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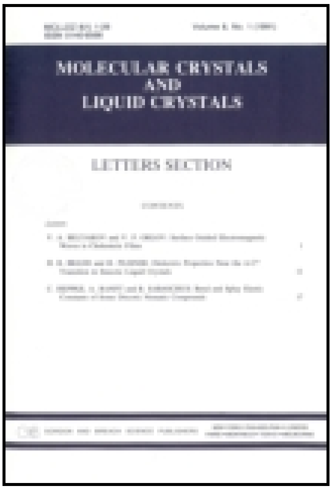

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Mechanical Properties of Highly Flexible Epoxy Systems Containing Nano-Sized Polymeric and Inorganic Particles

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Epoxy systems containing flexible epoxy and nano-sized particles were prepared and mechanical properties, such as lap-shear and impact-peel strengths were measured. Core-shell rubber (CSR), $CaCO_3$, and SiO_2 particles were used as nano sized particles. Polyurethane- and polyamide-modified epoxies were used to form flexible epoxy matrix. As curing agents, DDS (4,4-diaminodiphenyl sulfone) and DICY (dicyandiamide) were used, and 2E4MZ-CNS(1-cyanoethyl-2-4-metylimidazole) was used as catalyst. As an adhesion promoter, zirconate coupling agent was used. CSR has significantly improved impact-peel strengths especially at low temperature, −40°C, due to the presence of highly flexible segments in epoxy backbones. Furthermore, nano-sized inorganic particles, $CaCO_3$, and SiO_2, have improved the impact-peel strengths of the epoxy systems. However, the lap-shear strength was decreased as the content of flexible epoxy was increased in epoxy systems.

Keywords Core-shell rubber; epoxy; coupling agent; impact-peel strength; inorganic particles

Introduction

High performance epoxy systems, which possess excellent mechanical properties, can be used in many applications such as composites and structural adhesives [1–2]. In recent years, many studies on the toughness modification of epoxy system have been performed to overcome major disadvantages such as, low impact strength and low toughness [3–5]. In epoxy/thermoplastic blends, micro-sized phase-separated morphology, which is developed during cure process, contributes to low tensile strength and low combinable ability of other components [6]. In general, the phase behavior can be considered as one of the main factors to affect on mechanical properties.

Regarding the phase behavior, it is reported that in the presence of DDS(3,3 diamino diphenyl sulfone), the blends partially develop co-continuous phases [8, 9, 15]. In the same manner, the co-continuous phases were obtained in epoxy/thermoplstic blends when

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imidazole was introduced, as a catalyst. Furthermore, reactive thermoplastic enhanced the interaction between phases in epoxy system [10, 11, 13, 14].

CSR particles have been widely used to improve the mechanical performances of composite materials and structural adhesives at wide range of temperatures, especially at low temperatures [7–9, 16]. In this study, CSR and other nano-sized inorganic particles such as $CaCO_3$, and SiO_2 particles were incorporated into epoxy systems to improve the mechanical performances of flexible epoxy systems. Furthermore, as an adhesion promoter, zirconate coupling agent was introduced to increase the interfacial adhesion strength between polymer matrix and particles.

