P ₃		4.4
P ₄		3.8

a. Peak codes correspond to those on pyrograms in Fig. 1.

b. Effective carbon numbers for FID response.¹²

Results and Discussion

Reactive pyrolysis behavior of PETA

Figure 2 shows pyrograms of (a) uncured PETA containing BDMK and (b) UV-cured PETA obtained by pyrolysis in the presence of TMAH at 375°C. The assignments of the main peaks are summarized in Table 1 along with their chemical structures and effective carbon numbers for the FID response.¹² In the both pyrograms, methyl acrylate (MA) and tetra-, tri- and dimethyl ether of pentaerythritol (P₂–P₄) were typically observed along with a small amount of a related cyclic ether (P₁).⁷ Here, MA from UV-cured PETA was formed in markedly smaller amounts than that from uncured PETA. This observation clearly indicates that MA is formed from the remaining and original acryloyl groups in the cured and uncured PETA, respectively.

Meanwhile, pyrolysis products related to BDMK, methyl benzoate (MB) and (dimethoxymethyl)benzene (DB) were observed as minor constituents in the pyrogram of the uncured PETA, although the latter product was not found in the pyrogram of the UV-cured PETA. MB and DB observed in the pyrogram of the uncured sample were considered to arise from intact BDMK, since they were ascertained to be formed in almost the same amount through the reactive pyrolysis of BDMK, itself. The absence of DB in the pyrogram of UV-cured PETA suggests that almost all BDMK was decomposed by UV-irradiation. Therefore, MB in the pyrogram of the UV-cured sample should be exclusively produced from the initiator fragment incorporated in the resin structure. This observation agrees with the general concept that photopolymerization in the

Fig. 3 Possible formation pathways of reactive pyrolysis products from UV-cured PETA.

presence of BDMK is primarily initiated by the benzoyl radical, as shown in Fig. 1.¹⁰

Figure 3 summarizes possible formation pathways of the characteristic products formed from UV-cured PETA by reactive pyrolysis. MA and MB are produced from the unreacted acryloyl group and the initiator residue in the UV-cured resin, as described above. P₂–P₄ could be produced from the pentaerythritol moiety through hydrolysis and methylation at the ester linkages. In this case, the relative intensities among the P series products were almost the same as those observed in the pyrogram of the starting material, pentaerythritol, itself under the same pyrolysis conditions. Although PETA originally contained various byproducts, such as diacrylate having two hydroxyl groups, the formation of the pyrolysis products having hydroxyl groups could be mainly due to the low reactivity of aliphatic alcohol with TMAH. Moreover, the cyclic ether P₁ might be formed through an intramolecular dehydration reaction in the dihydroxyl compound, P₄. Meanwhile, the MA oligomer, which would be produced from a cross-linking structure in the UV-cured PETA,⁹ was scarcely observed in the pyrogram, mainly due to a lower volatility of the MA oligomers arising from the long sequence of the junctions prepared under the experimental conditions in this work.

Measurement of conversion of the acryloyl group

Since MA should arise from unreacted acryloyl groups in uncured and cured PETA, its relative yields could reflect the conversion of acryloyl groups. The relative yield of MA at a dosage of d mJ/cm² (Y_d) against the pyrolyzates of the PETA moiety (P₁–P₄) was calculated as

$$Y_d = \frac{I_{MA,d}/1.8}{I_{P1,d}/4 + I_{P2,d}/5 + I_{P3,d}/4.4 + I_{P4,d}/3.8}, \quad (1)$$

where $I_{MA,d}$, $I_{P1,d}$, $I_{P2,d}$, $I_{P3,d}$ and $I_{P4,d}$ are the observed peak intensities of MA, P₁, P₂, P₃, and P₄ for the same dosage, d , respectively. Meanwhile, the values 1.8, 4, 5, 4.4 and 3.8 are the effective carbon numbers for the FID response¹² of MA, P₁, P₂, P₃, and P₄, respectively.

Using the values of Y_d calculated from Eq. (1), the conversion

Fig. 4 Relationship between the UV dosage and the double-bond conversion, estimated by FT-IR and reactive Py-GC.

of acryloyl groups at d mJ/cm² irradiation (C_d) was estimated as

$$C_d(\%) = \frac{Y_0 - Y_d}{Y_0} \times 100, \quad (2)$$

where Y_0 and Y_d are the relative yields of MA of an uncured prepolymer sample and a cured one at d mJ/cm², respectively.

Figure 4 shows the double-bond conversions thus calculated from reactive Py-GC as a function of the UV dosage along with those estimated from the absorbance at 1635 cm⁻¹ in the FT-IR spectra. Apparently, the polymerization curve obtained by reactive Py-GC was almost comparable to that by FT-IR, although the conversions observed by reactive Py-GC were slightly higher than those by FT-IR in detail. This slight difference might be caused by the oxygen inhibition of polymerization promoted in a thinner UV-curable coating;² an uncured PETA solution applied on a KBr plate easily flowed down to generate a thinner film, because the plate was placed vertically during the FT-IR measurement. Since oxygen inhibition occurs especially in the early stage of photopolymerization, the difference in conversion should be somewhat larger at lower UV exposure of around 200–300 mJ/cm², as shown in Fig. 4. Furthermore, the relatively low final conversion (*ca.* 60%) of PETA might be mainly attributed

to a low polymerization temperature under the experimental conditions using an infrared cut-off filter.¹³ The reproducibility in Py-GC measurements was about 4% of the relative standard deviation for three repeated runs. These results suggest Py-GC in the presence of an organic alkali can be a complementary method to FT-IR for determining the conversion of UV-cured acrylic resins, even usable for pigmented and laminated samples.

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