MECHANICAL PROPERTIES OF IONOMER/CLAY NANOCOMPOSITE-MODIFIED EPOXY

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ABSTRACT

Epoxy resin was modified with ionomer / clay nanocomposite. The hardener (DDM) content was controlled from 5 to 26phr because ionomer is expected to react with epoxy resin. Effect of DDM content on mechanical properties was investigated. The dynamic viscoelastic tests showed that the glass transition temperature increased with decreasing the DDM content. For the epoxy with 7 and 9phr DDM, there is no apparent grass transition temperature, and thermal resistance was considerably improved. Fracture toughness decreased with decreasing the DDM content. Whereas the fracture toughness value of the modified epoxy with 26phr DDM was 20% higher than that of the unmodified one, that with 9phr DDM was 40% less. These results can be explained by increase of crosslink in epoxy matrix which were caused by the reaction with epoxy and ionomer.

KEYWORDS

Epoxy, Ionomer, Nanocomposite, Thermal resistance, Dynamic viscoelasticity, Fracture toughness

INTRODUCTION

Epoxy resin which is a representative network polymer has been widely used because of its high thermal resistant property and easy processing. The epoxy resin has been modified by inserting various types of the additives to improve mechanical, electrical and the other properties; carboxyl-terminated butadiene acrylonitrile (CTBN) rubber was very effective in the enhancement of the fracture toughness of the epoxy resin[1-4]. Recently, some researchers reported on the addition of clay into the polymeric materials to enhance the thermal resistance and the elastic modulus[5,6]. Addition of newly developed ionomer / clay nanocomposite is expected to give some special properties to epoxy resin. In this study, the epoxy resin was modified by the addition of the ionomer / clay nanocomposite particles. Effect of the addition of the nanocomposite on the thermal property and the fracture toughness was investigated.

EXPERIMENTAL PROCEDURE

Materials

The epoxy resin used in this study was diglicydyl ether of bisphenol A epoxy, Epikote 828. Curing agent was 4-4' diaminodiphenylmethane (DDM). Nanocomposite particles (Mitsui Du-pont polychemicals Co.Ltd.) which had 10μm diameter were used as additives. The nanocomposite particles were splay-dried from the dispersion of clay (montmorillonite) and thermoplastic resin, ethylene ionomer, in which 77% of carboxyl acids were neutralized with Zinc ion. The chemical structure of the ionomer was shown in Figure 1.

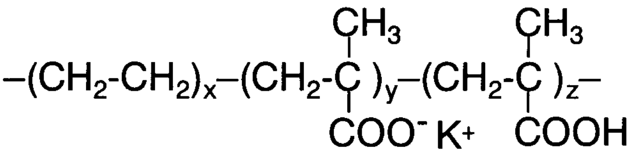


Figure 1: Chemical structure of ethylene ionomer.

The nanocomposite particles were added to the epoxy resin and mixed with a homogenizer. After degassing, this mixture was added to the DDM and mixed by hand. Curing condition was 120°C for 2hours and 180°C for 8hours. The formulation of the resins is given in Table1. As the ionomer can react with the epoxy resin, the ionomer content was varied from 5phr to stoichiometry, 26phr.

TABLE1
FORMULATIONS OF EPOXY MATERIALS

	Epoxy	Curing agent DDM	Clay / ionomer nanocomposite
Unmodified	100	26	0
Nanocomposite-modified	100	26	10
	100	20	10
	100	15	10
	100	9	10
	100	7	10
	100	5	10
	100	0	20

Dynamic viscoelasticity

Dynamic viscoelastic behavior was measured using rectangular specimens, 85 x 10 x 1mm, which were machined from the molded blocks. A specimen was mounted vertically in a testing machine, and the upper fixture was oscillated in torsion. The specimen was cooled to -50°C, and then heated to 300°C at constant heating rate, 1.38°C/min. Glass transition temperatures were defined as the temperature at the peak of the loss modulus, G".

Fracture toughness

Fracture toughness tests were conducted according to ASTM D5045 using compact tension specimens, 62 x 60 x 6mm, which were machined from the molded plates. Notches were introduced with a saw, and sharp precracks were formed by tapping a razor blade into the notch. Load in opening mode was applied through drilled holes in the specimen at displacement rate of 0.5mm/min. Testing temperature was 23°C. Fracture toughness values were calculated from the maximum load.

