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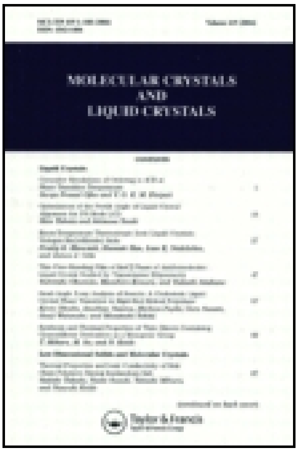

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Impact Optimized Performance of Epoxy/Polyamide/CSR(Core Shell Rubber)/Anhydride Blends at Low Temperature

Sunseong Ok [a] & Youngson Choe [a]
[a] Department of Chemical Engineering , Pusan National University , Busan , South Korea
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Impact Optimized Performance of Epoxy/Polyamide/CSR(Core Shell Rubber)/Anhydride Blends at Low Temperature

SUNSEONG OK AND YOUNGSON CHOE*

Department of Chemical Engineering, Pusan National University, Busan,
South Korea

In the present work, epoxy/polyamide/CSR (core-shell rubber)/anhydride blends were prepared to investigate the effects of soluble polyamide and core-shell rubber particles on the impact peel strength of the cured blends at room temperature and low temperature, 23°C and −40°C, respectively. A cure accelerator, 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN), has reduced cure time up to 10 sec at 200°C. Soluble polyamide and nano-sized CSR particles in epoxy systems had no influence on the cure kinetics. Both CSR particles and soluble polyamide significantly contributed to increasing the peel strength at room temperature. Soluble polyamide provided no impact resistance properties at low temperature, −40°C while CSR particles played a key role to improve impact optimized performance of epoxy systems at low temperature. Higher peel strength and impact resistance properties are strongly recommended for high performance structural adhesives in the various fields of industries.

Keywords Core-shell rubber; epoxy; impact peel strength; impact resistance; structural adhesive

Introduction

The epoxy resins possess excellent mechanical properties and can be used as base materials of high performance adhesives. Recently, highly improved impact strength at low temperature is needed in many applications such as mechanical and electronic assemblies. Basically, epoxy resins are very brittle and poorly resistant to crack propagation, exhibiting lower toughness and impact resistance especially at low temperature [1–3]. Epoxy resins can be modified to increase toughness and enhance resistance to crack propagation by incorporating toughening materials into the epoxy matrix. In general, as epoxy modifiers, thermoplastics or rubber-like polymers like poly(ether-sulfone)s [4–5], poly(ether-imide)s [6–7], polycarbonate, poly(2,6-dimethyl-phenylene-ether) [8] and polyamides [9] were widely used. Epoxy pre-polymer can be used to increase the miscibility with various soluble thermoplastic polymers. The blends of thermoset/thermoplastics generally present phase-separated morphology. However, phase-separated morphology causes a significant decrease in tensile and peel strengths. Mostly, co-continuous phases are preferred to obtain higher mechanical properties in epoxy/ thermoplastic or epoxy/rubber blends.

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*Address correspondence to Youngson Choe. Tel.: (+82)51-510-2396; Fax: (+82)51-512-8634. E-mail: choe@pusan.ac.kr

In the present work, among the possible approaches to improve the mechanical properties of epoxy systems, introduction of nano-sized core shell rubbers (CSR) into epoxy systems was considered [10–12]. Introducing micron-sized rubber particles into the epoxy systems should have an effect on the cure kinetics since the cure reaction path could be hindered by micron-sized domains. Furthermore, diallyl phthalate (DAP), multipurpose thermosetting resin, can be another alternative to improve the mechanical and water absorption properties [13–14]. DAP possesses the capability of preventing water absorption by participating in networking reaction in epoxy systems. Glass transition temperature (Tg) should be independent on the CSR contents in epoxy systems. Therefore, the size of CSR particles was carefully considered to improve the peel strength and to maintain the Tg of epoxy systems. In this work, the effects of nano-sized CSR particles on the mechanical properties of epoxy systems have been investigated.

