

# 자가손상복구용 복구액의 특성 분석

## Characterization of Healing Agent Candidates for Self-healing Applications

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### 국문요약

고분자 복합재 구조물의 경우 일반적으로 여러 층의 단층(laminar)이 적층된 구조로 이루어져 있으며, 모재균열, 층간분리 및 섬유파단과 같은 손상이 발생되어 파단에 이르게 된다. 자가손상 복구기법은 복합소재의 열경화성 수지 내에 손상복구액을 포함하고 있는 마이크로캡슐과 촉매를 투입하여 외부의 도움 없이 손상을 치료할 수 있는 방법으로, 소재의 디자인에 있어서 새로운 페리다임을 제공할 수 있는 것으로 현재 많은 연구가 진행되고 있다. 본 연구에서는 ENB(5-ethylidene-2-norbornene)와 DCPD(dicyclopentadiene)에 대하여 DMA(dynamic mechanical analysis)와 DSC(differential scanning calorimetry)를 이용하여 특성을 분석하였다. 또한 그들의 ROMP(ring-opening metathesis polymerization)반응과의 관계를 조사하였으며, ENB와 DCPD 블렌드에 대한 복구액으로서의 특성도 조사하였다. 본 연구실에서 합성된 두 가지 다른 종류의 ROMP 경화제에 대한 실제 자가손상복구에 있어서의 적용상 특성도 연구하였다.

## 1. INTRODUCTION

Thermosetting polymers and their composites, while used in a wide variety of applications, are susceptible to cracking damage of various forms (e.g. matrix microcracking, interlaminar fracture, fiber-matrix debonding). Matrix microcracks are the precursors to structural failure and limit the lifetime of structures while increasing required maintenance.[1] Microcracking induced by thermal and mechanical fatigue in thermosetting adhesives in bonded joints is a particularly long-standing problem in aerospace structures. In composite cryogenic tanks, damage caused by wide ranging service loading conditions and thermal cycling often results in increased leakage due to microcracks in the polymer matrix of the fiber-reinforced composite plies.

In these composite systems, as illustrated in Figure 1, healing is accomplished with no outside intervention by embedding microencapsulated heal-ing agent and a catalytic chemical trigger within a thermosetting matrix. Upon damage, internal cracks rupture the embedded microcapsules, releasing the healing agent into the crack plane where subsequent polymerization bonds the crack faces, effectively healing the material.[2]

Requirements for these autonomic healing agent systems are severe and include long shelf-life, excellent adhesive strength with the polymer matrix and reinforcement phases, rapid polymerization at room temperature, and insensitivities to nonideal mixing with the initiator. Improving the reaction kinetics of the healing agent system at room temperature is one important way to improve healing efficiency while reducing the required amount of costly catalyst.

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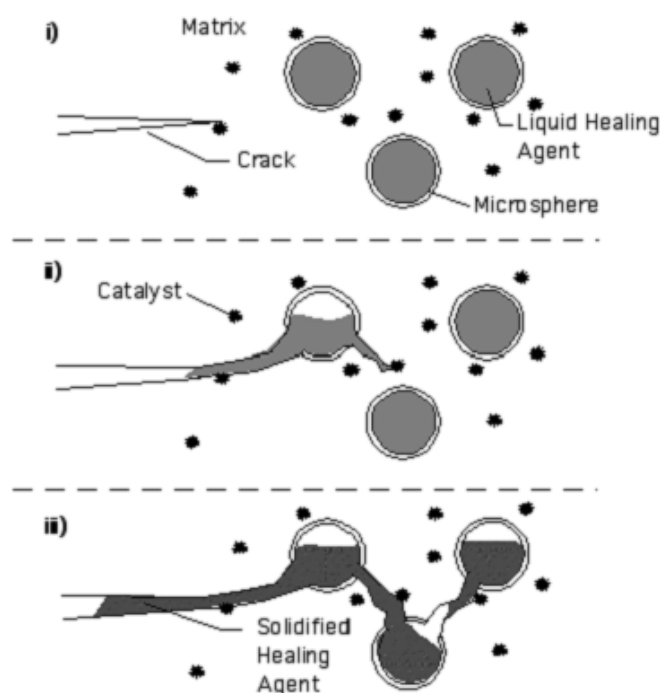


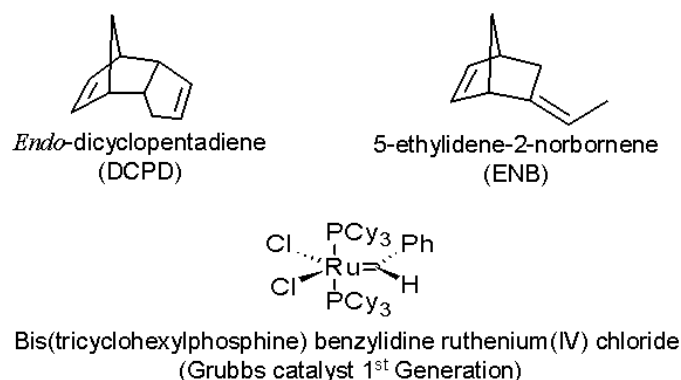
Figure 1. The self-healing concept. An encapsulated healing agent is embedded into a structural composite matrix containing a catalyst capable of polymerizing the healing agent.

