Properties of Photo-cured Networks using Polyglycerin Acrylates

Kimihiro Matsukawa, Yukiko Miyaji**, Shiori Kawabata***
*Material Innovation Lab., Kyoto Institute of Technology,
Kyoto, Japan
**Sakamoto Yakuhin Kogyo, Co., Ltd.
Osaka, Japan

Introduction

Glycerin is one of bio-based materials produced from palm oil, and it is attracted to contribute to reducing the use of petroleum resources. Bio-based polymer materials for industrial uses are possible candidates for achieving the SDGs. Polyglycerin, which is derived form glycerin, has some hydroxyl groups by the number of repeating units of glycerin. These hydroxyl groups can be applied for the preparation of crosslinked materials. Therefore, polyurethane linkage between glycerins might be made by the reaction with isocyanate compounds. However, as these polymers with pristine polyglycerin do not have sufficient distance between crosslinked points, the characteristics is not remarkable difference from ordinary network polymers. It seems that polyglycerin with longer side chains could be expected to provide a lot of unique functions. In this work, it has been examined the side chain extension of polyglycerin with ethylene oxide (EO) and the application to novel network polymers.

In the case of glycerin tetramer as a starting material, six terminated hydroxyl groups were reacted by some EOs for the side chain extension. And these six terminal hydroxy groups were successfully modified to acrylate groups as shown in Figure 1. These polyglycerin acrylates are expected to be multi-functional monomers for the preparation of new network polymers.

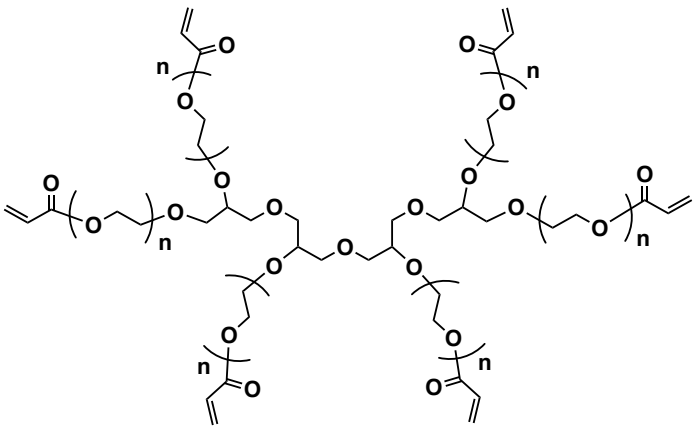


Figure 1 Polyglycerin based multi-functional acrylates.

Properties of Polyglycerin Acrylates

Two polyglycerin acrylates were used in this work, which is a short side chain type (SA-TE 6) and a long side chain type (SA-TE 60), and their molecular weight are correspondingly ca.900 and ca.3300. These are colorless liquid, and their viscosity of SA-TE6 and SA-TE-60 are 600 and 500 mPa·s/25°C, significantly lower than that of DPHA (6000 mPa·s/25°C or higher). Figure 2 shows the appearance of SA-TE60. In addition, while DPHA is insoluble in water, SA-TE 60 showed high water solubility and

could be dissolved in water at any concentration. As SA-TE6 and SA-TE-60 are dissolved in ethylene glycol monomethyl ether, acetone, MEK, toluene, and most of multi-functional acrylates such as DPHA, TMPTA, etc., it seems that they can apply to varieties of coating.

Photo-polymerization of Polyglycerin Acrylates

Photo-polymerization of SA-TE6 and SA-TE-60 were carried out by UV irradiation with 5 wt% of photo initiator (Irgacure 184) under air condition. It was found that these reactivities are very high by the realtime FT-IR measurement, compared with that of DPHA, as shown in Figure 3. Particularly, SA-TE60 indicate very fast curing rate, which was reached immediately to the conversion of 73%. Figure 4 shows the FT-IR spectra of photo-cured SA-TE6. After 125 sec irradiation (3000 mJ/cm^2), it was found that most of acrylic C=C bond were disappeared.

Figure 2 Appearance of SA-TE-60.