Experimental

Diglycidyl ether bisphenol-A type (EEW: 184–190, Kukdo Chemical), diglycidyl ether bisphenol-F type epoxy (EEW: 160–180, Kukdo Chemical) as epoxy resins, methyl tetrahydro phthalic anhydride (MeTHPA, Hitachi Chemical) as a curing agent, 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN, TCI) as an accelerator, and 3-glycidyloxypropyl trimethoxysilane (ShinEtsu) as a coupling agent were used as received. Two types of epoxy resins were partially modified with amine-terminated monomer. Amine-terminated epoxy was mixed with each type of epoxy resin. CSR particles (Rhom & Haas, Diameter: 150∼200 nm) and diallyl phthalate (DAP, TCI) as modifiers, polyether monoamine (PEA, Huntsman) as a dispersion agent were used. Macromelt, commercial polyamide (melting point at 133–143°C, viscosity 5500–8500 cps at 225°C) supplied from Henkel, was used as a modifier.

Two types of epoxy resin were mixed for 20 min with the weight ratio of 1:1 and then curing agent (equivalent ratio of 1:0.85), accelerator (2 phr), polyamide (5 phr) and coupling agent (0.5 phr) were mixed with epoxy resins for 45 min at 80°C. CSR particles (12.5 phr) were dispersed using an ultra-sonic dismembrator and homogenizer. As a final step, DAP monomer was poured into epoxy systems. The dynamic mechanical analysis (DMA, Perkin Elmer) was done at the heating rate of 5°C/min from room temperature to 250°C and at frequency of 1Hz in the air. Cure kinetics was monitored using the dynamic DSC. Impedance analyzer (Agilent E4991A) equipped with DEA (dielectric analysis) sensor was used to monitor the cure kinetics. The peel strength (ASTM D 1876) and impact peel strength (ISO 11343) were measured.

Results and Discussion

The size of CSR particle was carefully selected to improve the peel strength as well as to maintain the glass transition temperature of epoxy systems. In this study, CSR particle of 150 nm diameter was selected. CSR particles were dispersed with polyether monoamine for 1 h. Figure 1 shows the TEM images of CSR particle-dispersed epoxy systems. At the presence of polyether mono amine as a dispersion agent in epoxy system, both a homogenizer and a sonication were used to obtain uniform dispersion of CSR particles in epoxy system. TEM image indicates that CSR particles are well dispersed as shown in Fig. 1(a). However, when high shear-rate mechanical stirrer was used to disperse CSR particles, poor dispersion was obtained as shown in Fig. 1(b). Most of CSR particles were aggregated

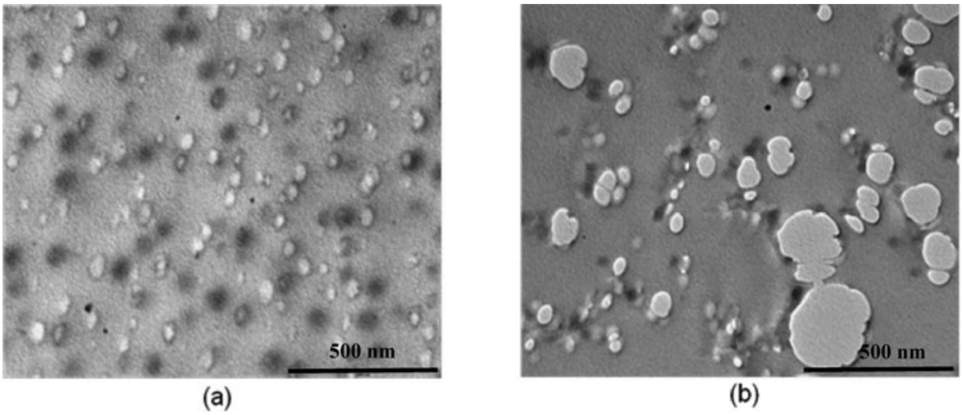


Figure 1. TEM images of well-dispersed CSR particles (using homogenizer and sonication) and poorly-dispersed CSR particles (using high shear-rate mechanical stirrer) in epoxy system.

in epoxy. Poor dispersion of CSR particles in epoxy can lead to increasing the viscosity of prepared epoxy systems and lead to significant decrease of mechanical properties.

