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Characterization of Dicyclopentadiene and 5-Ethylidene-2-norbornene as Self-healing Agents for Polymer Composite and Its Microcapsules

Jong Keun Lee*, Sun Ji Hong, and Xing Liu

Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Gyungbuk 730-701, Korea

Sung Ho Yoon

School of Mechanical Engineering, Kumoh National Institute of Technology, Gumi, Gyungbuk 730-701, Korea

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Abstract: Two different diene monomers [dicyclopentadiene (DCPD) and 5-ethylidene-2-norbornene (ENB)] as self-healing agents for polymeric composites were microencapsuled by *in situ* polymerization of urea and formaldehyde. We obtained plots of the storage modulus (G') and tan δ as a function of cure time by using dynamic mechanical analysis to investigate the cure behavior of the unreacted self-healing agent mixture in the presence of a catalyst. Glass transition temperatures (T_g) and exothermic reactions of samples cured for 5 and 120 min in the presence of different amounts of the catalyst were analyzed by differential scanning calorimetry. Of the two dienes, ENB may have advantages as a self-healing agent because, when cured under same conditions as DCPD, it reacts much faster in the presence of a much lower amount of catalyst, has no melting point, and produces a resin that has a higher value of T_g. Microcapsules containing the healing agent were successfully formed from both of the diene monomers and were characterized by thermogravimetric analysis. Optical microscopy and a particle size analyzer were employed to observe the morphology and size distribution, respectively, of the microcapsules. The microcapsules exhibited similar thermal properties as well as particle shapes and sizes.

Keywords: self-healing, microcapsules, diene, polymeric composite.

Introduction

In polymer matrix composites, the damage is mainly initiated at the interface between reinforcement and matrix, leading to interfacial debonding. Ply delamination due to the defects introduced 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 short 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] 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 the propagating cracks. Catalyst in matrix subsequently initiates polymerization of the released healing agent in the crack.

*e-mail: jklee@kumoh.ac.kr

In the recent works,[2-4] 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 composite. An artificial crack was introduced in the composite and normal stress was applied, inducing the crack propagation. Stress-strain behavior from double 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.[4] 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, DCPD was necessary to be cured for 48 h in the presence of as much as 5 wt% of catalyst in polymer matrix.[4] 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,[3] which means that the healing mechanism proposed may not work by freezing of the healing agent below the temperature. Development of healing agent

with no freezing is essential to the self-healing.

In this study, we introduce 5-ethylidene-2-norbornene (ENB) to overcome the above limitations as a candidate for new healing agent. Both DCPD and ENB are commonly used in manufacturing ethylene-propylene-diene terpolymers (EPDM), and ENB is known to be much faster in reaction. Therefore, we may expect reduction of catalyst amount and effective healing within a short time. DCPD was also analyzed and compared with ENB. Microcapsules for each healing agent were produced using a reactor system, which was assembled in this laboratory.

Experimental

In this study, two different dienes as healing agent, dicyclopentadiene (DCPD, Aldrich Inc., USA) and 5-ethylidene-2-norbornene (ENB, Aldrich Inc., USA), were characterized and microencapsulated by a urea-formaldehyde thermosetting material.

Thermal Analysis of Self-healing Agent. Thermal analysis to investigate cure behavior of the healing agents was performed by a rheological measurement (StressTech Rheometer, Reologica Instrument, Sweden) for two different uncured mixtures with a catalyst of 1.0 wt% for DCPD and 0.1 wt% for ENB. The sample was vigorously mixed for 10 sec in a vial at room temperature. Catalyst used was bis(tricyclohexylphosphine)benzylidine ruthenium (IV) dichloride (Grubbs's catalyst, Strem Chemicals, USA). Chemical structures of the diene healing agents and the catalyst are represented in Figure 1. In the measurements, two parallel plates of a stationary disc plate ($\phi = 30$ mm, thickness = 3.2 mm) and an oscillatory upper plate ($\phi = 8$ mm) accommodate approximately 50 mg of uncured sample. Oscillation was imposed to the sample with frequency of 1 Hz under applied stress of 5,000 Pa. Gap between the plates (or sample thickness) was fixed to be 0.3 mm during all the experiments.