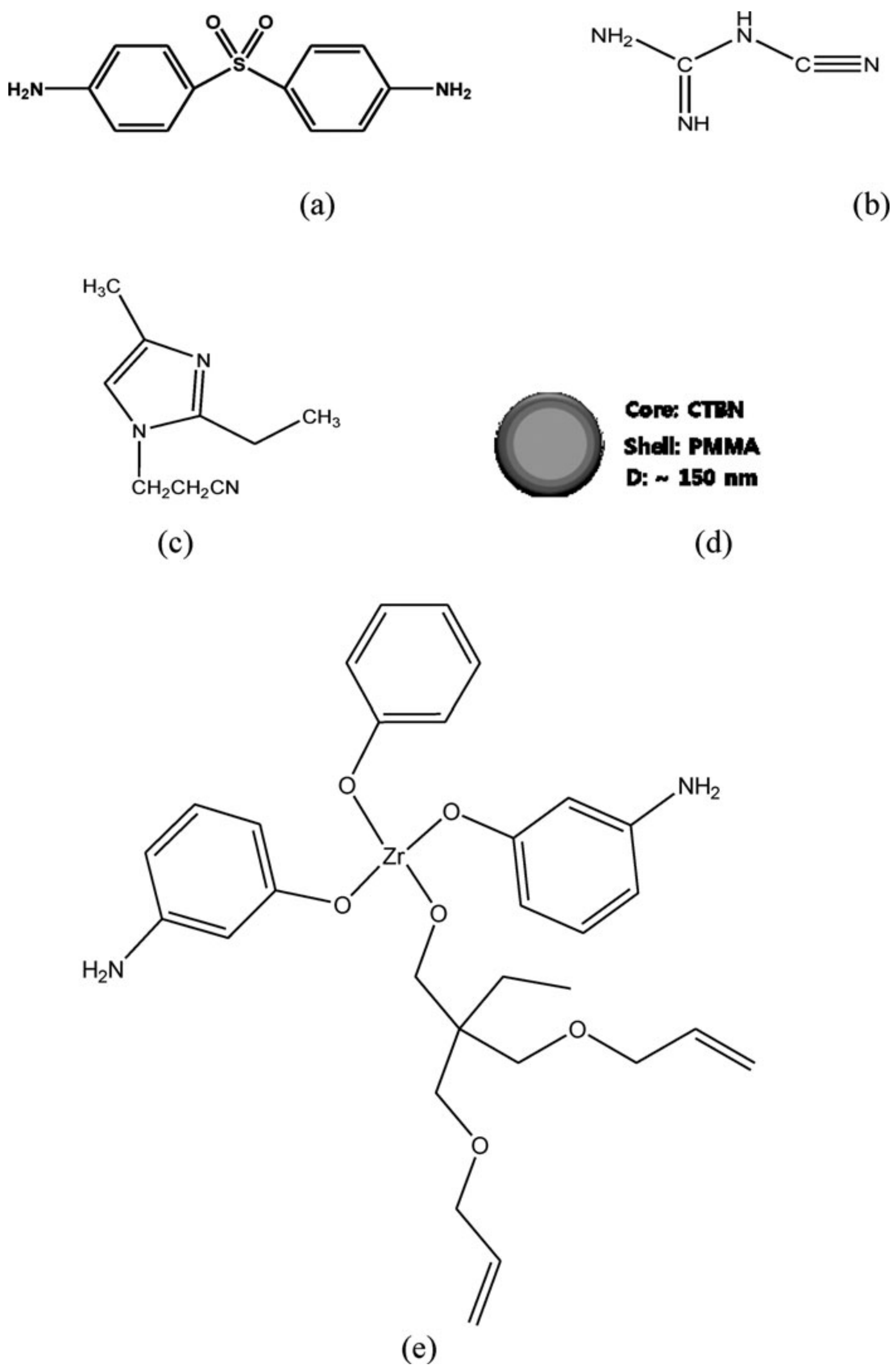
Experimental

Diglycidyl ether bisphenol-A (EEW: 184-190, Kukdo Chemical) as epoxy resin, DDS (4,4-diaminodiphenyl sulfone) and DICY (dicyandiamide, Aldrich)) as curing agents, and 2E4MZ-CNS(1-cyanoethyl-2-4-metylimidazole, Aldrich) as catalyst, and [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-O,O’,O”]zirconium (Kenrich) as a zirconium coupling agent are used as received. An epoxy resin were modified with polyamine(Dow Chemical). Polyurethane-modified epoxy(Bokwang) was used as received. Each modified epoxy was mixed with CSR particles (Rhom & Haas, Diameter: 150 nm in an equivalent ratio of 1:0.85), an accelerator (2 phr), and a coupling agent (0.5 – 1.0 phr). CSR and other inorganic particles (15 phr) were dispersed using an high frequency dismembrator and homogenizer. The lap shear strength and impact-peel strength (ISO 11343) were measured. The specimen of impact-peel strength test is shown in Figure 2.

Results and Discussion

In general, the modification of epoxy resin contributes to the improvement of wettability and adhesion capability of modified epoxy at substrate surface. Amine- or urethane-modified epoxy exhibits higher surface energy due to the hydrophillicity of amines or urethanes. As another approach to improve the mechanical properties of epoxy resin, nano-sized polymeric or inorganic particles are widely incorporated into very brittle epoxy resin. In this study, nano-sized particles were dispersed into relatively flexible epoxy system which already exhibits higher mechanical properties. The size of CSR and inorganic particles ($CaCO_3$, and SiO_2 particles) was carefully selected to improve the lap shear strength as well as impact-peel strength. The diameters of CSR and inorganic particles are about 150 and 30 nm, respectively. All the particles are very uniformly dispersed using a high frequency dismembrator and homogenizer. In addition, DICY and 2E4MZ-CNS were incorporated into epoxy-DDS cure process to partially increase the flexibility of cured epoxy system and to improve the adhesion properties of cured material. Imidazole can lead to increasing the interaction of thermoplastic and thermoset matrix, resulting in the increase of lap shear strength.

