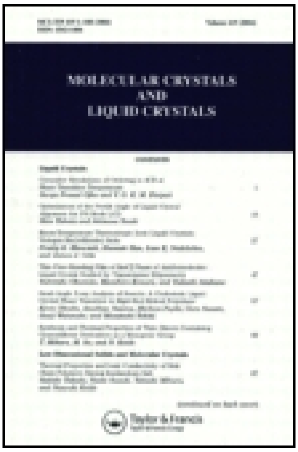

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Mechanical Properties of Core-Shell Rubber (CSR)/Diallyl Phthalate (DAP)/Epoxy Systems for Electronic Packaging Materials

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Modification of epoxy systems for electronic packaging materials, specially flip chip bonding materials, by introducing diallyl phthalate (DAP) and core-shell rubber (CSR) particles into epoxy systems have been investigated to improve the mechanical and water absorption properties. The cure behavior of CSR/DAP/epoxy/anhydride system was monitored by differential scanning calorimetry (DSC). Dynamic mechanical analyzer (DMA) was used to measure the glass transition temperature (T_g) of epoxy systems. CSR particles with the diameter of 150–200 nm played an important role in improving the peel strengths of non-conductive pastes (NCPs) while maintaining the thermodynamic properties such as the glass transition temperature of epoxy systems. Furthermore, introducing DAP into epoxy networks have improved both the water absorption properties and peel strengths of epoxy systems, in which the loading percent of DAP was limited to about 10% to obtain the lowered water absorption properties in this study.

Keywords Core-shell rubber particles; diallyl phthalate; electronic packaging materials; epoxy system; non-conductive pastes

Introduction

In electronic packaging areas, flip chip assembly using conductive or non-conductive adhesives is gaining gradual interests in chip packaging for its advantages compared with solder bumps. The typical advantages of flip chip assembly using conductive or non-conductive adhesives are lower processing temperature, finer pitch interconnection, cost efficiency, and a green technology [1–5]. For that reason, flip chip technology using non-conductive adhesives (NCAs) or pastes (NCPs) plays an increasingly important role in new electronic products and needs some properties such as high adhesion properties, low coefficient of thermal expansion (CTE), high Tg, and low water absorption [3]. Glass transition temperature (Tg) is the temperature at which the plastic changes from a rigid of harder material to a softer of glassy-type material, of where the physical properties of the resin change due to a weakening of the resin system's molecular bonds. Tg is important factor of

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Address correspondence to Youngson Choe, Department of Chemical Engineering, Pusan National University, Busan 609-735, Korea. Tel.: +82-51-510-2396; Fax: +82-51-512-8634; E-mail: choe@pusan.ac.kr packaging materials due to related to the other properties [15]. Tg can be determined from the dynamic mechanical analyzer (DMA) measurements as proposed by Lakshmi *et al.* [16]. The cross-linking density correlates directly to the glass transition temperature. Tan delta is plotted against temperature and glass transition is normally observed as a peak since the material will absorb energy as it passes through the glass transition. Non conductive adhesives (NCAs) offer a further pitch reduction less than 40 µm because they do not contain conductive particles which might give rise to short circuits [4] and thus NCAs can be an alternative to anisotropic conductive adhesives (ACAs) or pastes (ACPs) for fine pitch applications, offering a lead free, low temperature process. ACPs application in flip chip is able to achieve a pitch size of 70 µm [6]. In most NCPs applications, epoxy systems are used as a base material and higher chip bonding strength is needed. Among the possible approaches to improve the mechanical properties of epoxy systems, introduction of core shell rubbers (CSR) to epoxy systems can be considered [7–9]. Furthermore, diallyl phthalate (DAP), multipurpose thermosetting resin for electronic applications, can be another solution to improve the mechanical and water absorption properties [10,11]. DAP possesses a capability of preventing water absorption by networking reaction in epoxy systems. In this work, we have investigated the effects of nano-sized CSR particles and DAP on the mechanical properties of epoxy systems for electronic packaging.

Experimental

Materials

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-cyanoethl)-2-ethyl-4-methylimidazole (TCI) as a curing accelerator, and 3-glydidyloxypropul trimethoxy silane(ShinEtsu) as a coupling agent are used as received. CSR particles (Rhom & Haas, Diameter: 150~200 nm) and diallyl phthalate (DAP, TCI) as modifiers, polyether monoamine (Huntsman) as a dispersion agent were used, and the chemical and core shell structures are shown in Figure 1.

Two types of epoxy resin were mixed for 20 minutes with the weight ratio of 1:1 and then curing agent (equivalent ratio of 1:0.85), accelerator (2 phr) and coupling agent (0.5 phr) were mixed with epoxy resins for 45 minutes at 80°C. CSR particles (2.5, 7.5, and 12.5 phr) with polyether monoamine were dispersed in the prepared epoxy systems using an ultra sonic dismembrator for 1 hour at 80°C. As a final step, DAP monomer was poured into epoxy systems by 10, 20, and 30 phr in epoxy systems.