RESULTS AND DISCUSSIONS

Dynamic viscoelasticity

Effect of DDM content on dynamic shear modulus was shown in Figure 2. The shear modulus of the unmodified epoxy resin decreased gently with increasing temperature, and suddenly dropped to $2x10^7$Pa at 180°C, the glass transition temperature. For the nanocomposite-modified epoxy with 26phr DDM, the behavior was similar to that of the unmodified one. The glass transition temperature and the modulus at rubbery plateau region above the glass transition temperature was increasing with decreasing the content of DDM. For the modified epoxy with 7 and 9phr DDM, the shear modulus decreased gradually over whole temperature range and there is no apparent peak in the loss modulus. This fact shows that the glass transition doesn't occur in this epoxy system. When DDM content is 5phr, the shear modulus decreased largely from 100 to 200°C but the modulus at rubbery plateau region was much higher than the unmodified epoxy, which was similar to that of epoxy / ionomer resin system without DDM. The glass transition region and the rubbery plateau modulus has relations closely to the microstructure of the polymer, and the following suggestions are to be discussed. There is no significant difference in the network structure of the epoxy matrix between the stoichiometric epoxy with and without the nanocomposite. This means that DDM can react with the epoxy resin faster than ionomer. For the modified epoxy resin, ionomer can react with the unreacted epoxy matrix which remain after DDM reacted with epoxy, and the crosslink density rises in the epoxy matrix. Lower DDM content lead to higher crosslink density because an amount of reaction sites between ionomer and epoxy increases. For the epoxy with 7 or 9phr DDM, the densest network (almost perfect) may be achieved. In addition, each clay piece may restrained the movement of the molecular chains. When the content is less than 7phr, the property of the ionomer-epoxy product is superior to the other properties.

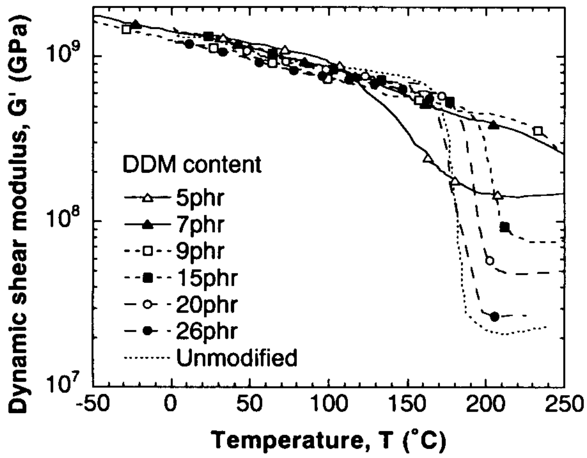


Figure 2: Effect of DDM content on dynamic shear modulus for nanocomposite-modified epoxy.

Fracture toughness

The fracture toughness values of unmodified and modified epoxies are shown as a function of DDM content in Figure 3. For the epoxy with stoichiometry DDM, the toughness value of the modified epoxy was 20% higher than that of the unmodified one. As to the modified epoxies, the fracture toughness was increasing with increasing DDM content. In particular, the toughness of the epoxy with lower DDM content was 40% less than that of the unmodified one.