The lap-shear and impact-peel strengths of neat and flexible epoxy systems were measured and summarized in Table 1. Impact load and impact energy data were measured at 23°C and −40°C, and typical plots of impact load data were shown in Figure 3. Impact-peel strength was calculated by integrating the load curve from ″A″ to ″B″ point. In principle, as the area below the load curve increases, impact-peel strength increases. For neat epoxy at room temperature, the value of impact-peel strength is to be near zero since the impact load values from ″A″ to ″B″ point are almost zero. The lap-shear strengths of polyurethane- and polyamine-modified epoxy were higher than that of neat epoxy. Brittleness generally decrease the mechanical properties of materials including lap shear strength. Modified



(a) (b) (c) (d) (e)

Figure 1. Structures of (a) 4,4-diamino diphenylsulfone (DDS), (b) dicyandiamide (DICY), (c) 2E4MZ-CNS (1-cyanoethyl-2-4-metylimidazole), (d) CSR, and (e) [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-O,O′,O″]zirconium.

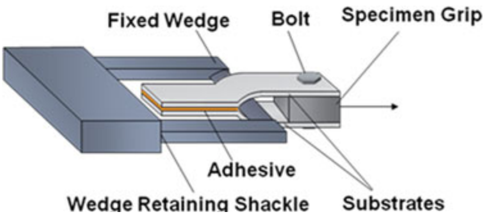


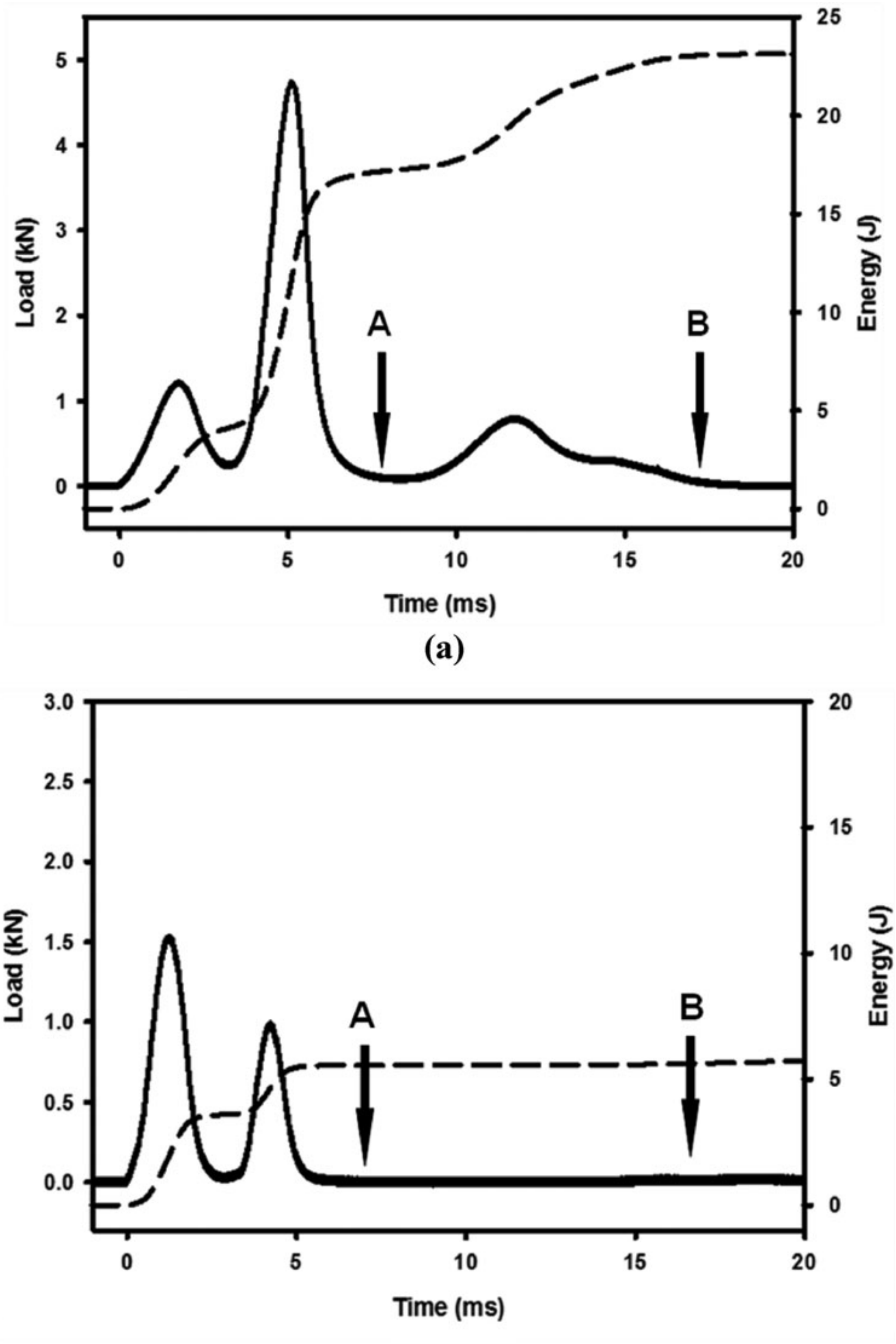
Figure 2. The specimen for impact-peel strength test.

