

RHEOLOGICAL MODIFICATION OF EPOXY RESINS WITH NANO SILICA PREPARED BY THE SOL-GEL PROCESS*

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Abstract Nano silica-modified epoxy resins were synthesized by the sol-gel process. The materials have the morphological structure of nano particales dispersed in the epoxy matrix. The dispersed phase formed a physical network in the resin and thus influenced the rheological behavior greatly. However, the nano silica did not show a significant influence on the mechanical properties of the cured resins.

Keywords Epoxy resin, Nano silica, Mechanical properties, Rheology, Sol-gel process

INTRODUCTION

The need for rheology control in adhesives for automobile assembly is evident. Automobile adhesives should be delivered by pump, and should not sag during curing, even on vertical surfaces. Therefore, rheology modifiers are usually incorporated to make the systems thixotropic. Typical commercial rheology modifier for epoxy resins is fumed silica. It provides yield stress and thixotropy at low concentrations through particle aggregation. However degradation of sag resistance during storage and irreversible change of rheological behaviors by the action of shearing are troublesome problems in conventional systems.

In our previous papers^[1, 2] reversible gels of poly(butylene terephthalate) (PBT) and poly(butylene terephthalate)-*b*-poly(tetramethylene glycol) (PBT-*b*-PTMG) in epoxy resins were studied as rheological modifiers. They were found to be effective in modifying the rheological properties of epoxy resins. The resins were made thixotropic by PBT or PBT-*b*-PTMG spherulites.

In this paper we describe an alternative approach to the rheology control of the epoxy resins. Nano silica prepared by *in situ* hydrolytic polycondensation of tetraethoxysilane in epoxy resins is used as rheology modifier. The rheological properties of the modified resins prior to the curing process and the mechanical properties of the cured resins are reported.

EXPERIMENTAL

Materials

The epoxy resin used in this study was Epikote 828, produced by the Kumho Shell Chemical Co.. Tetraethoxysilane (TEOS) was a chemical reagent produced by the Shanghai Resins Factory. The

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catalyst for the hydrolysis of the silica precursor was N-benzyltrimethylamine (BDMA), a chemical reagent produced by Beijing Chemical Factory. The curing agents for the epoxy resins were 4, 4'-diaminodiphenyl methane (DDM), a chemical reagent from Fengguang Chemical Factory, Hubei province, and triethylenetetramine (TETA), a chemical reagent from Beijing Chemical Factory.

Preparations

For the preparation of nano silica-modified epoxy resins TEOS and BDMA were dissolved in the epoxy resin, and a given amount of water was added^[3]. The mixture was stirred thoroughly at room temperature. The system became thixotropic within about 3 h. The volatile was then removed *in vacuo* at 60~70°C. For the preparation of specimens for mechanical tests, the resins were mixed with a curing agent and deaerated *in vacuo*, and then it was cast into a mold and cured. Single-edge notched specimens were prepared for the three-point bending tests.

Measurements

The morphology of the cured resin was studied using a Hitachi H-300 transmission electron microscope (TEM). For the steady shear measurements a Rheometrics Dynamic Stress Rheometer was used, and the dynamic rheological measurements were taken using a Rheometric Mechanical Spectrometer RMS 605 using a parallel plate geometry of radius 25 mm and a gap of 2 mm. Three-point bending tests were conducted on an Instron 1122 test machine at a crosshead moving rate of 2 mm/min. G_{1c} was calculated according to Ref. [4].

RESULTS AND DISCUSSION

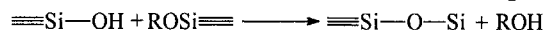
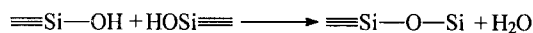
The Preparation of Nano Silica-Modified Epoxy Resins by the Sol-Gel Process

The sol-gel process for the preparation of nano silica involves the hydrolysis and the condensation of TEOS:

Hydrolysis



Condensation



These reactions can be catalyzed by both acids and bases. Since the oxirane groups are vulnerable to acid, an acid catalyst is not suitable in the presence of epoxy resin.

