

# Mechanical and Dielectric Properties of Epoxy Resin Modified Using Reactive Liquid Rubber (HTPB)

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**ABSTRACT:** In the present study, hydroxyl-terminated polybutadiene (HTPB) liquid rubber was employed to modify epoxy resin using 2,4,6-tri (dimethylaminomethyl) phenol as a catalyst, and methyl hexahydrophthalic anhydride as a curing agent. The reactions between HTPB and epoxy were monitored by Fourier transform infrared (FTIR); the mechanical and dielectric properties of HTPB modified epoxies were evaluated and the morphology was investigated through scanning electronic microscopy (SEM). The FTIR analysis evidenced the occurrence of a chemical reaction between the two components. The mechanical results indicated that the impact strength of HTPB-modified epoxy was superior to that of the pure epoxy. As the HTPB content increased up to 10 phr the best

mechanical performances in terms of tensile and flexural properties were achieved when compared to the unmodified epoxy. Higher concentration of HTPB resulted in larger particles and gave lower mechanical strength values. The incorporation of HTPB into epoxy decreased the dielectric constant and dissipation factor over a wide frequency range from 1 to  $10^6$  Hz, and improved the electrical resistivity. SEM micrographs showed that the modified epoxy exhibited a two-phase morphology where the spherical rubber domains were dispersed in the epoxy matrix. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4346–4351, 2012

**Key words:** resin; microstructure; mechanical property; dielectric property; modification

## INTRODUCTION

Epoxy resins are widely used in several important applications such as structural adhesives, surface coatings, advanced composites for the aerospace, and electronic industries, owing to their outstanding performances including high rigidity and strength, chemical resistance, adhesive properties, formulation latitude, and reactivity with a wide variety of chemical curing agents.<sup>1–5</sup> However, the major drawback is its brittleness in the cured state, and for this reason, the toughness has been extensively studied in the last decades.<sup>2–6</sup> Several methods have been proposed to increase the toughness of epoxy, and one of the most successful involves the addition of a suitable rubber to the uncured epoxy, and then con-

trolling the polymerization reaction in order to induce phase separation.<sup>7–9</sup> The great majority of the studies involves, the chemical modification of epoxy with reactive liquid rubber, particularly carboxyl-terminated butadiene acrylonitrile copolymer (CTBN),<sup>3,5,6</sup> hydroxyl terminated butadiene acrylonitrile copolymer (HTBN).<sup>9</sup> The rubber particles finely dispersed in the epoxy matrix with particle size of few micrometers, enhance the toughness of epoxy considerably with only a minimum adverse effect on the thermal and mechanical properties.<sup>8</sup> However, the electrical insulating properties of the CTBN or HTBN modified epoxy decline slightly.

The obvious characteristic of hydroxyl terminated polybutadiene (HTPB) liquid rubber is its immiscible nature with epoxy and hence it stays in a phase separated state from the major epoxy matrix throughout the cure reaction.<sup>5</sup> This is a consequence of its weak polarity compared to the strong polar liquid rubber, i.e., CTBN and HTBN. Several investigations on the physical and morphological aspects of HTPB modified epoxy have been reported except for the electrical and dielectric properties.<sup>1,5,6,9</sup> The objective of this study is to investigate the morphology, the mechanical, electrical, and dielectric behavior of HTPB-modified-epoxy. The importance of this work is that a cyclic anhydride was used as curing agent because when used as curing agent the very low viscosity at room temperature of the cyclic anhydride reduces

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obviously the viscosity of anhydride-HTPB-epoxy mixture, thus, the mixture free of solvents can be processed easily. To enhance the compatibility between the two components we first react HTPB with epoxy using 2,4,6-tri (dimethylaminomethyl) phenol as a catalyst. On the basis of mechanical and electrical testings, morphological observations, the microstructure, the mechanical and electrical properties of HTPB-modified-epoxy have been studied. We anticipate the improvements in the impact strength and dielectric properties of modified epoxy can be observed with the inclusion of HTPB into epoxy, which are of great importance to some application fields such as electronic packaging, substrate materials, etc.