Measurements

Curing kinetics were taken with dynamic mode differential scanning calorimetry (DSC, Perkin Elmer) at a 10°C/min heating rate from 50 to 250°C. 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 1 Hz in the air. The adhesion strength, 90 degree peel strength, was measured by ASTM-D6862

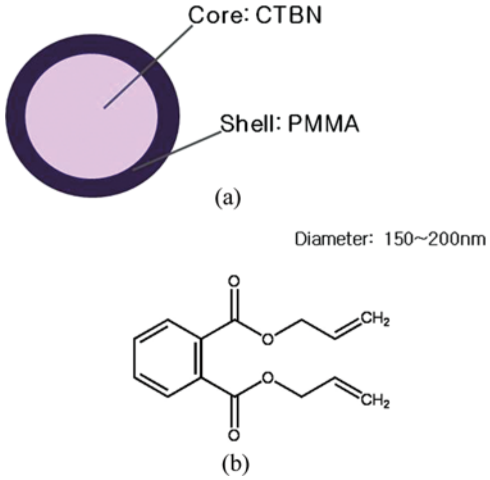

Figure 1. Structure of core-shell rubber (core; CTBN (carboxyl terminated butadiene acrylonitrile), shell; PMMA (polymethyl methacrylate)) (a) and DAP (diallyl phthalate) (b).

standards [12]. The prepared NCPs were applied on to the interface of pre-patterned ITO glass and coffer foil. The test specimens were cured at 200°C for 5 minutes including holding time and 30Mpa of pressure was applied on to the specimen during the curing process.

Water absorption was measured by ASTM-D570 standards [13], the specimen size was $25 \times 50 \times 1.5$ mm. Specimens were dried for 30 hours in the vacuum oven at 80°C and their initial weights were measured and then specimens were immersed in water for 100 hours at 60°C. After removing the reminder of water at surface of sample, the weight of specimens were measured. Water absorption was calculated from the ratio of [wet weight – conditioned weight] to [conditioned weight] of the specimen.

Result and Discussion

Cure kinetics was monitored using the dynamic DSC, as shown in Figure 2. While the contents of CSR particles in the prepared NCPs increased, cure peak temperatures on the heat flow curves maintained almost constant, near 146°C. This indicates that introducing nano-sized CSR particles into the NCPs does not affect on the cure kinetics. However, if there exist micro-sized domains in epoxy systems, those domains could affect on the cure kinetics. At the presence of micro-sized domains in epoxy systems, in general, cure peak temperatures on the heat flow curves slightly increase since the cure reaction path could be hindered by micro-sized domains [14]. In that reason, nano-sized domains are strongly recommended for high Tg epoxy systems and the Tg of NCPs, containing nano-sized domains in the present epoxy systems, was also independent on the CSR particle contents as expected, as shown in Figure 3. Because of the effect of CTBN contents that is CSR core material, there are shown a small peak between 90°C and 110°C. But it is too small to ignore. In two aspects, the size of CSR was carefully selected; 1) to improve the peel strength and

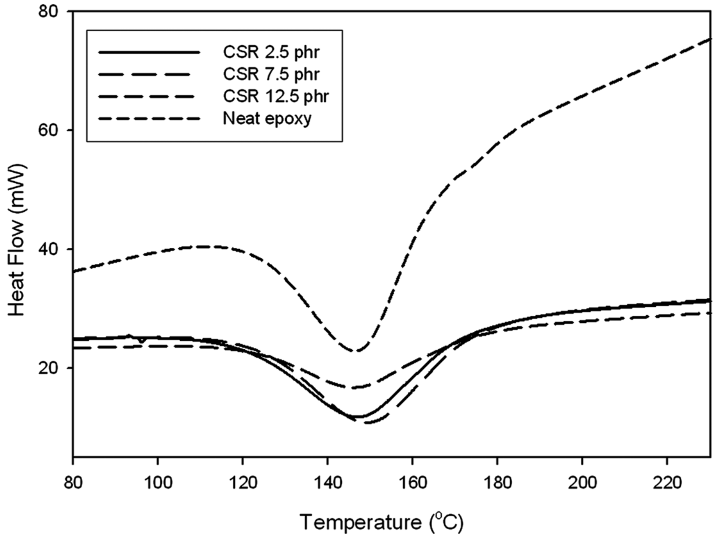

Figure 2. Dynamic DSC results of epoxy systems containing different amount of CSR (2.5, 7.5 and 12.5 phr).

2) to maintain the glass transition temperature of epoxy systems. Therefore, 150–200 nm of CSR in diameter was selected in this study.

