G2-02

Development of a novel adamantane cross-linker

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Abstract-- Cross-linked polymers with multi-functional (meth)acrylate such as DPHA and TMP-3A show higher thermal and chemical stabilities as well as excellent mechanical strength. However, water absorption property and dielectric constant of these conventional cross-linkers were far from satisfactory. We recently developed a novel adamantane cross-linker having low water absorption property and low dielectric constant. We introduce characteristics of this adamantane cross-linker.

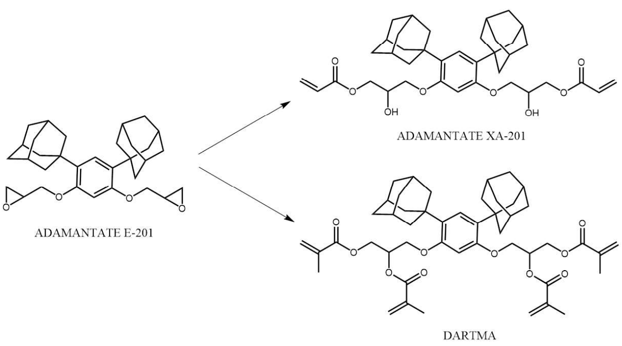
I. Introduction

The multi-functional (meth)acrylate is well known as chemical and mechanical strength improve agent, so that it is used in various applications. However, water absorption property and dielectric constant were high in the conventional multi-functional (meth)acrylate, and its application was limited [1]. On the other hand, the compound having adamantyl structure has high heat-resistant, low water absorption property and low dielectric constant [2]. We produce a lot of (meth)acrylates having adamantyl structure and provide these materials for electronic materials application. Recently, we developed new multi-functional (meth)acrylate having adamantyl structure. In this paper, we report the characteristics of these adamantane cross-linkers.

II. Preparation

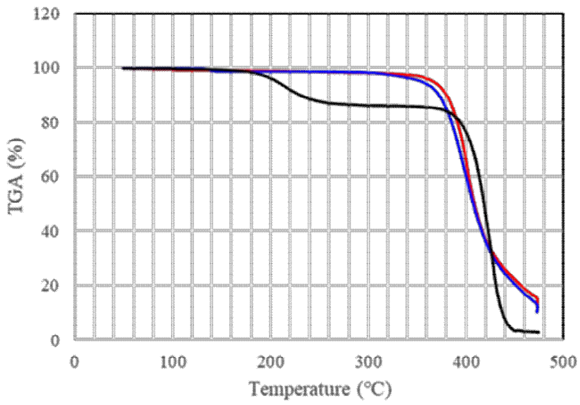
The chemical structure of adamantane cross-linkers (ADAMANTATE XA-202 and DARTMA) are shown in the Fig.1. Those materials were synthesized from ADAMANTATE E-201.

Fig. 1. Chemical structures of adamantane cross-linker.



As a result of thermal gravimetric analysis (Fig.2.), ADAMANTATE XA-202 and DARTMA show low volatility than that of Tricyclodecane dimethanol diacrylate (TCDDA) which are widely used as low water absorptivity cross-linker.

Fig. 2. Thermal gravimetric analysis of cross-linkers.



ADAMANTATE XA-202 (red line), DARTMA (blue line), TCDDA (black line)

III. Evaluation as Cured Film

First, photo or thermal curable formulations were coated onto a glass substrate to target film thickness (10~15 um), then baked at 90 °C for 2 min on the hot plate. In the case of photo curable formulations, coating films after baking were irradiated at 3,000 mJ/cm^2 with intensity of 300mW/cm^2 at 365 nm. In the case of thermal curable formulation, coating film after baking was baked at 150 °C for 60 min.

Properties of cured films using different cross-linkers are shown in Table 1.

Table 1. Properties of photo or thermal cured films.

cross-linker	cure type	reaction rate	pencil hardness	heat resistance	water absorption rate	dielectric constant
ADAMANTATE XA-202	photo	54%	HB	298°C	4.6%	3.62
DARTMA	photo	30%	HB	340°C	1.6%	3.37
DARTMA	thermal	77%	H	315°C	0.1%	-
TCDDA	photo	87%	H	363°C	0.6%	3.45
DPHA	photo	52%	4H	360°C	1.7%	4.14
DPHA/DATRMA = 80%/20%	photo	38%	4H	363°C	1.1%	-
DPHA/DATRMA = 40%/60%	photo	35%	2H	357°C	0.6%	-

Photo curable formulation: cross-linker / Omnirad 379EG / Toluene = 39% / 1% / 60%

Thermal curable formulation: cross-linker / Perbutyl_P / Toluene = 39% / 1% / 60%