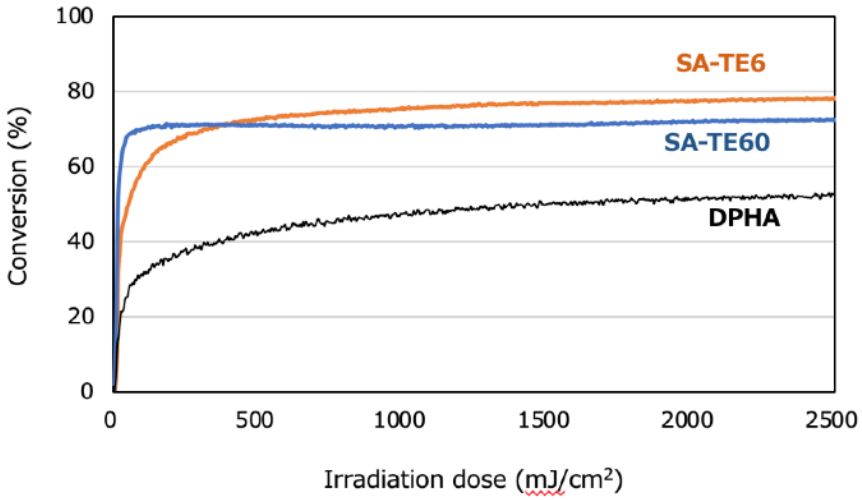


Figure 3 Conversion of acrylic groups in monomers observed by real-time FTIR measurement.

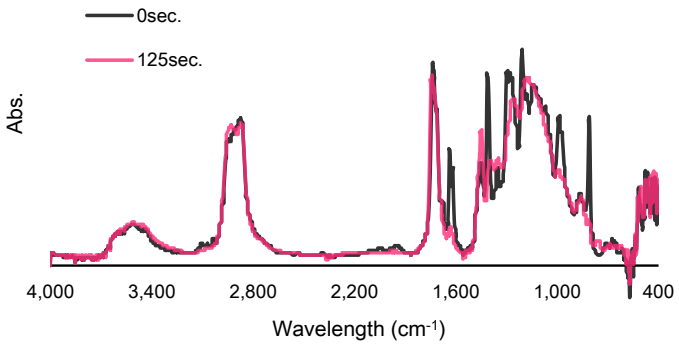
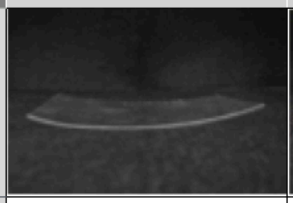
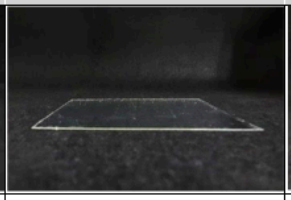


Figure 4 Change of FT-IR spectra of SA-TE6 after UV irradiation.

Several properties of photo-cured acrylates (SA-TE6, SA-TE60, and DPHA) are summarized in Table 1. After photo-cured coating on PET film, there are big difference on appearance of films. Although DPHA coating indicated heavy curling generated by its shrinking, curling of polyglycerin acrylate coating was not observed much. Especially, SA-TE60 showed no curling, but it was low surface hardness. It was found that there is a relation between the reduction of curling and the surface hardness. From the result of Mandrel bending test, the coating of SA-TE60 could be survived more than bending of 10,000 times. This should be noted as an important multi-functional monomer for flexible coatings.

Table 1 Properties of photo-cured coating of SA-TE6, SA-TE60, and DPHA.

		SA-TE6	SA-TE60	DPHA
Curl after photo-cure	Appearance			
	Lift height	4.1 mm	0.6 mm	N.D.
Pencil hardness		H	<6B	3H
Steel wool scratch test (500g, 10 times)		Almost no scratch	Many scratch	No scratch
Mandrel bending test	One bend	No crack (<2mm)	No crack (<2mm)	8mm
	10K times	6mm	No crack (<2mm)	N.D.