Therefore, it is necessary to characterize the thermal properties of the healing agents after ROMP to generate improved self-healing materials and to develop more effective healing agents over wide temperature ranges. In this study, the thermal properties of endo-DCPD, ENB, and their mixtures cured at RT with a Grubbs catalyst are investigated using DMA and DSC.

## 2. EXPERIMENTAL

### 2.1 Sample preparation

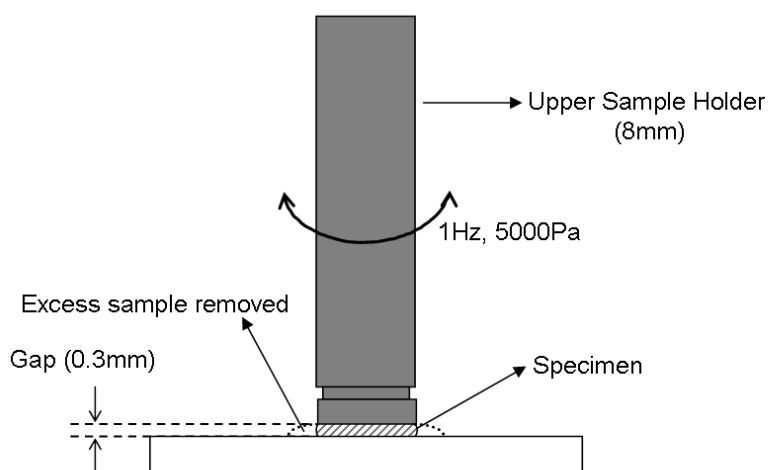
Two monomers, dicyclopentadiene (DCPD with 95% *endo*-isomer, Acros Chemical Co., Belgium) and 5-ethylidene-2-norbornene (ENB, Aldrich Chemicals Inc., USA), and Grubbs first generation catalyst (bis (tricyclohexylphosphine) benzylidene ruthenium (IV) chloride, Aldrich Chemicals Inc., USA), were used in this study. Chemical formulae of the reactants are represented in Figure 2. The two monomers and catalyst were blended together with a magnetic stir bar at room temperature for 10 sec in a vial. This short initial mixing time (with vigorous agitation at the highest stirring level of a magnetic stirrer) was necessary to prevent unwanted premature exothermic reaction during mixing, especially in the fast reacting ENB or ENB-rich samples. For DMA experiments, monomer mixing ratios of DCPD to ENB were 3:1, 1:1, and 1:3 by weight with two different levels of catalyst for each ratio. The monomer and catalyst compositions of samples used in this study are shown in Table 1; the catalyst loading levels were based on previous works, considering the rate of reaction of DCPD and ENB.[3,4]



**Figure 2.** Chemical structures of materials used in this study.

## 2.2 Dynamic mechanical analysis

Dynamic mechanical measurements provide a convenient means for generating the themomechanical spectra of polymeric materials. A wide variety of useful material parameters are attainable with the use of DMA. These include storage modulus ( $G'$ ) or elastic modulus, glass transition and sub-glass transition relaxation, quantification of crosslinking density, determination of gelation and vitrification transitions, and rate and extent of polymerization. In this experiment, a rotational dynamic mechanical analyzer (StressTech Rheometer, Reologica Instrument, Sweden) was employed to characterize the thermal and mechanical properties of curing and polymerized candidate healing agent systems. Figure 3 shows a schematic drawing of a sample holder of the DMA. About 40 mg of liquid sample is placed at the center of a stationary lower plate, followed by moving down an oscillating upper sample holder (diameter=8 mm) to a fixed gap distance between the parallel plates. Lowering the upper plate onto the sample resulted in the specimen being distributed across the lower plate, with the excess material flowing out around the upper plate as shown in Figure 3.