Figure 2 shows the dynamic DSC results of epoxy systems containing different amount of CSR particles. As the content of CSR particles in epoxy systems increased, temperatures at highest peak on the heat flow curves maintained almost constant. This indicates that introducing nano-sized CSR particles into the epoxy systems does not affect the cure kinetics. In presence of the catalyst, 2E4MZ-CN, cure temperature was slightly decreased as shown in Fig. 3. Cure time was adjusted to about 10 seconds at 200°C for fast cure

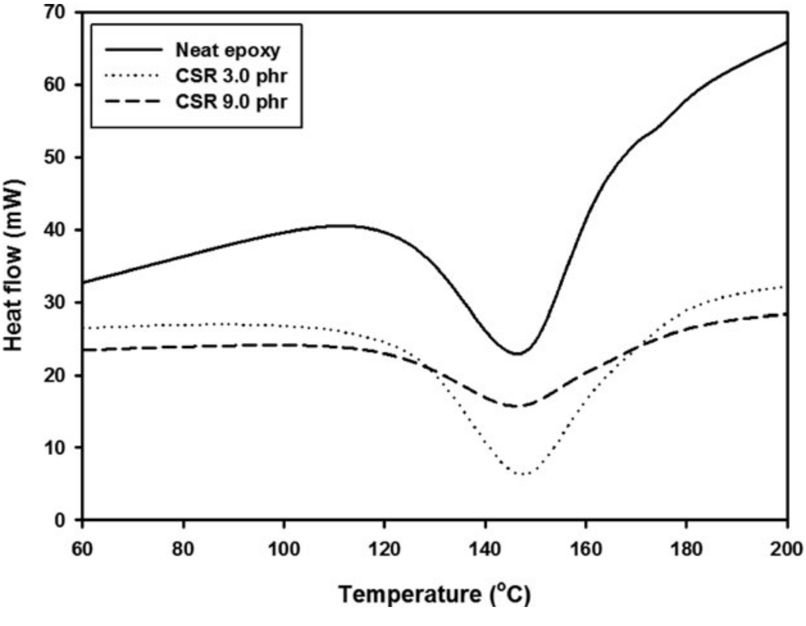


Figure 2. Dynamic DSC results of epoxy systems containing different amount of CSR particles (polyamide : 5 phr, 2E4MZ-CN 1 phr).

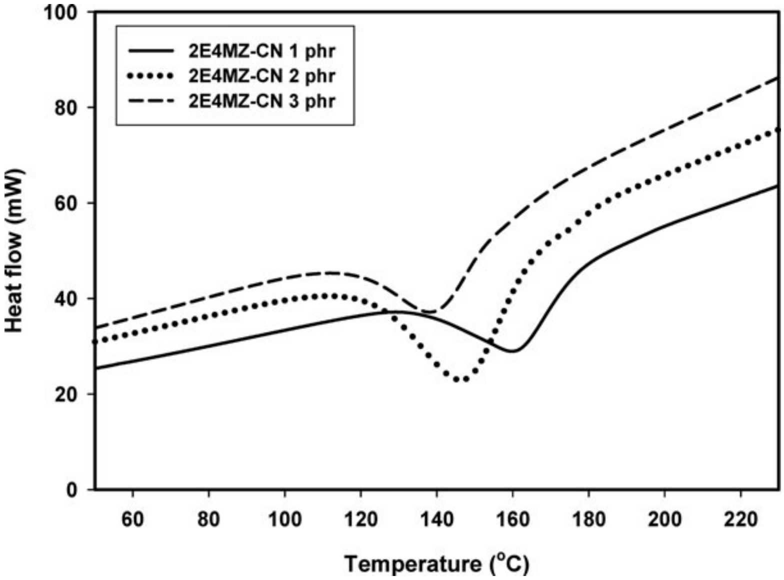


Figure 3. Dynamic DSC results of epoxy systems containing different amount of 2E4MZ-CN (polyamide: 5 phr, CSR: 12.5 phr).

applications. Fast cure epoxy adhesives are essential in various fields of mass production industries. Cure kinetics was monitored using DSC and impedance analyzer and the results are shown in Figs. 4 and 5. In both measurements, cure time was less than 10 sec. From the results of impedance analyzer, it can be concluded that as the content of catalyst increases,