## EXPERIMENTAL

### Materials

The epoxy resin was liquid diglycidyl ether of bisphenol-A (D.E.R-331, Dow) with an average epoxy value of 0.52. The curing agent was methyl hexahydrophthalic anhydride (MeHHPA) from Shanghai Shengyuan, China. 2,4,6-tri (dimethylaminomethyl) phenol (DMP-30) used as the accelerator, was obtained from Shanghai Haitai, China. HTPB liquid rubber, supplied by Zibo Qilong Chemical, China, presents a  $\overline{M}_n$  of 2500 and hydroxyl number of 0.8–1.0 g/mequiv.

### Sample preparation

Preparation of epoxy-HTPB pre-polymer

The synthesis of HTPB modified epoxy prepolymer was performed by reacting epoxy (100 g) with the HTPB whose content ranged from 0 to 40 phr in the presence of DMP-30 (0.6 wt % of epoxy) as a catalyst. These reagents were added into a three-necked reaction flask swept with nitrogen. The flask was placed in an oil bath at 130°C and allowed to react under stirring conditions for 1–2 h. After that, the formed HTPB-epoxy prepolymer was promptly cooled down to room temperature.

Preparation of anhydride cured HTPB-epoxy pre-polymer

The prepared HTPB-epoxy prepolymer was mixed with the anhydride and the accelerator in the weight of 100 : 85 : 1 in weight ratio. Then, the mixture was gently stirred for 5 min to ensure proper dispersion of the hardener, degassed for 10 min in order to get rid of trapped bubbles, and poured into appropriated molds. The cure was performed in an oven following the curing procedure: 100°C for 1 h, and 150°C for 3 h.

### Characterization

Infrared (FTIR) analyses were performed in a Perkin Elmer spectrometer (model Paragon1000, USA) at a  $2\text{ cm}^{-1}$  resolution averaged over 20 scans.

Scanning electron micrography (SEM) was performed using a JEOL JSM-7000F SEM, Japan. The fractured surfaces of samples were prepared in liquid nitrogen, and were sputtered with gold in vacuum prior to observation.

The tensile tests were conducted in a New SANS ZMGI 250 testing machine (Shenzhen, China) at a crosshead speed of 2 mm/min according to ASTM D-638. The values were taken from an average of at least five specimens. Flexural tests were also conducted using a New SANS ZMGI 250 testing machine fitted with a three-point bending fixture at a crosshead speed of 2 mm/min, according to ASTM D-790. The specimens for flexural strength measurement were made in the form of a rectangular bar with 80 mm in length, 4 mm in thickness, 10 mm in width, and 64 mm in span. The impact strength of the unnotched specimens was determined by using a SANS ZBC1251Charpy tester (Shenzhen, China) according to ASTM D-256. The specimens for impact strength test were made in the form of a rectangular bar with 125 mm in length, 13 mm in thickness, 13 mm in width, and 95 mm in span. All the mechanical tests were carried out at room temperature and the values were taken from an average of six specimens.