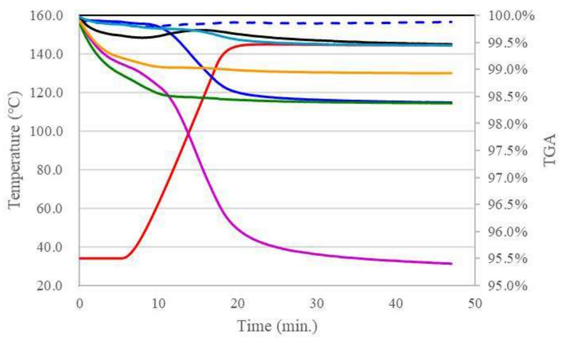
The pencil hardness of ADAMANTATE XA-202, DARTMA and TCDDA cured film is lower than that of Dipentaerythritol hexa/pentaacrylate (DPHA). The low pencil hardness of adamantane cross-linkers can be explained by acryl equivalent weight.

The heat resistance that mean 5% mass reduction temperature of ADAMANTATE XA-202 and DARTMA is lower than that of general cross-linkers. The low heat resistance of adamantane cross-linkers is considered to be due to low crosslinking density.

The water absorption rate (Fig.3.) was obtained by thermal gravimetric analysis of cured film which dipped in the water at 23 °C for 24 hr. The water absorption rate of ADAMANTATE XA-202 cured film is higher those of other cross-linkers. ADAMANTATE XA-202 has two hydroxyl groups. These hydroxyl groups negatively effect the water absorption property. The water absorption rate of DARTMA thermal cured film is very low, but that of DARTMA photo cured film isn't. The difference is due to the reaction rate of acryl group. The DARTMA photo cured film has improved the water absorption property by combining with DPHA. This results indicate that crosslinking density positively effects the water absorption property.

The dielectric constant of DARTMA cured film is lower than that of other cross-linkers.

Fig. 3. Water absorption rate of cured film.



ADAMANTATE X202 (purple line), DARTMA photo (blue line), DARTMA thermal (blue broken line), TCDDA (black line), DPHA (green line), DPHA/DARTMA(80/20) (yellow line), DPHA/DARTMA(40/60) (light blue line), Temperature (red line)

IV. Evaluation as Photo Resist

As application of DARTMA, We evaluated negative tone acrylic resists shown Table 2.

Table 2. Negative tone acrylic resist formulations

Sample	PR-1	PR-2	PR-3
Acryl photo polymer	54%	54%	54%
DPHA	32%	16%	16%
TCDDA		16%	
DARTMA			16%
Epoxy resin	10%	10%	10%
Silane coupling agent	1%	1%	1%
Photo initiator	3%	3%	3%

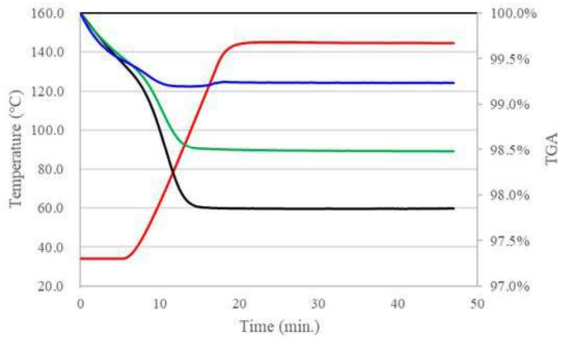
Negative tone acrylic resists were evaluated by the standard process conditions shown Table 3.

Table 3. Standard process conditions

Item	Process condition
Film thickness	10 um
Soft bake	90 °C 2 min.
Exposure	200 mJ/cm^2 at I line 20 mW/cm^2
Development	60 sec. / 2.38% TMAH aq.
Hard bake	230 °C 30 min.

Fig.4. shows the water absorption rate of negative tone acrylic resist film. The water absorption rate of PR-3 is very low and PR-3 shows good insulation reliability. Also PR-3 shows good patterning ability.

Fig. 4. Water absorption rate of negative tone acrylic resist film.



PR-1 (black line), PR-2 (green line), PR-3 (blue line), Temperature (red line)

V. Conclusions

In this study, a novel adamantane cross-linker was developed to improve water absorption property of acrylic curing film. The water absorption rate of DARTMA thermal cured film is lower than conventional cross-linkers.

The negative tone acrylic resist used DARTMA shows good water absorption property and insulation reliability. Also this resist shows good patterning ability and it is expected to be used as an insulating coating material.

References

[1] Gijutsujouhoukyoukai LTD, first ed., "How to choose, how to use functional monomer casebook", pp. 133-141, July 2017 (in Japanese).

[2] Gijutsujouhoukyoukai LTD, first ed., "How to choose, how to use functional monomer casebook", pp. 247-257, July 2017 (in Japanese).