Characterization of Microcapsules for Self-Healing in Polymeric Composites

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ABSTRACT

Two different diene monomers [dicyclopentadiene (DCPD) and 5-ethylidene-2-norbornene (ENB)] as self-healing agent for polymeric composites were microencapsuled by *in-situ* polymerization of urea and formaldehyde. The healing agents were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Exothermic reaction and glass transition temperature from DSC and storage modulus (G') and tan δ from DMA curves were analyzed for the samples cured for 5 min and 24 h in the presence of different amounts of catalyst. Microcapsules were successfully formed for both diene monomers. Microcapsules containing the healing agent were manufactured and its thermal properties were characterized by thermo gravimetric analysis (TGA). Optical microscope (OM) and particle size analyzer (PSA) were employed to observe morphology and size distribution of microcapsules, respectively. Comparison of the two self-healing agents and their microcapsules with the two was made in this study.

1. INTRODUCTION

In polymer matrix composites, the damage is known to initiate mainly at the interface between reinforcement and matrix, leading to interfacial debonding. Ply delamination due to the defects introducing during manufacture may also take place. Brittle matrix of the composite material is susceptible to microcracks under load. Once these irreversible damages occur within the composites, mechanical strength decreases and the life time becomes shorten greatly. An autonomic damage repairing technique in polymer composites has been recently of great interests since the methodology for the repair was reported in the literature.[1,2] The new repair concept involves recovery of mechanical strength by means of a liquid healing agent to be filled and vitrified between crack planes. The healing agent microencapsuled and then embedded in matrix with catalyst is supposed to be released into cracks by capillary action when microcapsules are ruptured by propagating cracks. Catalyst in matrix subsequently initiates polymerization of the released healing agent in the crack.

In the recent work[1, 2], the microcapsules for self-healing were manufactured using a dicyclopentadiene (DCPD) healing agent surrounded by a urea/formaldehyde (U/F) thermosetting resin thin wall, and showed substantial healing effects in a fiber-reinforced polymer matrix composites. An artificial crack was introduced in the composite and applied normal stress, inducing the crack propagated. Stress-strain behavior from cantilever beam tests showed that about 45% at room temperature and over 80% at 80°C for 48 h of healing were recovered in fracture toughness. However, there are several points to be considered for more effective healing by the self-healing concept. First of all, it should be considered the amount of catalyst and the rate of polymerization of healing agent. For the substantial recovery in facture toughness, it is necessary to cure for 48 h in the presence of as much as 5 wt% of catalyst. The large amount of catalyst and the long period of cure time are not desirable in practical applications. Therefore, it is essential to develop more reactive healing agent with smaller amounts of catalyst. Secondly, DCPD used as a healing agent in the study has a melting point of around 10°C,[2] which means that the healing mechanism proposed may not work by the freezing of the healing agent below this temperature. Development of healing agent with no freezing is essential to the self-healing.

In this study, a new healing agent [5-ethylidene-2-norbornene (ENB)] to overcome the above limitations is introduced and investigated the possibility as healing

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agent for the self-healing method. Microcapsules were produced using a reactor system which was assembled in this laboratory.

2. EXPERIMENTAL

Diene monomer is capable of forming crosslinked structure with high toughness and strength from a low molecular weight monomer with a low viscosity through a ring opening metathesis polymerization mechanism.[3] Therefore, this monomer is considered to be an appropriate candidate for the purpose of healing cracks due to damages in polymeric composite materials. In this study, two different diene monomers, dicyclopentadiene (DCPD) and 5-ethylidene-2-norbornene (ENB), were characterized and microencapsulated by a urea-formaldehyde thermosetting material.

2.1 Characterization of Self-Healing Agents

Thermal analysis to investigate the cure behavior of the healing agents was performed by differential scanning calorimetry (DSC, Dupont 982, USA) and dynamic mechanical analysis (DMA, StressTech Rheometer, Reologica Instrument, Sweden) for two different samples (i.e., DCPD and ENB) at the various amounts of catalyst. Catalyst used in this study was bis(tricyclohexylphosphine)benzyllidine ruthenium (IV) dichoride (Grubbs's catalyst, Strem Chemicals, USA). Chemical structures of the diene monomers and the catalyst are represented in Figure 1. Amount of catalyst was determined from a series of preliminary experiments. DSC temperature scans were made from -40 to 225°C for samples with no catalyst and from room temperature to 225°C with catalyst. For the liquid samples with no catalyst, about 5mg was poured into a hermetic pan and tightly clamped with cap on which four tiny holes were made to allow vaporization of sample during testing.