Differential scanning calorimetry (DSC, Dupont 982, TA Instrument, USA) was also employed to examine the glass transition temperature (T_g) and exotherm for samples cured at room temperature for 5 and 120 min. DSC temperature scans were made from −40 to 225 °C for samples with no catalyst and from RT to 225 °C with catalyst. Amount of catalyst for DSC experiment was determined to be DCPD = 0.65~5.0 wt% and ENB = 0.03~0.1 wt% from a series of preliminary experiments. Mechanical mixing was made for DSC samples as in DMA tests. For the liquid mixture with no catalyst, about 5 mg 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. For cured specimens, the uncured mixture was spread into thin film on Teflon sheet immediately after mixing to prevent further reaction due to severe exothermic heat in a bulk form of the diene monomers with catalyst. Around 10 mg of small pieces was taken from film cured on the Teflon sheet. The glass transition temperature of the cured samples was determined from the inflection point of a stepwise transition on the DSC thermogram when it appears. All DSC experiments were made at a heating rate of 10 °C/min under a dry nitrogen atmosphere.

Manufacture and Characterization of Microcapsules. DCPD and ENB were microencapsuled by a urea-formaldehyde thermosetting material. Micro-droplets of diene monomer were formed in distilled water by vigorous stirring at 1,000 rpm. Poly(ethylene-*co*-maleic anhydride) (EMA, Aldrich Inc., USA) 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.[3] The microcapsules for DCPD and ENB produced were observed by an 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).

Results and Discussion

Characterization of Healing Agents. Thermosetting resins normally transform from liquid to rubbery and finally to glassy during cure. 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. Time positions can be taken as the extrapolated onset of the initial rise in storage modulus (G') for gelation[5,6] and as the peak position

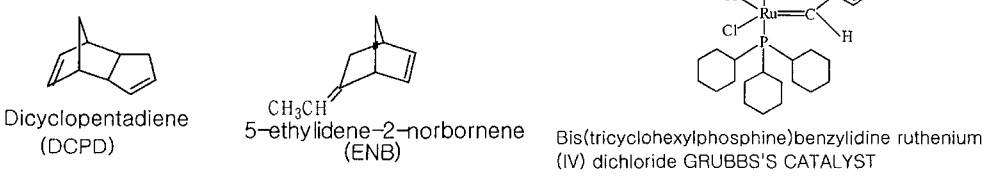

Figure 1. Chemical structures of diene monomers and catalyst used in this study.

