Synthesis and characterization of photosensitive methacrylates to give heat-resistant polymers

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Abstract

New photosensitive monomers having multiple methacryloyloxy groups were synthesized by the reaction of naphthalene and biphenyl derivatives containing two or more glycidyloxy groups with methacrylic acid. The obtained photosensitive monomers were mixed with polymerization initiators (1 wt% AIBN and/or BIPE) and a reactive diluent (20 wt% DPCA60). The mixtures were termed as compounds. The compounds were converted into the insoluble gel products by heating or photo-irradiation with an ultra high-pressure mercury lamp. We also measured the heat resistance of the insoluble gel products by thermogravimetry and investigated the correlation between the heat resistance and the chemical structures of photosensitive methacrylate composites. All of the insoluble gel products showed the heat-resistance over 260 °C and particularly the compound having the largest number of methacryloyloxy groups had the highest heat-resistance among them. This compound exhibited the highest consumption rate of the photosensitive group and it was in accordance with the result of the reactive photo-polymerizability measured by the gray scale method.

Keywords: Epoxy-compounds; Methacrylate; Photosensitive compound; Heat-resistance

1. Introduction

Various photosensitive polymers have significantly contributed to high-tech and general industries. They included bichromates, cinnamyl compounds, diazo compounds, azides, and acrylates, and have been referred to as five common photosensitive compounds. Among them, the polymers having acryloyloxy group (acrylate-type photopolymer [1–8]) surpassed the others in terms of the extent of utilizing fields and consumption, because of their advantages to form transparent, flexible, strong, and thick films. One of their uses is solder resist [9–12] in which the key structure is epoxyacrylate [13–16]. ‘Epoxyacrylate’ is an idiomatic expression and, precisely expressing, it should be referred to as epoxymethacrylate compound. In this study four new epoxyacrylates were prepared as main component of the heat-resistant solder resist, expecting that they are superior to existing ones. If their components have the heat-resistance over 260 °C, they will be capable to be used as the solder resist for the lead-free solder which has recently developed considering the environmental safeguards.

To develop new heat-resistant photopolymers, we consulted some commercially available heat-resistant resins. Some of these epoxy-compounds have a heat-resistant framework structure [17] such as naphthalene or biphenyl derivatives having multiple glycidyl groups. Our new epoxyacrylates were started from these naphthalene and biphenyl derivatives, that is, diglycidyl ether of naphthalene (1), the triglycidyl and, tetraglycidyl ethers of naphthalene derivatives ((2) and (3), respectively), diglycidyl ether of biphenyl (4), and diglycidyl ether of bisphenol-A (5).

New photosensitive monomers having methacryloyloxy groups were synthesized via the reaction using epoxy-compounds mentioned with methacrylic acid. This paper presents the synthesis and characterization of the products, focusing on their characteristics for use as the photosensitive compounds. Bisphenol-A type methacrylate starting from (5) was synthesized for the sake of comparison although the methacrylate from (5) has already been developed.

2. Experimental

2.1. Materials

Epoxy-compounds used as starting materials in this study are shown in Scheme 1. All of them are commercially available as encapsulating materials, being called as ‘epoxy compound’ even if they are glycidyl compounds. The epoxy-compounds...
of 1–3 were produced by Dainippon Ink & Chemical Co. as HP-4032D, and EXA-4750, and EXA-4700, respectively, and 4 and 5 by the Japan Epoxyresin Co. as YX-4000 and Epitope828, respectively. The molecular equations in Scheme 1 indicate the ones which have the maximum number of glycidyl groups. Instead, the real average numbers of glycidyl groups, which were calculated from epoxy equivalent of each epoxy compound, are about 2.5 for epoxy-compound 2, about 3.0 for epoxy-compound 3, although they are almost 2.0 for epoxy-compounds 1, 4 and 5. DPCA-60 (Scheme 2), which serves as a plasticizer as well as a supplementary crosslinker, was purchased from Nippon Kayaku Co. Methacrylic acid (MAA), triethyl-benzyl-ammonium chloride (TEBAC), azobis-isobuthyro-nitrile (AIBN), and benzoin-isopropyl-ether (BIPE) and toluene were used as monomer, catalyst, thermal and photo initiators and solvent, respectively. They were purchased from Wako Pure Chemicals Co.