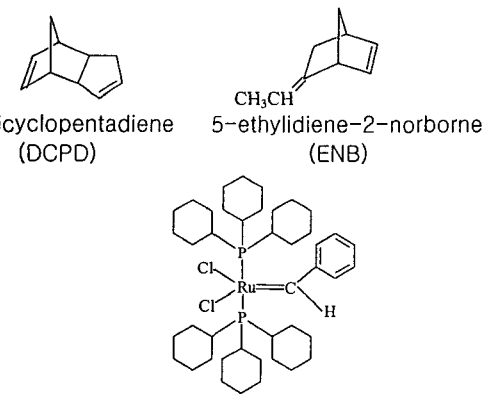

Figure 1. Chemical structures of diene monomers and catalyst.

The diene monomers with catalyst were mixed for 2 min in a vial by a mechanical stirrer. The mixture was spreaded into thin film on Teflon sheet and allowed to cure at room temperature for 5 min and 24 h. The reason of making film immediately after the mixing is to prevent further reaction due to severe exothermic heat in a bulk form of the dienes under catalyst. 10 mg of the solid sample in aluminum pan was taken from film cured on the Teflon sheet. The glass transition temperature (T_g) of the cured samples was determined from the infection point of a stepwise transition on the DSC thermogram. All DSC experiments were made at a heating rate of 10°C/min under a dry nitrogen atmosphere.

For a dynamic mechanical analysis technique used in this experiment, two parallel plates of a stationary disc plate (ϕ=30 mm, thickness=3.2 mm) and an oscillatory upper plate (ϕ=8 mm) accommodate approximately 50 mg of a liquid sample. Oscillation was imposed to the sample with frequency of 1 Hz under applied stress of 5000 Pa. Gap between the plates (or sample thickness) was fixed to be 0.3 mm during all the experiments.

2.2 Manufacture and Characterization of Microcapsules

DCPD and ENB were microencapsuled by a urea-formaldedyde thermosetting material. Microcapsules were formed for both diene monomers in distilled water by vigorous stirring at 1000 rpm. Poly(ethylene-co-maleic anhydride) (EMA) was used as an emulsifier. System conditions for the production of microcapsules were pH=4.0 and reaction temperature=55°C for both monomers. Details of the manufacturing process have been reported.[4] The produced microcapsules containing of DCPD and ENB were observed by optical microscope (OM, Epiphot 200, Nikon, Japan) and characterized by thermogravimetric analysis (TGA, Dupont 931, TA instrument, USA) and particle size analysis (PSA, Microtrac-S3000, USA).

3. RESULTS AND DISCUSSION

3.1 Characterization of healing agents

Figure 2 shows DSC thermograms for diene monomers (DCPD and ENB) with no catalyst and different amounts of catalyst after 5 min of cure at room temperature. DCPD with no catalyst shows two endothermic peaks; while a small one at 15°C and a big at 143°C, corresponding to melting transition and evaporation of the monomer, respectively. Onset of evaporation of monomer occurs at 55 and 35°C and a peak temperature of the evaporation at 140 and 105°C for DCPD and ENB, respectively. After the 5 min of cure, liquid sample with catalyst became solidified but DSC thermogram shows an exothermic peak, indicating that cure reaction was not completed yet. The exothermic peak shifts to lower temperature from 55°C (0.65 wt% catalyst) to 50°C (5 wt% catalyst) for DCPD.