The peel strength of NCPs was strongly dependent on the contents of CSR and DAP, as shown in Figure 4. As the CSR content was increased, the peel strength was proportionally increased from 9×10^4 Pa to 1.4×10^4 Pa. The value of 1.4×10^4 Pa, as a goal in this study, is strongly recommended for finer pitch interconnections applications. In most electronic package applications, the normal value of peel

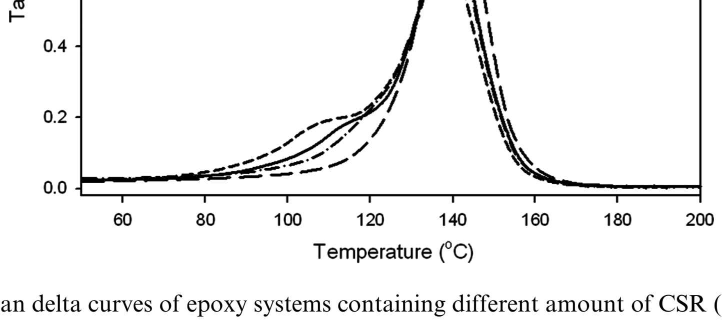

Figure 3. Tan delta curves of epoxy systems containing different amount of CSR (2.5, 7.5 and 12.5 phr).

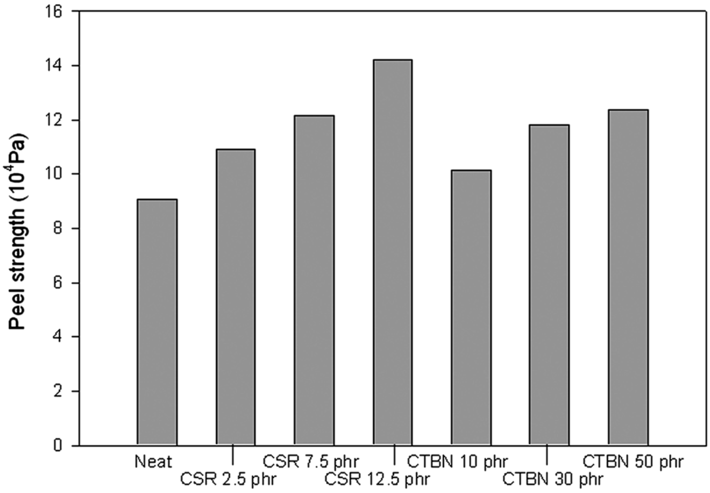

Figure 4. 90 degree peel strengths of epoxy systems containing different amount CSR (2.5, 7.5 and 12.5 phr) and DAP (10, 20 and 30 phr).

strength is about 1.1×10^4 Pa. As the DAP content was increased, the peel strength was slightly increased. However, over 20 phr DAP, the peel strength began to decrease since, at higher contents of DAP in epoxy systems, the epoxy matrix tends to be rigid, leading to decreasing the toughness of epoxy systems.

Water absorption results are shown in Figure 5. Epoxy systems modified with 10 phr DAP showed much lower water absorption percent than neat epoxy system. However, over 30 phr DAP in epoxy systems, water absorption percent was not reduced and the glass transition temperature was slightly lowered by about 5°C compared to neat epoxy system. This indicates that the cross-linking density was lowered

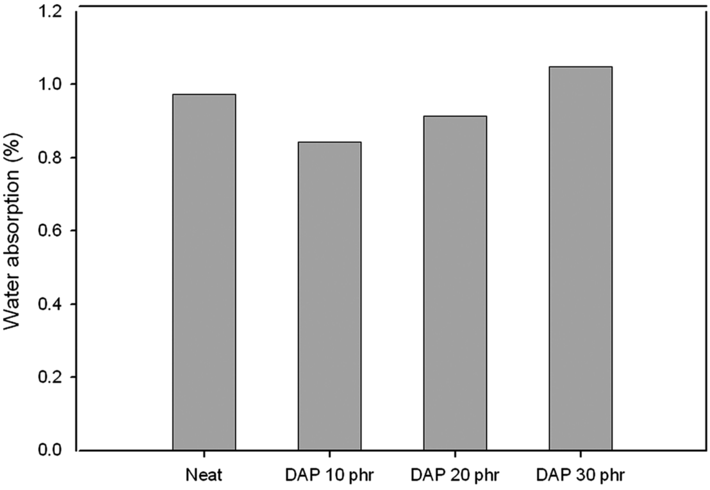

Figure 5. Water absorption percents measured for epoxy systems containing different amount of DAP (0, 10, 20 and 30 phr).

at higher blending percent of DAP with neat epoxy and water absorption properties, partially depending on cross-linking density in epoxy systems, have been consequently changed. Consequently, epoxy systems for electronic packaging materials can be modified by introducing DAP and CSR to improve the mechanical and water absorption properties while maintaining the thermodynamic properties of epoxy systems in this study.

Conclusion

Epoxy systems for electronic packaging materials, especially flip chip bonding materials, have been modified by DAP and CSR particles to improve the mechanical and water absorption properties. CSR particles with the diameter of 150–200 nm played an important role in improving the peel strengths of NCPs while maintaining the thermodynamic properties such as the glass transition temperature of epoxy systems. Furthermore, introducing DAP into epoxy networks have influenced on both the water absorption properties and peel strengths of epoxy systems. The loading percent of DAP was limited to about 10 phr in epoxy systems to obtain the lowered water absorption properties in this study.

Acknowledgment

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