2.2. Synthesis of methacrylate monomers

The procedure for the synthesis of multi-functional methacrylate monomers is shown in Scheme 3. After setting up a 500 ml flask with a thermometer, cooling tube, air-blowing glass tube and mixing glass tube, the reaction mixture was prepared at a capacity of about 1/2 the volume (250 ml) in the flask.

Equivalent amounts of epoxy-compound and MAA, 0.25 wt% TEBAC, and toluene (70 wt%) were mixed under air flow of 100 ml/min at 105 °C. To calculate the rate of reaction of MAA (photosensitive group) with epoxy-compounds, about 0.3 g was taken out from the reaction mixture in the flask at certain time intervals and it was poured into 10 ml of toluene-ethanol (1:1) solution with one drop of bromothymol blue solution (BTB). Then the solution was titrated with NaOH–ethanol (0.1 mol/l) and calculated the acid value of the solution. The reaction was continued until the acid value decreased to less than 10, and then the mixture was kept in a refrigerator after adding 25 ppm of hydroquinone to prevent any spontaneous chemical reaction. The reaction products, multi-functional methacrylates of epoxy-compounds, were designated as 1’, 2’, 3’, 4’, and 5’, from their starting materials, 1, 2, 3, 4, and 5, respectively.

![Scheme 1](image1)

![Scheme 2](image2)

![Scheme 3](image3)
2.3. Characterization of methacrylate monomers 1′–5′

The reaction products were characterized with an HPLC (C-R5A, Shimadzu) using three serial GPC columns, the KF806, 804, and 801 (Showa Denko Co.). They were eluted with THF at the rate of 0.8 ml/min at 40 °C. MALDI-TOF MS (Matrix-Assisted Laser Desorption Ionization Time-Of-Flight Mass Spectrometry) was carried out for the chemicals 1 and 1′ with a Bruker ultraflex mass spectrometer. The spectrometer was equipped with a nitrogen laser. The detection was in the reflection mode. Chemical structures of the methacrylate monomers were also examined by using IR (JIR-5500, JEOL), FTIR (2000, Perkin-Elmer Co.), NMR (EX-400, JEOL), and UV spectroscopy (UV-3100PC Shimadzu). Thermal analysis was carried out using a thermo-gravimetric balance (Bruca-AX).

2.4. Polymerization of methacrylate composites

To obtain good films by polymerizing 1′–5′, added were initiators, AIBN and/or BIPE (1 wt% of 1′–5′) and a plasticizer, DPCA-60 (20 wt% of 1′–5′), to 1′–5′. We named the above-mentioned reaction mixtures as methacrylate composites 1′′–5′′ corresponding to 1′–5′. Because monomers have two or more double bonds per molecule, 1′′–5′′ finally formed insoluble cross-linked polymers by heating or photo-irradiation. In the case of heating, we utilized an electric furnace, and in the case of photo-irradiation, we used the instrument shown in the lower part of Fig. 1. About 10 mg of the sample was needed for thermal gravimetry to check the extent of reaction. To obtain the quantity of photo-polymerized sample sufficient for several measurements, 1.2 g of samples were placed horizontally on the glass plate within a circle of 2.5 cm diameter and 100 μm thickness and irradiated using a light reflected from an aluminum oxide plate (JIS-A1080-P-H26). The aluminum oxide plate was set over the sample at the distance of 10 cm with an angle of 45 degrees, and the horizontal UV light was reflected downward by the angle of 90 degrees. 46.9% of direct lighting reached the sample, corresponding to 15.1 mW/cm².

Thermal polymerization of the same composites was done as follows. After 1′′–5′′ were coated in the same thickness on the glass plate, they were heated under several conditions. The products were put into THF and treated with an ultrasonic cleaning instrument for 0.5 min. then allowed to stand for 4.5 min. After that, the solubility of the samples was assessed by visual observation of them.