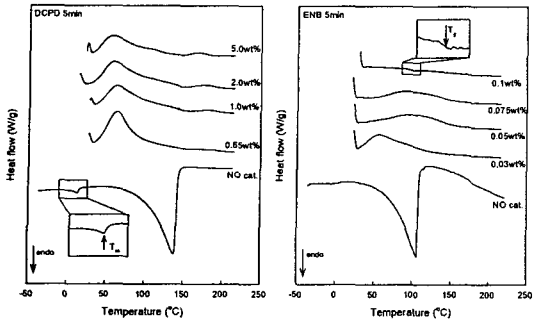

Figure 2. DSC thermograms of DCPD and ENB for samples cured for 5 min at room temperature with no catalyst and with different amounts of catalyst.

DSC curve for ENB has a big endothermic peak at 105°C due to evaporation of monomer, but no melting peak was observed. An exothermic peak occurs at 50°C in this monomer with the catalyst amount of 0.03 wt%. However, the exothermic peak temperature increases with the increase of catalyst up to 0.075 wt%, which is opposite to DCPD. At 0.1 wt%, a stepwise transition was observed at 90°C on the DSC curve corresponding to the glass transition temperature but no exotherm above the temperature. Note that cure reaction proceeds much faster in ENB than DCPD at less than 1/10 of catalyst.

In Figure 3, DSC thermograms are represented for DCPD and ENB cured for 24 h at room temperature. For DCPD, all the DSC curves exhibit two exotherms; a big and broad one at lower temperature and a small at higher temperature. As the amount of catalyst increases from 0.65 to 5.0 wt%, the big peak temperature shifts from 95 to 75°C, and a small peak temperature shifts from 185 to 170°C with increase in peak area. Glass transition appears for the catalyst of 0.65 and 1.0 wt% right before the exothermic peak around 50°C. However, no glass transition was observed at higher catalysts (i.e., 2.0 and 5.0 wt%). The glass transition does exist but may be hidden by the exotherm due to the faster reaction at higher amount of catalyst. Note also that, at 0.1 wt% of ENB, the glass transition appears around 90°C, above which no exothermic peak exists.

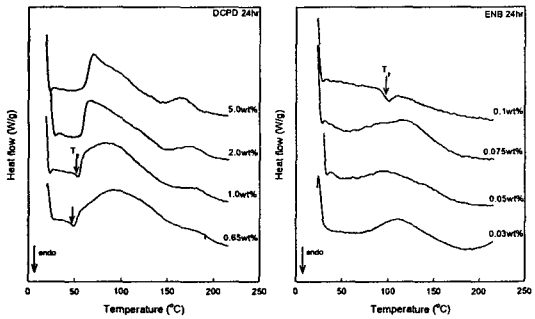

Figure 3. DSC thermograms of DCPD and ENB for samples cured for 24 h at room temperature with no catalyst and with different amounts of catalyst.

For the thermosetting materials, the material normally proceeds from liquid to rubbery and finally to glassy. Transformation from liquid to rubbery is known as gelation and that from rubbery to glassy as vitrification. Gelation is defined by the incipient formation of infinite size of molecule at a molecular level and abrupt increase of viscosity at a macroscopic level. Although many methods to determine gel time were reported, the gelation can be defined by onset of increase in G'.[5,6] Vitrification time can be easily determined by the peak position of tan δ. Samples of DCPD with 1.0 wt% and ENB with 0.1 wt% were tested by a dynamic mechanical analyzer, and storage modulus (G') and tan δ vs. time data were obtained. From the DMA data (storage modulus and tan δ vs time at room temperature) in Figure 4, time of initial increase and level off were determined from the intersection method and also times at tan δ peaks were determined. While G' starts to increase after 5 min and to level off from 66 min for DCPD, G' increases after 0.3 min rapidly and only needs 12 min for the G' increase to be level off for ENB. The tan δ peak position at which material transforms from rubbery to glassy state is vitrification time at 50 and 8 min for DCPD and ENB, respectively. This result shows the much faster cure reaction of ENB at much lower amount of catalyst.