**Figure 3.** Schematic drawing of the DMA sample holder.

## 2.3 Differential scanning calorimetry (DSC)

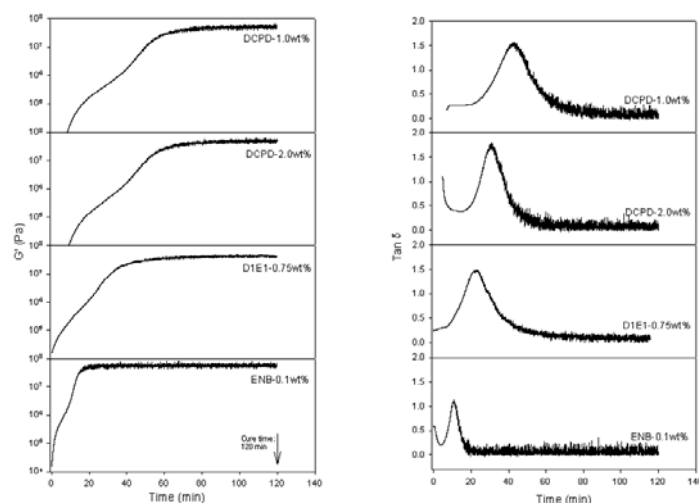
Temperature scans using DSC (Perkin Elmer Pyris-1, USA) as a complementary method to DMA were performed for the samples cured at RT for 120 min. For the DSC experiments, the uncured mixture was

dropped into liquid N<sub>2</sub> immediately after mixing in order to prevent further reaction due to the severe exothermic heat in a bulk form. For each experiment, about 8 mg of frozen sample was removed from the liquid N<sub>2</sub>, placed into an aluminum DSC pan, cured isothermally at 25°C for 120 min, and followed by two successive temperature scans. The first temperature scan was from -50 to 250°C and the second was from RT to 200°C, both at a heating rate of 10°C/min under a dry nitrogen atmosphere.

### 3. RESULTS AND DISCUSSION

#### 3.1 Isothermal cure behavior of DMA

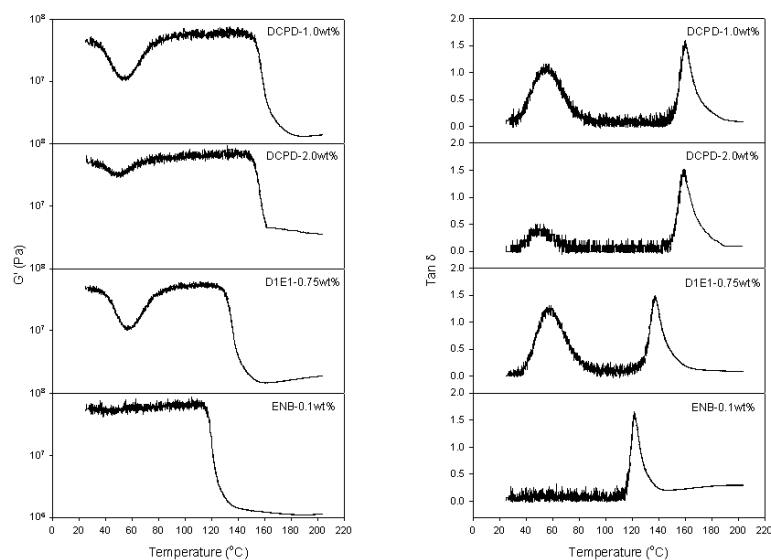
The ruthenium catalyst induced ROMP of the healing agent candidates was monitored by measuring storage modulus ( $G'$ ) and  $\tan \delta$  as a function of time at RT using DMA. The results for DCPD (1.0 and 2.0 wt% of catalyst), D1E1 (0.75 wt%), and ENB (0.1 wt%) are displayed in Figure 4. As shown in the figure, initially  $G'$  increased with time and then leveled off, showing a shoulder during the  $G'$  increase. A peak appeared on the corresponding  $\tan \delta$  curves. The peak on the  $\tan \delta$  curve is known to be due to vitrification[5], which is a transition from rubbery or liquid to glassy solid as a result of an increase in molecular weight. It can be seen that higher catalyst loadings and larger ENB portions in the samples lead to the shift of  $G'$  curve and  $\tan \delta$  peak to a shorter time scale, indicating the acceleration of the reaction.



**Figure 4.** Typical storage modulus ( $G'$ ) and  $\tan \delta$  vs. time data during isothermal cure at RT for different samples.