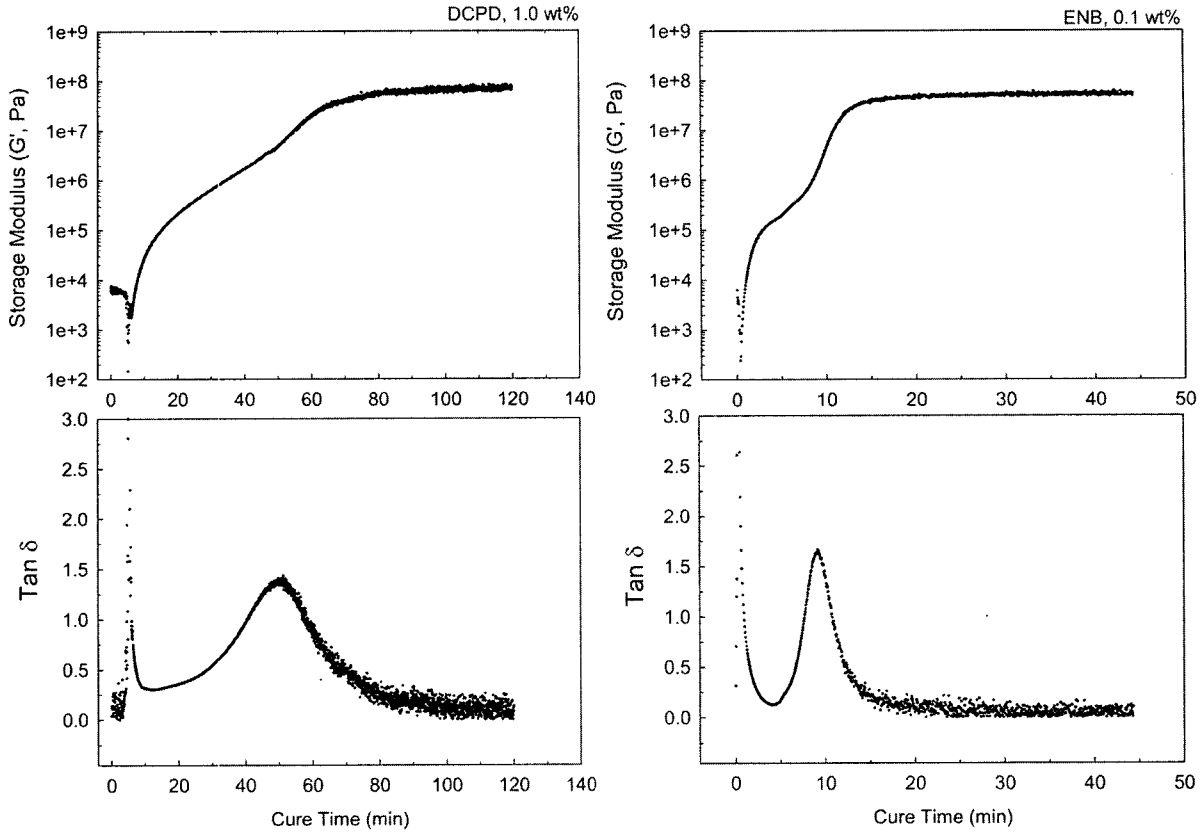

Figure 2. Storage modulus (G') and tan δ vs. time for unreacted samples with catalyst of 1.0 wt% for DCPD and 0.1 wt% for ENB.

of tan δ for vitrification by means of dynamic mechanical analysis.

Dicyclopentadiene (DCPD) is capable of forming crosslinked structure with high toughness and strength from a low molecular weight monomer through a ring opening metathesis polymerization mechanism.[7-9] Therefore, this monomer was studied as an appropriate candidate for the purpose of healing cracks due to damages in polymeric composite materials.[1-4] In this study, DCPD with 1.0 wt% and ENB with 0.1 wt% catalyst were tested, and storage modulus (G') and tan δ vs. time data were obtained during cure at room temperature. For DCPD and ENB, a linear polymer should be formed if only the highly strained norbornene ring opened. However, the double bond in the cyclopentene ring for DCPD and the ethylidene for ENB may undergo reaction, giving rise to crosslinking.

The G' and tan δ curves during isothermal cure are shown in Figures 2 for DCPD and for ENB sample. As shown in the figure, G' initially increases rapidly, and slows down for a while, and then increases rapidly again, and levels off thereafter for both samples. Onset of initial rise of the modulus, corresponding to the gelation time, was determined to be 5 min for DCPD and 0.8 min for ENB. Time position for the tan δ peak, corresponding to vitrification time, was 50 min for DCPD and 8 min for ENB. The transformations (i.e., gelation and vitrification) occurs much earlier in ENB, indicating that cure reaction of ENB proceeds much faster compared to DCPD at much lower amount of catalyst. It should be noticed that the amount of catalyst used was 1/10 in ENB.

Figure 3 shows DSC thermograms for DCPD and ENB with no catalyst and different amounts of catalyst (0.65~5.0 wt% for DCPD and 0.03~0.1 wt% for ENB) after 5 min of cure at room temperature. DCPD with no catalyst shows two endothermic peaks; a small one at 15 °C and a big at 143 °C, corresponding to melting transition and evaporation of the monomer, respectively. Sample with catalyst became solidified after the 5 min of cure time. DSC thermogram of solidified DCPD shows an exothermic peak, shifting to lower temperature from 55 °C (0.65 wt% catalyst) to 50 °C (5.0 wt% catalyst). Since the exotherm is due to the further reaction of remaining functional groups, 5 min for cure is not enough for completing cure of DCPD. For ENB with no catalyst in this figure, there is one big endothermic peak at 105 °C due to evaporation of monomer. Notice that no melting peak was observed in this monomer. An exothermic peak appears at 50 °C for ENB sample with 0.03 wt% catalyst cured for 5 min. The exothermic peak temperature

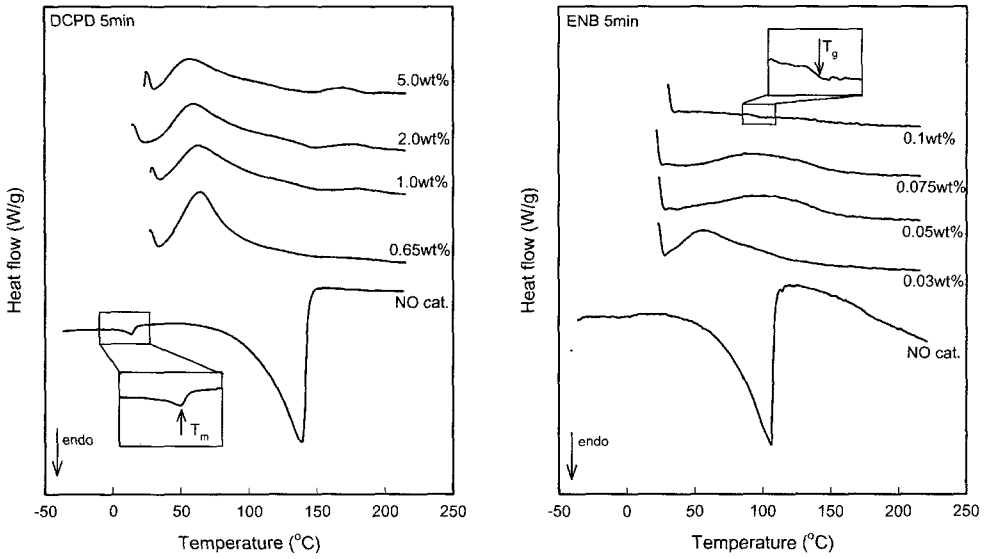

Figure 3. DSC thermograms of DCPD and ENB for samples cured for 5 min at room temperature without and with different amounts of catalyst.