2.5. Rate of consumption of the photosensitive group in methacrylate composites

The methacrylate composite containing 1 wt% AIBN or BIPE without DPCA-60 was put on a KBr plate with 10 μm thickness or put between two KBr plates and then irradiated with direct horizontal UV light in air. The IR absorbance was measured at 945 cm⁻¹ to time to time to calculate the rate of consumption of the photosensitive groups or unsaturated double bonds. To investigate the influence of negative film on the transcription of the image to photosensitive polymer, the relative photosensitivity of the methacrylate composites was measured using the Kodak step tablet No. 2 film (thickness: 300 μm). Polymerization was performed using a system shown in the upper part of Fig. 1. The sample (thickness: 20 μm) was placed directly on the horizontal Kodak step tablet No. 2 film and irradiated just from downwards, in contrast to the case of the thermo-gravimetric sample (irradiated from upards as shown in the lower part of Fig. 1). The step tablet film was set on thin stainless steel (90×60×0.05 mm) with an opening (50×30 mm) in the central region on the circular holder (7 cm in diameter). After irradiation, the film was developed in toluene for 1 min. and then rinsed with methanol for 2 min. After the film dried, the photosensitivity of the methacrylate composites on the film was measured by determining from where the developed images began to appear on the step tablet [15].

2.6. Thermo-gravimetric measurement of the polymethacrylates obtained by thermal or photo polymerization

Photosensitive methacrylate composites 1′′–5′′ were heated in an electric furnace or photo-irradiated with an ultra high pressure Hg lamp, which altered the composites to the insoluble cross-linked polymers. Heat-resistance was measured by thermo-gravimetry in which 9 mg samples were heated at 10 °C/min.

3. Results and discussion

3.1. Synthesis of multi-functional methacrylate monomers

MALDI-TOF MS clarified that the epoxy-compound 1 is composed of two glycidyl groups-carrying molecules (M_w = 272) with very small amounts of no or one glycidyl group-carrying molecules (M_w = 160 and 216, respectively).
The amount of MAA mixed with epoxy-compounds was set to be equivalent to the amount of glycidyl groups existing in each epoxy-compound. Table 1 shows the recipe and conditions for reaction, and some results of the reaction, that is, the acid value at the end of each reaction, the amount of the photosensitive group (MAA) introduced into the product, and the appearance of the product. The rate of MAA introduction to each epoxy compound was calculated from the $(a_o-a_t)/a_o$ where $a_t$ and $a_o$ were the acid values at time 0 and t. The kinetics was analyzed in terms of concentration of remaining MAA, and the reaction was found to be nearly of the first order kinetics at the initial stage of reaction as shown in Fig. 2. The epoxy-compounds 1, 2 and 3 exhibited a high rate of reaction and formed rigid solids, but the rests, 4 and 5, resulted in the formation of viscous solids. The products for 4 and 5 retained the high acid values even after the reaction was continued for a long time. The reaction was stopped after the acid value decreased to less than 10. The crude products were refined by four repetitions of precipitation and dissolution with an insoluble solvent, methanol, and a good solvent THF, and dried.

### 3.2. Structural analysis of the multi-functional methacrylate monomers

The purity of all of the extracts was measured by HPLC measurement and that of 1 and 1' by mass spectroscopy. The clear retention time of each sample appeared on HPLC spectrum and it showed the reasonable increment in the molecular weights of the product compared with the respective starting materials. MALDI-TOF MS revealed the molecular weight of main product was 444 as expected and that the product included small amounts of the compounds having unreacted end group(s) whose molecular weights were 358 and 272.

The IR and NMR spectra of 1'–5' was measured. In the IR spectrum of 1', peaks of the 1250, 909 and 833 cm$^{-1}$, (8, 9 and 11 μm) assigned to the stretching vibration of the epoxy ring disappeared. Several new peaks appeared in the spectrum of 1', the peaks at 3630 and 1100 cm$^{-1}$ were assigned to OH stretching and deformation vibration of the secondary alcohol; 1735 and 1240, 1165 cm$^{-1}$ were assigned to C=O stretching and C–O–C deformation vibration of the ester group; and 947 cm$^{-1}$ to end methylene deformation vibration of the methacryloyloxy group.