epoxy exhibits higher wettability on to the substrate surface and contains flexible segments in the epoxy backbone, which leads to the improvement of adhesion properties of epoxy systems. Impact-peel strengths of two modified epoxy systems at room temperature were relatively low, 0–17 N/mm, compared to commercial grades of high performance structural adhesives (Dow and Henkel) and at −40°C, the values were almost zero. This indicates that other effective impact-absorbing mechanisms should be necessary and incorporated into the current flexible epoxy systems especially at low temperature, at −40°C.

Nano-sized particles and silane or zirconate coupling agents are incorporated into amine- or urethane-modified epoxy, and then the lap-shear and impact-peel strengths of flexible epoxy systems were measured. The measured mechanical properties are summarized in Table 2. CSR, SiO_2 and $CaCO_3$ particles are highly effective in improving the lap-shear strengths of flexible epoxy systems. CSR containing epoxy systems showed relatively lower value of lap shear strength since the coupling agent could not work with CSR particles. Zirconate coupling agent in flexible epoxy systems was not effective in improving the impact-peel strengths at both 23°C and −40°C, indicating that a coupling agent can not contribute to crack-blocking mechanism during crack propagation process. For a CSR particle-containing flexible epoxy system, higher values of impact peel strength were measured at 23°C and −40°C, indicating that nano-sized CSR particles can be a most effective impact-absorbing agent in flexible epoxy systems at room temperature as well as at low temperature, −40°C. In flexible epoxy systems, nano-sized SiO_2 and $CaCO_3$ particles are not effective as toughening agents at room temperature as well as at low temperature, mainly due to the very rigid interface between flexible epoxy and particles regardless of introducing a coupling agent. Consequently, nano-sized CSR and inorganic particles and a coupling agent can be used together in flexible epoxy systems to improve both impact-peel resistant and adhesion properties at room and low temperatures.

Table 1. Mechanical properties of amine- and urethane-modified epoxies

Epoxy systems	Lap-shear strength (MPa)	Impact-peel strength at 23°C (N/mm)	Impact-peel strength at −40°C (N/mm)
Neat epoxy	19	0	0
Amine-modified epoxy	30	17	0
Urethane-modified epoxy	11	12	0



(a)

(b)

Figure 3. Typical impact load and impact energy vs. impact time plost at (a) 23°C and (b) −40°C.

Table 2. Mechanical properties of amine- and urethane-modified epoxies blended with nano-sized CSR, SiO_2, and $CaCO_3$ particles, and zirconate coupling agent

Epoxy systems		Lap-shear strength (MPa)	Impact-peel strength at 23°C (N/mm)	Impact-peel strength at −40°C (N/mm)
CSR 10phr	+Neat epoxy	20	11	7
	+Urethane-modified epoxy	24	22	15
	+Urethane-modified epoxy + zirconate	24	23	16
	+Amine-modified epoxy	28	28	20
	+Amine-modified epoxy +zirconate	28	26	21
SiO_2 10phr	+Neat epoxy	19.2	0	0
	+Urethane-modified epoxy	24	14	0
	+Urethane-modified epoxy + zirconate	26	14	0
	+Amine-modified epoxy	30	16	0
	+Amine-modified epoxy +zirconate	33	16	0
$CaCO_3$ 10phr	+Neat epoxy	16	0	0
	+Urethane-modified epoxy	21	13	0
	+Urethane-modified epoxy + zirconate	23	13	0
	+Amine-modified epoxy	28	14	0
	+Amine-modified epoxy +zirconate	30	15	0

Conclusions

Amine- or urethane-modified flexible epoxy, exhibiting hydrophillicity, was blended with nano-sized particles and a zirconate coupling agent, and then the lap-shear and impact-peel strengths of flexible epoxy systems were measured. Nano-sized CSR, SiO_2 and $CaCO_3$ particles are highly effective in improving the lap-shear strengths of flexible epoxy systems. However, nano-sized inorganic particles are not effective as toughening agents in flexible epoxy matrix, regardless of introducing a coupling agent into the epoxy system in this study.

Acknowledgments

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