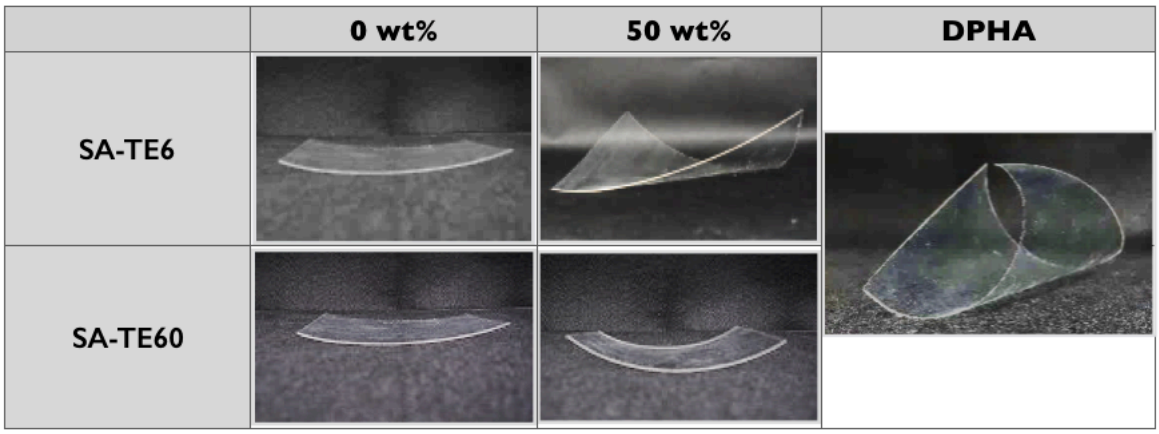


Figure 5 Different curling of poly glycerin acrylates/DPHA mixtures.

DPHA is well-known as a hard coating material, but there are some disadvantages such as curlings, cracks, and non-flexible. In addition of polyglycerin acrylates to DPHA, it is thought that these disadvantages can be overcome. The curling of polyglycerin acrylates/DPHA mixture were much smaller than DPHA, as shown in Figure 5. These results reveal that SA-TE6 and SA-TE60 are effective additives for modifing the properties of multi-functional acrylates.

As it was found that SA-TE60 improved the photo-radical polymerization in Figure 3, the photopolymerization of mixture of SA-TE60 with usual monomers might be proceed well by using even small amount of photo-initiators. In this point of view, photo-curing of SA-TE60/TMPTA (50/50) was examined with different amount of photo-initiators. The photo-polymerization with smaller amount of photo-initiator was occurred effectively by less irradiation dose, as shown in Figure 6. From the above results, it was found that SA-TE60 is an useful monomer that can provide advantageous reaction conditions.

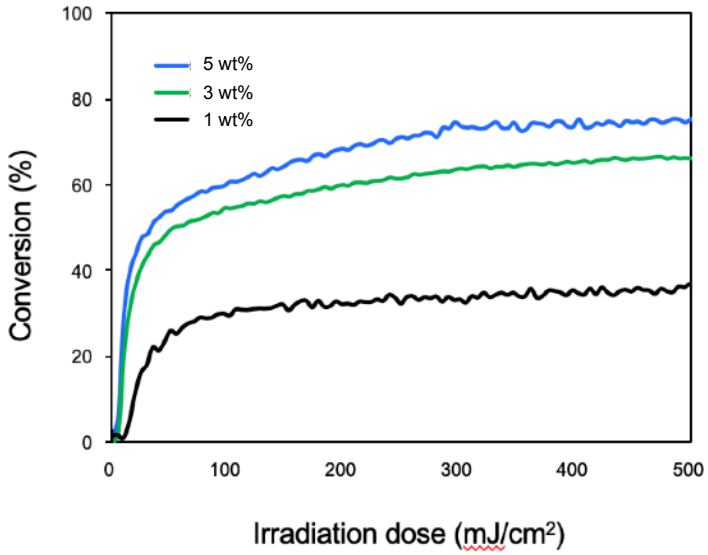


Figure 6 Conversion of photo-cured network polymers (SA-TE60/TMPTA) with different amount of photo initiator (1 wt%, 3 wt%, 5 wt% of Irgacure 184).