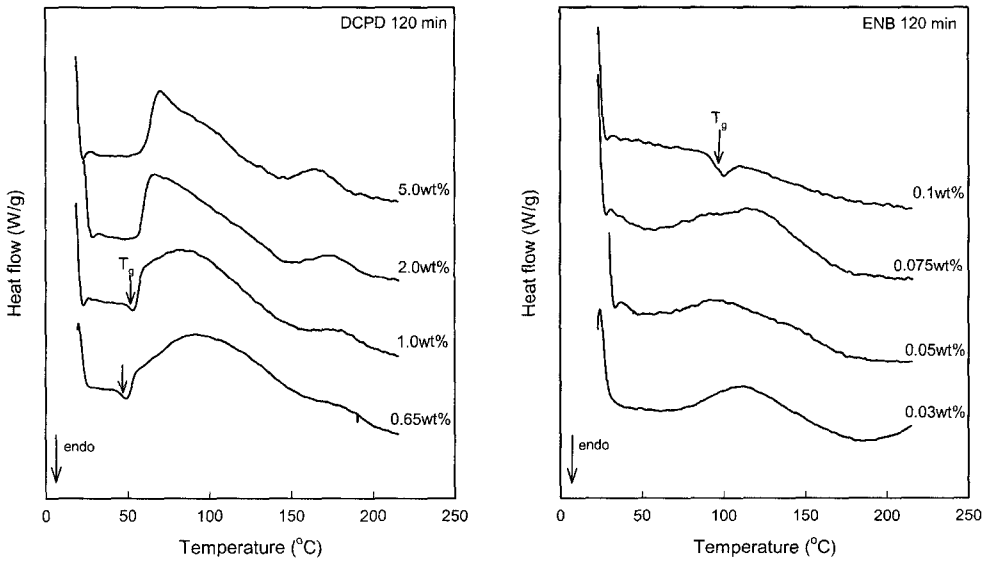

Figure 4. DSC thermograms of DCPD and ENB for samples cured for 120 min at room temperature without and with different amounts of catalyst.

increases with increase of catalyst up to 0.075 wt%, which is opposite to DCPD. The opposite trend is not clearly understood. Further study may be necessary to explain it. A stepwise transition was observed at 90 °C on the DSC curve for ENB with 0.1 wt% catalyst, corresponding to the glass transition temperature, above which no exotherm appears.

Same samples were cured for 120 min at room temperature and DSC thermograms of the samples are shown in Figure 4. For DCPD, all the DSC curves exhibit two exotherms; a big one at lower temperature and a small at higher temperature. The big peak due to residual reaction becomes sha per and its temperature shifts from 95 to 75 °C with increase of catalyst. The small peak shifting from 185 to 170 °C becomes distinct with increase of catalyst. Further investigation may be necessary for the occurrence of the small peak at the higher temperature. As shown in the figure, the glass transition appears around 50 °C for the sample with catalyst of 0.65 and 1.0 wt%, followed immediately by an exothermic peak. However, the glass transition was not observed at higher amount catalyst (i.e., 2.0 and 5.0 wt%). For ENB, there is an exothermic peak with 0.03, 0.05 and 0.075 wt% catalyst and the glass transition at 90 °C with 0.1

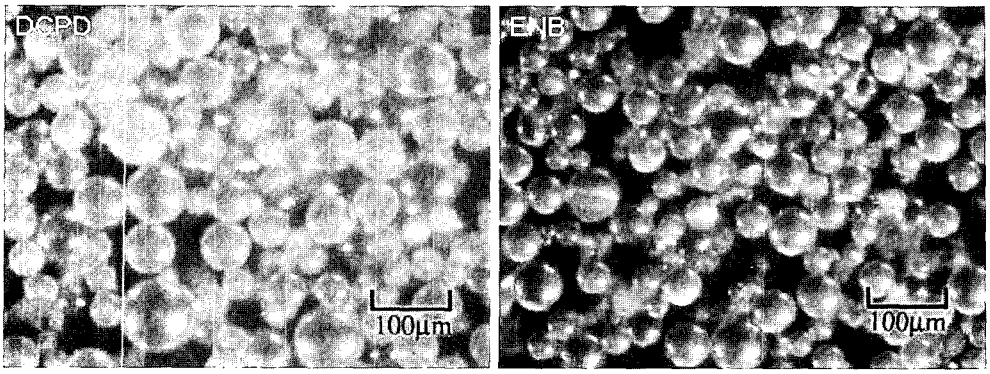

Figure 5. Optical microscope observation of DCPD and ENB microcapsules.