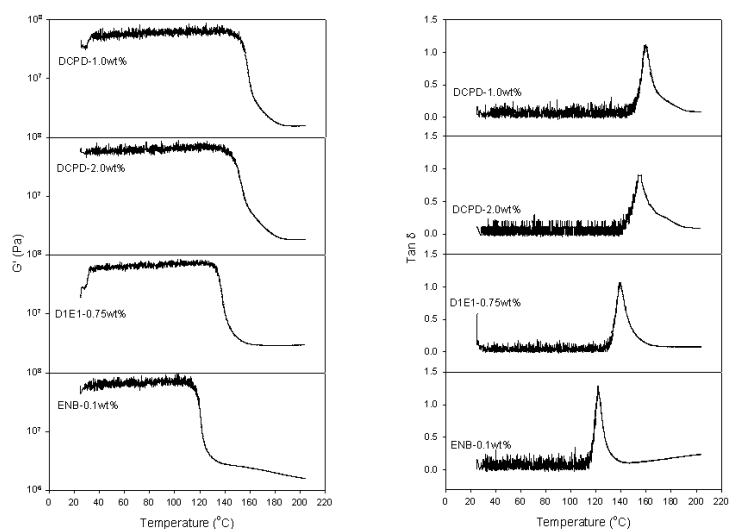
#### 3.2 Subsequent DMA temperature scans

Figure 5 shows storage modulus ( $G'$ ) and  $\tan \delta$  vs. temperature data (the first temperature scans) for the samples cured isothermally at RT for 120 min in Figure 4. For the DCPD and D1E1 samples, a downward peak on the  $G'$  curves near the beginning of the temperature scans (between 45 and 60 °C) can be observed in the figure. The corresponding  $\tan \delta$  curves show an upward peak in the similar temperature range. In great contrast, these low temperature peaks do not appear in the ENB sample. It seems that the amplitudes of the downward and upward peaks became smaller with increasing catalyst loading or ENB portion in the sample. However, a large-scale  $G'$  decrease and a sharp  $\tan \delta$  peak were observed for all samples at higher temperature.



**Figure 5.** Storage modulus ( $G'$ ) and  $\tan \delta$  vs. temperature data during a first temperature scan for the samples cured after an isothermal scan.

The subsequent temperature scan in Figure 6 displays storage modulus ( $G'$ ) and  $\tan \delta$  vs. temperature data for samples scanned from RT to 200  $^{\circ}\text{C}$  in Figure 5. The peaks on the  $G'$  and  $\tan \delta$  curves at lower temperatures during the first temperature scan disappeared in the second temperature scan, but the large-scale  $G'$  decrease and the corresponding  $\tan \delta$  peak at a higher temperature remain as in the first temperature scan.

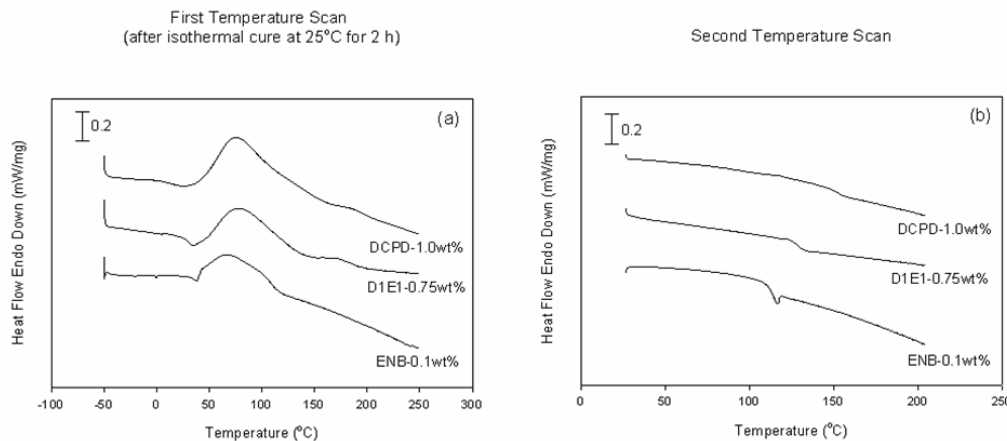


**Figure 6.** Storage modulus ( $G'$ ) and  $\tan \delta$  vs. temperature data during a second temperature scan for the samples after the first temperature scan.

### 3.3 DSC temperature scans

Figure 7 has the first (a) and the second (b) DSC temperature scans of DCPD with 1.0 wt%, D1E1 with 0.75 wt%, and ENB with 0.1 wt% of catalyst cured isothermally at RT for 120 min. A stepwise transition

appeared and a subsequent exothermic peak followed in the first scan, and only a stepwise transition was present in the second scan for all samples tested. Note that the curves in Figure 7 were vertically displaced by arbitrary amounts for clarity.



**Figure 7.** Two consecutive DSC temperature scans for samples cured for 120 min at room temperature (a) the first (b) the second scan.

## ACKNOWLEDGEMENT

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