BDMA was used as catalyst in this study. The reactions proceeded rapidly in the presence of 1~1.25 parts of BDMA per hundred parts of epoxy resin (phr) and excess of water for the hydrolysis. In a typical run, 10 phr of TEOS and 1.25 phr of BDMA were dissolved in the epoxy resin and 2.5 phr of water was added. The mixture was stirred thoroughly at ambient temperature. The viscosity of the mixture increased rapidly and the resin became thixotropic in 3 h. The volatile were then removed *in vacuo* at 60~70°C. According to the weight gain 2.8 phr of silica was formed in the resin.

Although BDMA is a curing agent for the epoxy resin, the resin in the presence of 1.25 phr of BDMA and 2.8 phr of the sol-gel silica, was quite stable at ambient temperature, as shown by the change of the epoxy value. The epoxy value, determined by titration, was 5.2 meq/g at the beginning. After storing at room temperature for 35 days, the epoxy value was 5.1 meq/g. The stability of the resin modified by the sol-gel silica was also demonstrated by the change of the rheological properties. This will be discussed below.

The Morphology of the Nano Silica-Modified Epoxy Resins

Microtomed sections of the nano silica-modified epoxy resin, cured with TETA, were studied by TEM. In Fig. 1 a micrograph of the resin with a magnification of 5000 times is given. It can be

seen that silica particles of ca. 60 nm diameter form aggregates dispersed over the resin matrix.



Fig. 1 TEM micrograph of the epoxy resin modified with 2.8 phr nano silica magnification: 5000X

At a silica content of 2.8 phr, the clusters likely formed a physical network in the resin as demonstrated by dynamic mechanical measurements. In Fig. 2 the storage modulus G' and the loss modulus G'' versus the frequency are shown. G' is very sensitive to the structure. For the neat epoxy resin G' was negligible. For the resin containing 2.8 phr of silica, however, G' was close to G'' at low frequencies. $G'=G''$ is a criterion of gelation of a system.

Rheological Behavior of Nano Silica-Modified Epoxy Resins

The nano silica exerted great influences on the rheological behaviors of the epoxy resin. As mentioned above, the epoxy resin containing 2.8 phr nano silica behaved like a gel in dynamic measurements.

The dependence of viscosity on shear rate was studied by steady shear measurements. It can be seen in Fig. 3 that the low-shear-rate viscosity was enhanced for two orders of magnitude by 2.8 phr nano silica, and the modified resin was highly shear thinning.

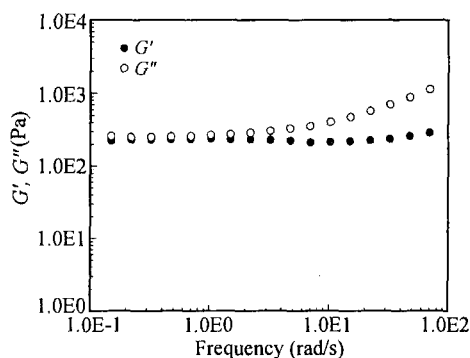


Fig. 2 G' and G'' versus frequency at 19°C for the epoxy resin modified with 2.8 phr nano silica

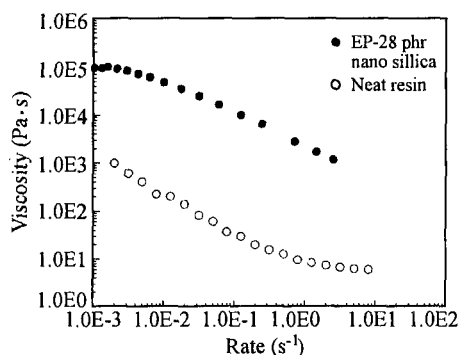


Fig. 3 Viscosity versus shear rate at 25°C for the epoxy resin modified with 2.8 phr nano silica and the neat resin

The effect of storage on the viscosity is shown in Fig. 4. It is seen that the viscosity at low shear rates increased significantly upon storage. This may be attributed to the perfection of the particle aggregation. At the high-shear-rate end, on the contrary, the viscosity increase was insignificant after storage for 190 days.