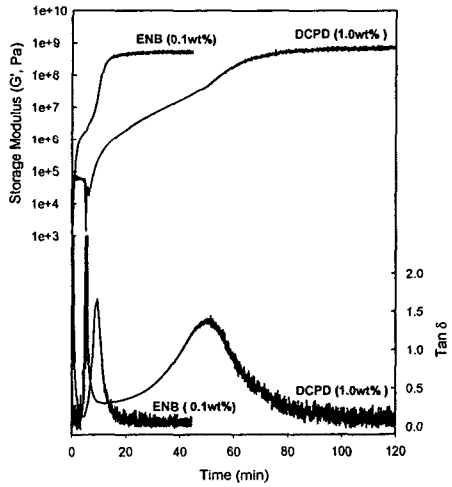

Figure 4. Storage modulus (G') and tan δ vs time data for unreacted samples with catalyst of 1.0 wt% for DCPD and 0.1 wt% for ENB.

3.1 Manufacture of microcapsules

Microcapsules containing DCPD and ENB surrounded by a urea/formaldehyde thermosetting resin at a stirring rate of 1000 rpm were observed by optical microscope (OM). The photograph from OM in Figure 5 shows that spherical shape of microcapsules were produced for both healing agents. Thermal stability of the DCPD and ENB microcapsules from TGA is very similar, dropping suddenly in weight at 210°C as shown in Figure 6. The sudden decrease is found to be due to

the explosion of microcapsules, leading rapid evaporation of healing agent during heating. Degradation of urea/formaldehyde shell starting at 200°C with increasing internal pressure of microcapsules gives rise to the explosion at the temperature. Particle size distribution of the microcapsules produced for both diene monomers are shown in Figure 7. The particle sizes are ranged 20-300 μ for DCPD and 10-230 μ for ENB.

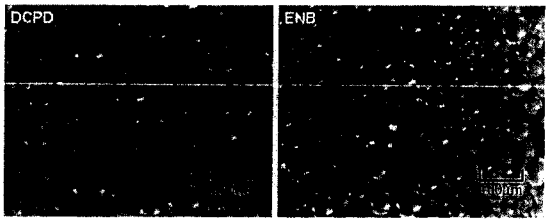

Figure 5. Optical microscope observation of microcapsules containing DCPD and ENB.

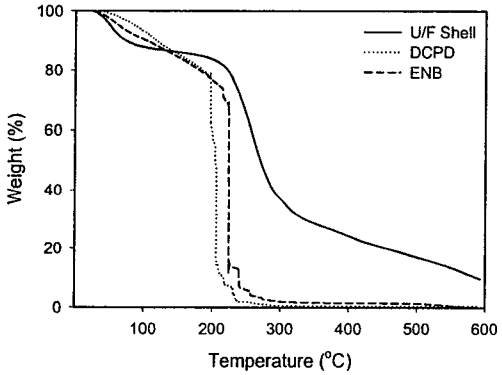

Figure 6. TGA thermograms for microcapsules (containing DCPD and ENB) and U/F shell

4. CONCLUSION

In this study, cure behavior of diene monomers was examined in the presence of different amounts of catalyst. The two diene monomers exhibited quite different in cure behavior. DCPD becomes solidified below 15°C, while ENB has no freezing. Reaction rate of ENB is much faster than that of DCPD at much lower amounts of catalyst. The characteristics of the nonfreezing and high reactivity of self-healing agent are considered to be very important for further development of self-healing concept toward practical use in polymeric composites. We successfully manufactured microcapsules for both DCPD and ENB. Observation of microcapsules with the healing agents showed similar in thermal resistance from TGA, shape from OM, and particle size distribution from PSA.

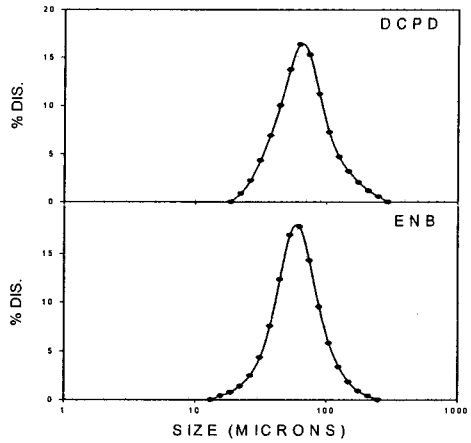

Figure 7. Particle size distribution of DCPD and ENB microcapsules.

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