Anti-fogging Properties of Photo-cured Polyglycerin Acrylates

SA-TE60 is a multi-functional hydrophilic monomer, and also there is a hygroscopic properties (moisture absorption and release). These properties can be estimated to contribute to anti-fogging properties. Anti-fogging coating is generally performed by the treatment of surfactants, however the disadvatage of these coatings are very low durability. On the other, SA-TE60 coating is tough and stable, which has a property of moisture release. Therefore, these coating have very unique properties of anti-fogging coating, which can be repeatedly. The picture of Figure 7 indicates that the coated part of SA-TE 60 is not fogged placing for 1 min over hot water of 50°C. This phenomenon is useful as a practical anti-fogging coating. Most important factor for the anti-fogging properties is the thickness of coating, because the amount of moisture absorption is determined by the coating thickness. As shown in Figure 8, ca.50 μm thickness of coating provided the anti-fogging property over 3 min.

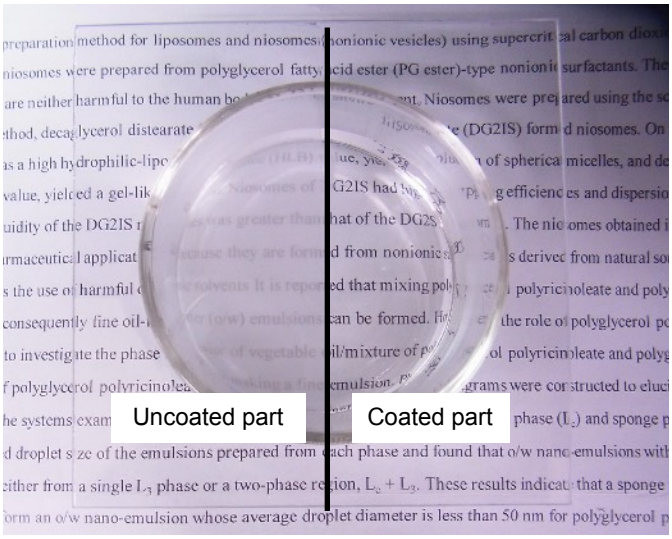


Figure 7 Picture of anti-fogging coating using SA-TE60 on polycarbonate sheet putting over hot water of 50°C for 1 min.

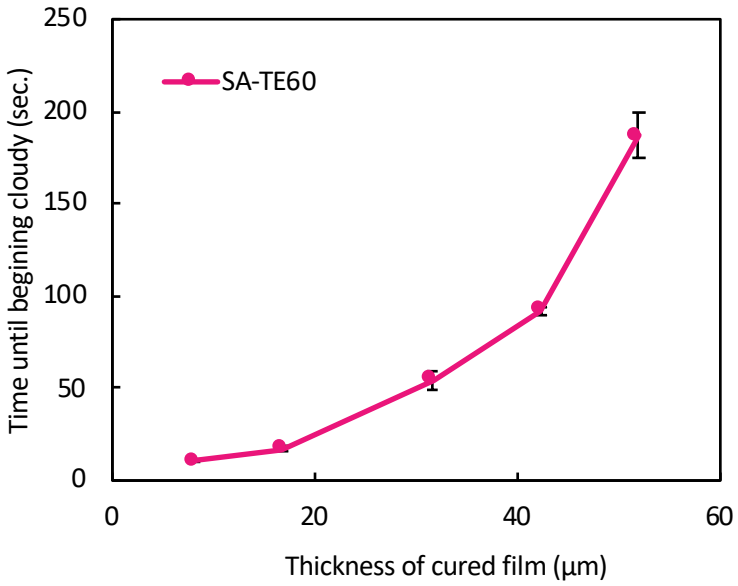


Figure 8 Time until beginning cloudy depend on thickness of SA-TE60 cured coating.

Conclusions

Polyglycerin acrylates, SA-TE6 and SA-TE60, are multi-functional acrylic monomers, which have many interesting properties such as high reactivity, high flexibility, anti-fogging, etc. Mixture of polyglycerin acrylates with usual multi-functional monomers, DPHA and TMPTA, provided outstanding properties such as low curling, low shrinkage, flexible, and so on. These materials are expected to become practical use in a wide range of industrial fields.