As to the NMR spectra of 1', peaks at 2.85 and 2.75 ppm (doublet) originated in methylene, and one at 3.4 ppm originated in methine of epoxy group in 1, disappeared. The new peaks that appeared in 1' were 6.18 and 5.60 ppm, which were assigned to the end methylene of methacryloyloxy group: 1.92 ppm (singlet) to the methyl group, and 3.2 ppm to OH group. The peaks of methylene and methine formed with the ring-opening of the epoxy group appeared near 4.4 and 4.1 ppm. The low chemical shift of them was due to their position adjacent to the oxygen atom. In this area, the typical peaks of the methylene adjacent to oxygen atom combining with phenyl ring appeared. Thus, the peaks had complicated shapes, but all the peaks were clarified without any contradiction and were coincident with the theoretical peaks. In a similar manner, we certified the spectra of 2'–5' and consequently could determine their respective chemical structures. The spectra of 1',2', and 3' were almost the same each other, indicating the similarity of their chemical structures.

Fig. 3 shows UV spectra of 3' and 5'. The absorbance of 3' had a skirt over longer wavelength to near 365 nm. The UV spectra of 1'–3' were closely similar but the skirts of 1' and 2' were not spread to 360 nm. And the absorbance of 5' fell down to zero at 300 nm. Commercially available ultra high-pressure
mercury lamp emits continuous ultraviolet rays and a line spectrum of 366 nm [18] is one of the strongest emissions. Consequently the fact that 30 had the strong absorbance over a wide range of wavelength suggests that 30 is the most sensitive to the UV light of the ultra high-pressure mercury lamp among the samples examined. Table 2 shows the various characteristics obtained from the UV spectra of 1–5. And the data supported that 30 would be the most photosensitive material among 1–5. But, as the photosensitivity is affected by many other factors, for instance, the composite’s viscosity and alkaline concentration, the above-mentioned conclusion is not the decisive one.

3.3. Thermal polymerization of the methacrylate composites

Preliminary polymerizations using various catalysts and initiators revealed that use of 1 wt% AIBN, 1 wt% BIPE, and 20 wt% DPCA-60 are recommendable to obtain the satisfactorily insoluble film of 1–5 by heating or photo-irradiation, although only 30 could give a fairly good insoluble solid without DPCA-60 under the standard conditions. But, in order to investigate the heat-resistance under the same conditions, we decided to add the upper three reagents (AIBN, BIPE, and DPCA-60) to all of the polymerization recipes.

The products by thermal polymerizations of methacrylate composites were investigated in terms of their durability against solvents, that is, whether the products are dissolved with THF or not. The results are shown in upper three columns in Table 3. Crosslinked polymers were formed the fastest in the polymerizations of 4 and 5 then followed by that of 30.

3.4. Photosensitivity of 1–5 to UV irradiation

3.4.1. Rate of the decrease in photosensitive group in IR spectra

The change of IR spectra of 1–5 was investigated when they were UV-irradiated with 1 wt% BIPE, which is known as the photo-initiator for acrylate photosensitive polymers. The peak (~945 cm⁻¹) of the vinyl group [−C(CH₃)=CH₂] decreased with the increase of irradiation time from 1, 2, 5, 166
15, to 30 min, whereas the peak at 1720 cm\(^{-1}\) of the C=O stretching vibration assigned to the ester group did not change even after 30 min UV irradiation. From the ratio of peak at 945 to 1720 cm\(^{-1}\) at each reaction time, by so-called base-line method [19], we investigated the rate of consumption of the unsaturated double bonds, that is, vinyl groups of methacrylates in the course of photo-polymerization. The double bonds of methacrylates decreased with increasing irradiation time in all systems, among which the system of methacrylate 3\(^{\prime}\) lost the double bonds fastest, as shown in Fig. 4.