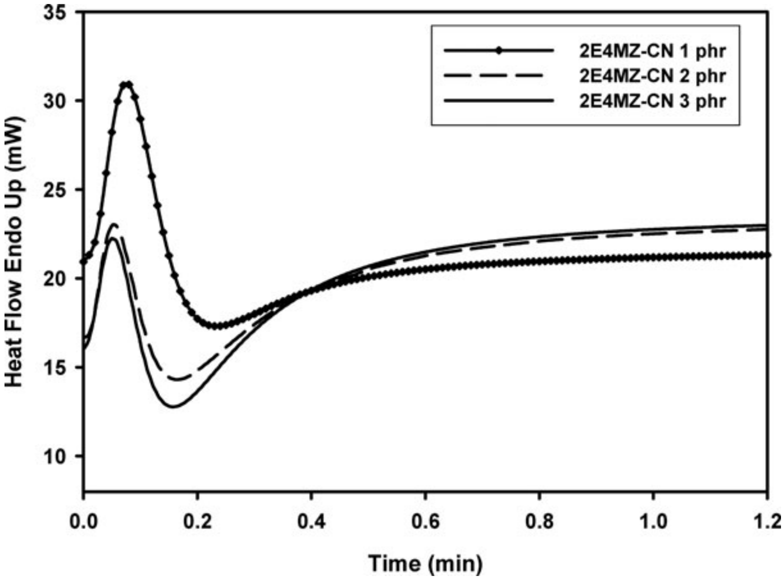


Figure 4. Isothermal DSC results of epoxy systems containing different amount of 2E4MZ-CN (polyamide: 5 phr, CSR: 12.5 phr).

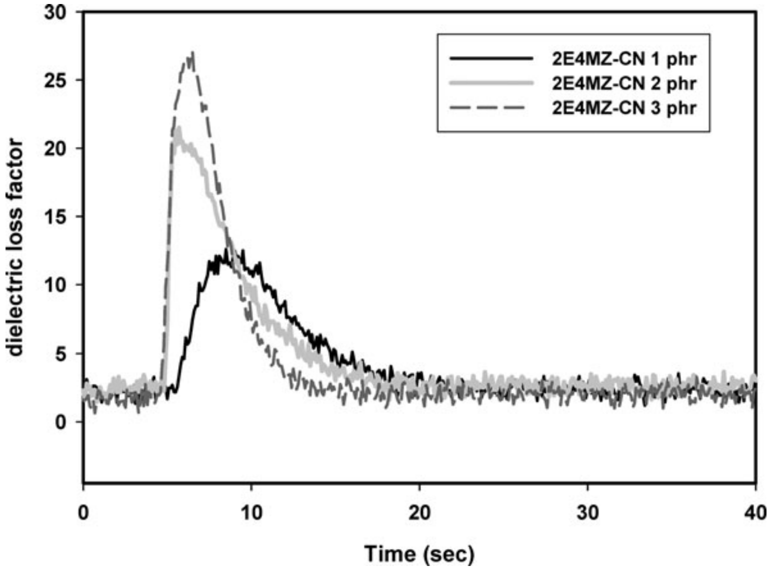
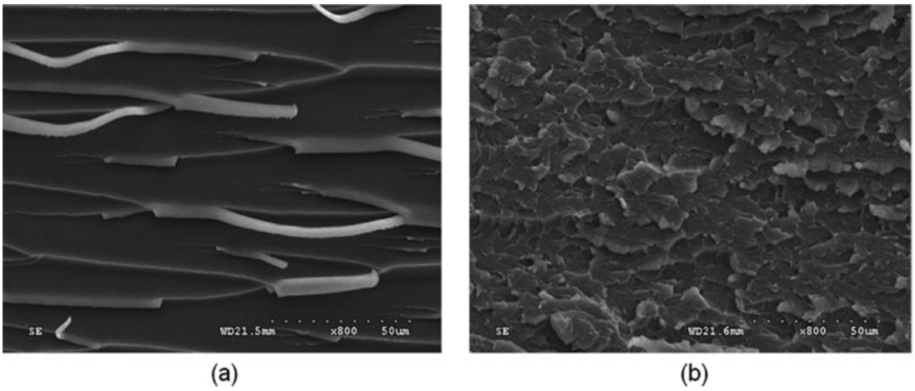


Figure 5. The dielectric loss factor of epoxy systems containing different amount of 2E4MZ-CN (polyamide: 5 phr, CSR: 12.5 phr).

cure time can be reduced up to 7 or 8 sec at the CSR particle content of 12.5 phr, indicating that nano-sized CSR particles in epoxy system does not affect the cure kinetics. The glass transition temperatures of CSR particle-dispersed epoxy systems were 146 and 185°C respectively at the cure temperatures of 200 and 280°C for a cure time of 10 sec. The glass transition temperatures of epoxy systems containing CSR particles of 0, 2.5, 7.5 and 12.5 phr are 143, 142, 141 and 142°C, respectively. Nano-sized CSR particles do not affect the Tg of CSR-particle dispersed epoxy systems.