A yield stress is desirable for many applications such as coatings, sealants and adhesives. The sol-gel silica is advantageous in imparting yield stresses to the resin. The yield stress was determined using a controlled stress rheometer, in which shear stress was increased from zero to 1000 Pa in 100 steps in 100 seconds, the strain was measured and the apparent viscosity calculated by the computer. The stress under which the viscosity began to fall off was taken as the yield stress

(Fig. 5). The epoxy resins modified by 2.8 phr nano silica showed a yield stress in the range of 300–500 Pa. In contrast, the epoxy resin containing fumed silica, a commonly used rheology modifier, of the same concentration did not show a yield stress. It can be seen in Table 1 that the yield stress provided by nano silica does not lost after storage for long times.

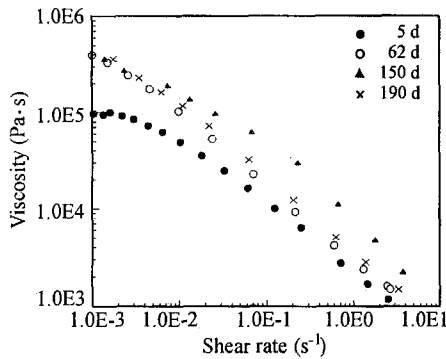


Fig. 4 Viscosity versus shear rate for the epoxy resin modified with 2.8 phr nano silica after storage

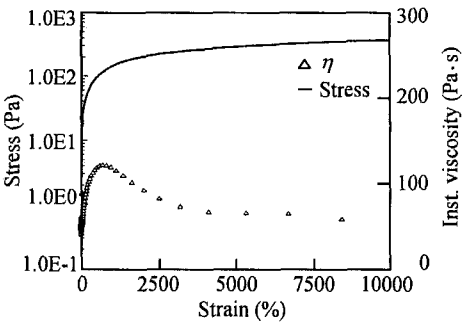


Fig. 5 Stress ramp for the epoxy resin modified with 2.8 phr nano silica at 25°C

Inorganic fillers are usually incorporated for preventing sag. By using the conventional technology, the loss of sag resistance during storage may be a problem in many industrial products. However, the yield stress of the nano silica-modified epoxy resins was not reduced after storage for long times, as shown by the data given in Table 1.

Table 1. The effect of storage on the yield stress of the epoxy resin modified with 2.8 phr nano silica

Storage period (day)	5	40	150	190
Yield stress (Pa)	396	476	450	450

Nano Silica Modified Epoxy Adhesives

For the study of the influence of the nano silica on the mechanical properties of the cured epoxy resins, DDM was used as curing agent. A set of experimental results is given in Table 2. It can be seen that there is a minor improvement in the flexural strength and the modulus by the sol-gel silica at the expense of the fracture energy G_{IC} .

Table 2. The mechanical properties of the epoxy resin modified with 2.8 phr nano silica

Composition (by wt.)	Epoxy resin nano	100	100
	SiO ₂ BDMA	0	2.8
	DDM	0	1.25
		28	28
K_{IC} (MPa • m ^{1/2})		0.72	0.74
G_{IC} (J/m ²)		210	204
Modulus (GPa)		2.20	2.36
Flexural strength (MPa)		116	129

* Curing conditions: 100°C/4h, 165°C/4h

Table 3. The sag resistance and adhesion strength of epoxy adhesives

Curing agent	Triethylene tetramine		4, 4'-Diaminodiphenyl methane		
Curing conditions	60°C / 3h		160°C / 3h		
Modifier	—	2.8 phr nano silica	—	2.8 phr nano silica	2.8 phr fumed silica*
Sag (cm)	> 10	0	> 10	0	7.5
Lap-shear strength (MPa)	9.6	10.9	19.9	20.5	20.4

*Fumed silica #3 from Shen Yang Chemical Factory

Although the sol-gel silica is not a valuable reinforcer for the epoxy resin, yet it is a good rheology modifier for the resin. A comparison is given in Table 3. The epoxy resin modified with 2.8 phr nano silica can be used for making very good sag-resistant adhesives. Even when a curing temperature as high as 160°C was used, the adhesive with the nano silica as modifier did not drip down on a vertical surface. By contrast, the adhesive using the same amount of fumed silica as a rheology modifier showed a sag of 7.5 cm during the curing. A slight improvement in bonding strength was found for the rheology modifiers.

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