The results in Table 3 indicate that the products from methacrylates 4\(^{\prime}\) and 5\(^{\prime}\) remained soluble in THF after the treatment with AIBN under UV irradiation for scheduled period. This fact suggested that AIBN does not act as a photo-polymerization initiator for 4\(^{\prime}\) and 5\(^{\prime}\). To investigate further, we conducted the IR spectra analysis in the UV irradiation to 3\(^{\prime}\), 4\(^{\prime}\), and 5\(^{\prime}\) in the presence of AIBN, and found that AIBN caused consumption of vinyl groups of 4\(^{\prime}\) and 5\(^{\prime}\) as well as 3\(^{\prime}\), but the rates of consumption of the vinyl groups were in the order of 3\(^{\prime}\) > 4\(^{\prime}\) > 5\(^{\prime}\), to which the negligible polymerization of 4\(^{\prime}\) and 5\(^{\prime}\) might be attributed. To confirm this point, we irradiated the samples covered with blank division corresponding to 0 step part of Kodak step-tablet No. 2 film and found that the rates of consumption of the photosensitive group in 4\(^{\prime}\) and 5\(^{\prime}\) were much less than those for 3\(^{\prime}\). Considering these experimental results, AIBN was found to be a good thermal initiator but not necessarily good photo-initiator for 4\(^{\prime}\) and 5\(^{\prime}\) comparing with the other monomer systems.

3.4.2. Relative photosensitivity by gray-scale method

The relative photo-polymerizability of five kinds of methacrylate monomers 1\(^{\prime}\)–5\(^{\prime}\) with 1 wt% AIBN or BIPE without DPCA-60 followed by gray-scale method [20] under various conditions is shown in Fig. 5. The photo-polymerizability of the samples was in the order of 3\(^{\prime}\) > 2\(^{\prime}\) > 1\(^{\prime}\) > 5\(^{\prime}\) > 4\(^{\prime}\). Additionally, we investigated the same polymerization of 3\(^{\prime}\) and 5\(^{\prime}\) in the presence of 20 wt% DPCA – 60 (So, the systems correspond to 3\(^{\prime}\), and 5\(^{\prime}\), respectively). As a result, we found that 3\(^{\prime}\) became insoluble at the 6th step (transmittance: 0.17, this value is shown in the guarantee by Kodak) for 3 min irradiation, which meant that 3\(^{\prime}\) had good quality in terms of the photopolymer’s function. It is considered that, in the plate-making field of screen-printing, the photopolymer must be insoluble at the Fourth step (transmittance: 0.32) for 3 min irradiation. With regard to image resolution, we found that all of the polymers obtained from 1\(^{\prime}\) to 5\(^{\prime}\) showed the good image resolution of short line of 50 μm by the development at a coating thickness of 20 μm. These results suggested that the methacrylate composites could be sufficiently used as photopolymerizable compounds.

3.5. Heat-resistance of 1\(^{\prime}\)–5\(^{\prime}\) by heating or UV irradiation

TG patterns of 3\(^{\prime}\) polymerized by heating and UV irradiation showed a sufficient heat-resistance over 260°C, which was the temperature we first aimed for our polymer. We investigated the relation between the temperature and the rate of decreasing mass by measuring the TG patterns of 1\(^{\prime}\)–5\(^{\prime}\) polymerized by heating and UV irradiation. The results of the latter are shown in Fig. 6. The heat-resistance of the photo-irradiated polymers was slightly higher than that of the thermally polymerized polymers under our experimental conditions. The polymer from 3\(^{\prime}\) showed the highest heat-resistance in both cases of thermal and photo-polymerizations. Thus, the polymer 3\(^{\prime}\) is considered the most suitable photopolymer among the five compounds (1\(^{\prime}\)–5\(^{\prime}\)). Namely the monomer having a larger number of methacrylate groups exhibits the best performance as the photosensitive resist.
4. Conclusions

New acrylate-type photosensitive monomers containing multiple methacryloyloxy groups were synthesized by the reaction of the corresponding epoxyresins with methacrylic acid. They were made new photosensitive composites with initiators (AIBN and BIPE) and a plasticizer (DPCA60). The composites were changed into insoluble polymers by thermal and photo-polymerizations. Among them, four-functional monomer was found to be the best in terms of the conversion of the photosensitive group and in terms of the reactive photo-polymerizability assessed by the gray-scale method. All of the thermally polymerized and photo-polymerized polymers were durable over 260 °C, and 3° showed the highest heat-resistance. Finally, we concluded that the 3° the most suitable composite among the composites investigated.

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