The fractured surfaces of cured epoxy systems are shown in Fig. 6. With the presence of CSR particles in epoxy system, a rough fractured surface was observed, which indicates that the crack propagation can be effectively blocked in the epoxy matrix, as shown in



(a) (b)

Figure 6. The fractured surfaces of epoxy systems without CSR (polyamide: 5 phr) (a) and with CSR (polyamide: 5 phr, CSR: 12.5 phr, 2E4MZ-CN: 1 phr) (b) cured at 200°C.

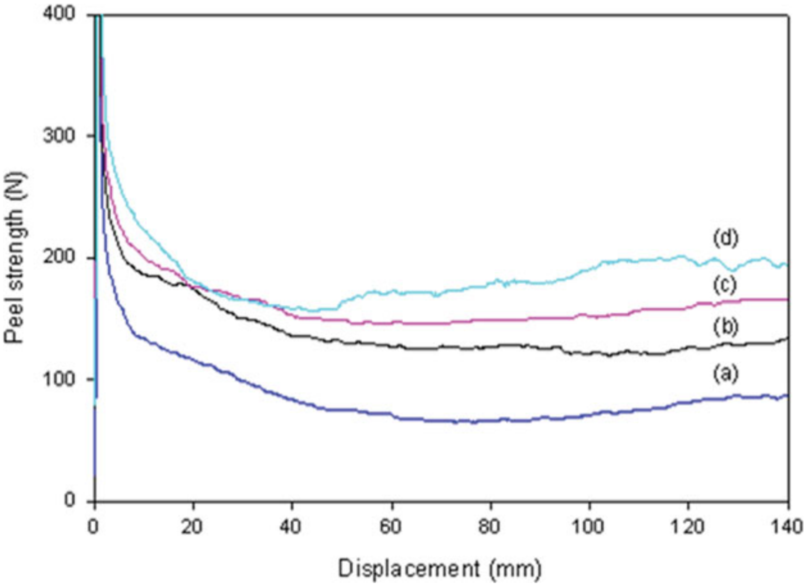


Figure 7. Peel strength of epoxy systems cured at 200°C (2E4MZ-CN: 1 phr); neat epoxy (a), with polyamide (5 phr) (b), with CSR (12.5 phr) (c), and with polyamide (5 phr) and CSR (12.5 phr) (d).

Fig. 6(b). Without CSR particles in epoxy system, the fractured surface is relatively clean, which indicates that there exists no toughening mechanism in the epoxy matrix, as shown in Fig. 6(a).

Peel (180 degree) strengths were significantly increased by introducing nano-sized CSR particles and soluble polyamide into epoxy systems, as shown in Fig. 7. By employing CSR particles and soluble polyamide, the peel strength was increased almost two times compared to neat epoxy. CSR particles might contribute to toughening the epoxy matrix and soluble polyamide to improving adhesion strength in current epoxy systems. Higher peel strength is strongly recommended for high performance structural adhesives.

Impact peel strengths were measured at 23°C and −40°C, respectively, and the results were summarized in Table 1. For a neat epoxy system, the impact peel strength was almost zero at 23°C and −40°C, respectively. For a polyamide-containing epoxy system, low value of impact peel strength was measured at room temperature and zero value of impact peel strength at −40°C, indicating that the system possessed no impact resistance properties at low temperature, −40°C. For a CSR particle-containing epoxy system, higher values of impact peel strength were measured at 23°C and −40°C, indicating that CSR particles can be considered as an effective modifier to improve the peel strength and impact resistance properties of epoxy system at room temperature and temperatures as low as −40°C.

Table 1. Impact peel strength of epoxy systems measured at 23°C and −40°C

Test item	Temperature	Neat epoxy	Polyamide	CSR	CSR + polyamide
Imact peel [N/mm]	23°*C*	0.0	6.0	24.2	27.4
	−40°*C*	0.0	0.0	14.7	15.2

Conclusion

Epoxy/polyamide/CSR (core-shell rubber)/anhydride blends were prepared for the application to high performance structural adhesives. Incorporating nano-sized CSR particles into epoxy systems can be an effective solution to improve the toughness of epoxy system at low temperature, −40°C, without sacrificing the thermodynamic properties such as Tg and cure kinetics, achieving less than 10 seconds of cure time at 200°C by employing 1-(2-cyanoethyl)-2-ethyl-4-methylimidazole (2E4MZ-CN) as a cure accelerator. Consequently, soluble polyamide and nano-sized CSR particles in epoxy system acted as effective modifiers to provide an excellent impact optimized performance of epoxy systems at low temperature for fast cure applications in the various fields of industries.

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