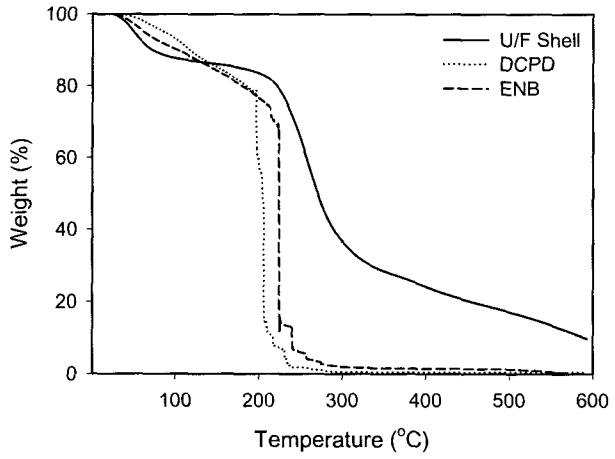

Figure 6. TGA thermograms for DCPD and ENB microcapsules and U/F shell.

wt% catalyst. Glass transition does exist for sample without showing stepwise transition on DSC curve but is hidden by the exotherm for sample with faster reaction at higher amounts of catalyst. Note that the glass transition temperature of 5 min-cured ENB sample with 0.1 wt% catalyst was not changed after 120 min of cure, indicating that the ENB can be completely cured within 5 min.

Manufacture of Microcapsules. Microcapsules containing DCPD or ENB surrounded by a urea/formaldehyde thermosetting material at a stirring rate of 1,000 rpm were produced and observed by an optical microscope (OM). The photograph from OM in Figure 5 shows a spherical shape of microcapsules for both healing agents. Thermal stability of the DCPD and ENB microcapsules from TGA is similar as a whole, dropping suddenly in weight around 200 °C for DCPD and 225 °C for ENB microcapsules as shown in Figure 6. The sudden decrease is due to the explosion of microcapsules, causing 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 of microcapsules at the temperature. Particle size distribution of the microcapsules produced for both diene monomers are shown in Figure 7. The particle sizes are similarly ranged 20-300 μm for DCPD and 10-230 μm for ENB.

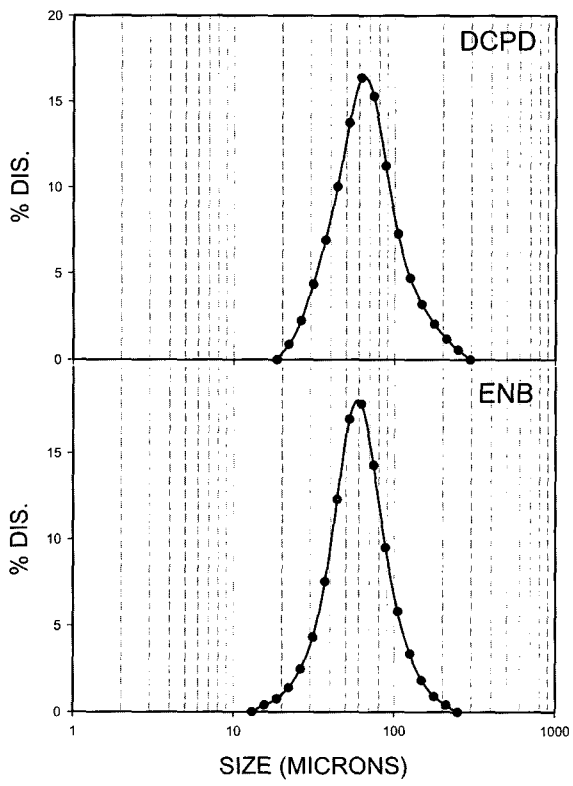

Figure 7. Particle size distribution of DCPD and ENB microcapsules.

Conclusions

In this study, cure behavior of diene monomers as self-healing agent was examined in the presence of different amounts of catalyst. The two diene monomers exhibited quite different 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 ENB are essential 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 similarity in thermal resistance from TGA, shape from OM, and particle size distribution from PSA.

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