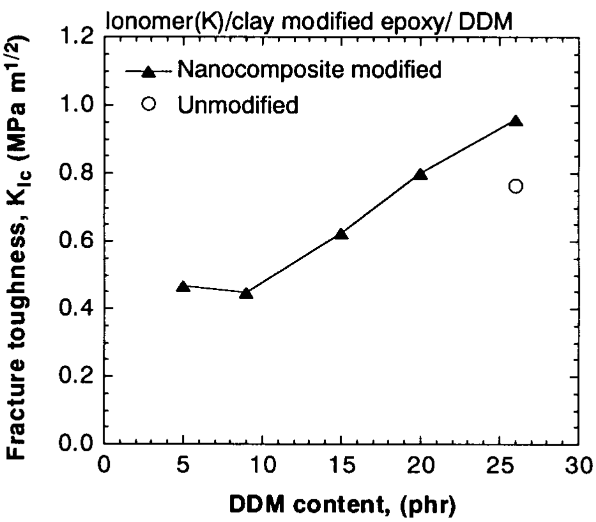
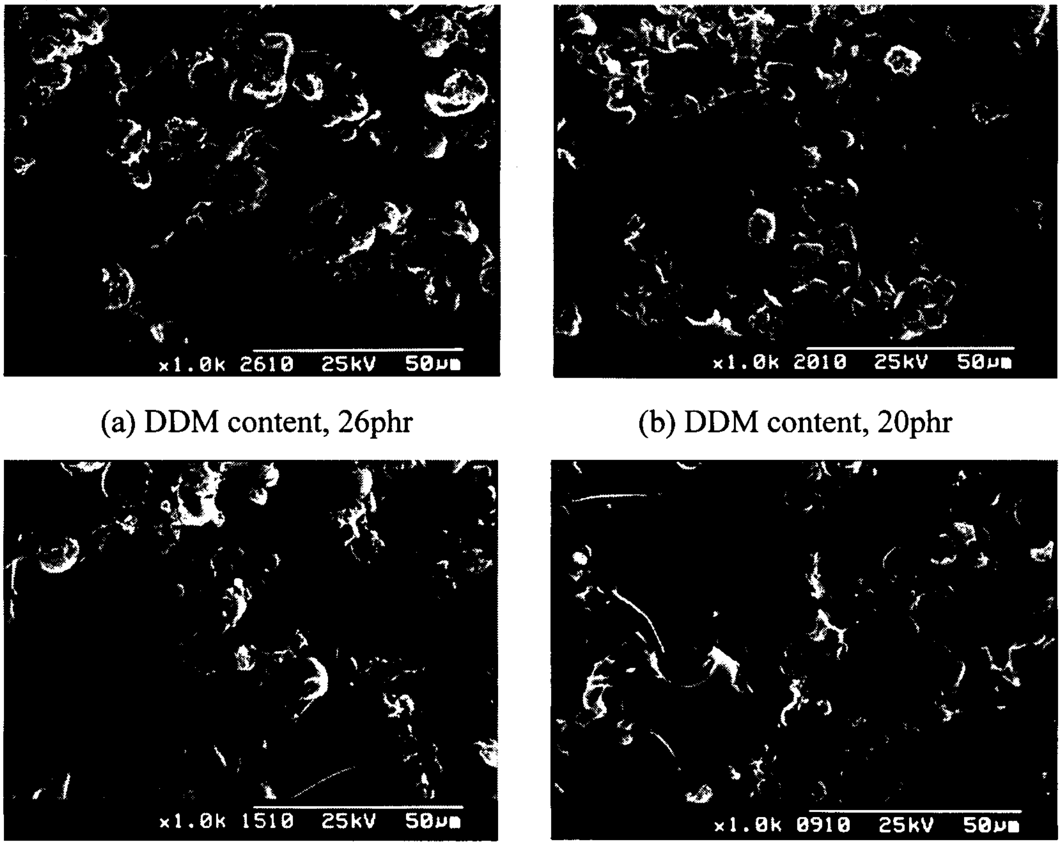


Figure 3: Fracture toughness of nanocomposite-modified epoxy.

Fractographic observations are shown in Figure 4. The particles were dispersed on the surfaces of all the epoxy system, and the size the particle after curing was larger than the original size. It is suggested that epoxy penetrated into ionomer rich region in the particles. For the modified epoxy with 26phr DDM, the crack propagated along



(a) DDM content, 26phr

(b) DDM content, 20phr

(c) DDM content, 15phr

(d) DDM content, 9phr

Figure 4: Scanning electron micrographs of fracture surfaces for nanocomposite-modified epoxy.

the particle / epoxy interfaces. For that with 20phr DDM, the crack propagated partly inside the particles. The rate of the fracture inside the particle increased with decreasing the DDM content. When DDM content is 9phr, the crack propagated mostly inside the particles. These facts show that high thermal resistant epoxy (9phr DDM) has strong interfaces where ionomer reacted enough with epoxy, and that the epoxy with higher DDM content has poor interfaces.

Fracture mechanism were discussed on the basis of the fractographic observation. For the modified epoxy with 26phr DDM, because the interfacial debonding by poor interfaces causes the crack blunt, stress intensity in the vicinity of the crack tip is lowered and the fracture toughness increases. On the other hand, the epoxy with lower DDM which has high crosslink density become brittle because high crosslink restrain the region of the plastic deformation. In addition, the crack blunt cannot be expected because of strong interfaces.

CONCLUSIONS

Epoxy resin was modified with ionomer / clay nanocomposite particles. Effect of hardener (DDM) content on mechanical properties was investigated. The dynamic viscoelastic tests showed that the glass transition temperature increased with decreasing the DDM content. For the epoxy with 7 and 9phr DDM, there is no apparent glass transition temperature, and thermal resistance was considerably improved. The fracture toughness decreased with decreasing the DDM content.

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