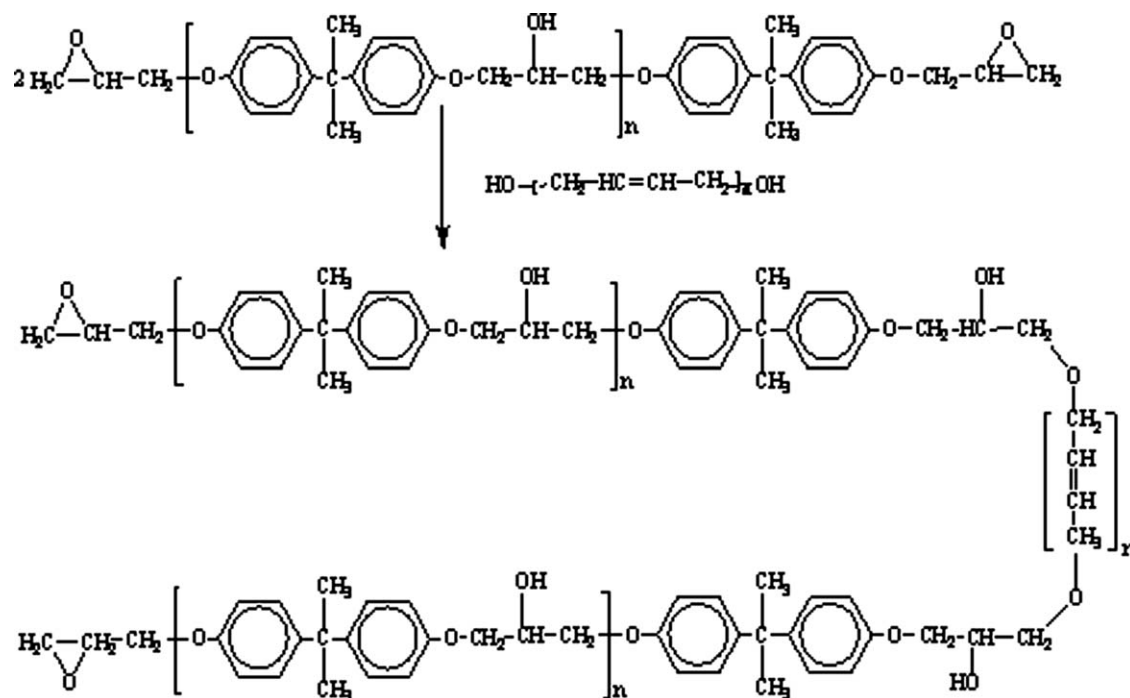
The dielectric measurements were performed on a broadband dielectric spectrometer (Novocontrol Technology Company, Germany) with Alpha-A high performance frequency analyzer. The measurements were carried out in the frequency range from  $10^{-1}$  to  $10^7$  Hz at room temperature. The specimens for dielectric measurements were made in the form of circular discs with 1 mm in thickness and 20 mm in diameter. Both sides of the discs were suitably sprayed with gold powder to improve electrical contact. All measurements were carried out in the cryostat to avoid possible environmental effects.

The volume and surface resistivity measurements were performed on an ultrahigh electric resistor (model: ZC-36, Shanghai, China) at room temperature. The dimension of the samples for tests is 80 mm in diameter, 1 mm in thickness.

## RESULTS AND DISCUSSION

### The FTIR spectroscopy

It is well known that hydroxyl group reacts with epoxide group at a temperature above 100°C using tertiary amine as a catalyst. So, the hydroxyl group of HTPB liquid rubber can react with the epoxide group of epoxy resin in the presence of DMP-30 as a



**Figure 1** Scheme showing the formation of functional group ether in the reaction between epoxy and HTPB rubber.

catalyst, thus leading to a chemical linkage between the two components. The reaction to link HTPB to the epoxy is illustrated in Figure 1.

FTIR spectra of HTPB, pure epoxy, and epoxy modified with 10 and 20 phr HTPB are shown in Figure 2. A comparative study of such spectra allows the drawing of conclusions related to the chemical linkages formed during the HTPB-modified epoxy reaction. The pure epoxy resin shows peaks at  $915$  and  $831 \text{ cm}^{-1}$  because of the oxirane group of epoxy.<sup>1</sup> The addition of HTPB to epoxy caused chemical interaction between the oxirane ring of epoxy and functional hydroxyl group of HTPB, and led to a decrease in the peaks at  $915$  and  $831 \text{ cm}^{-1}$  for the 10 and 20 phr HTPB modified epoxy. Moreover, the absorption bands at about  $1040 \text{ cm}^{-1}$ , which can be ascribed to the ether bond of epoxy, were observed to increase, as expected, in the HTPB-modified-epoxy prepolymer compared to pure epoxy. Therefore, the FTIR analysis evidenced the occurrence of a chemical interaction between epoxy and HTPB, which enhances the compatibility between the two components.

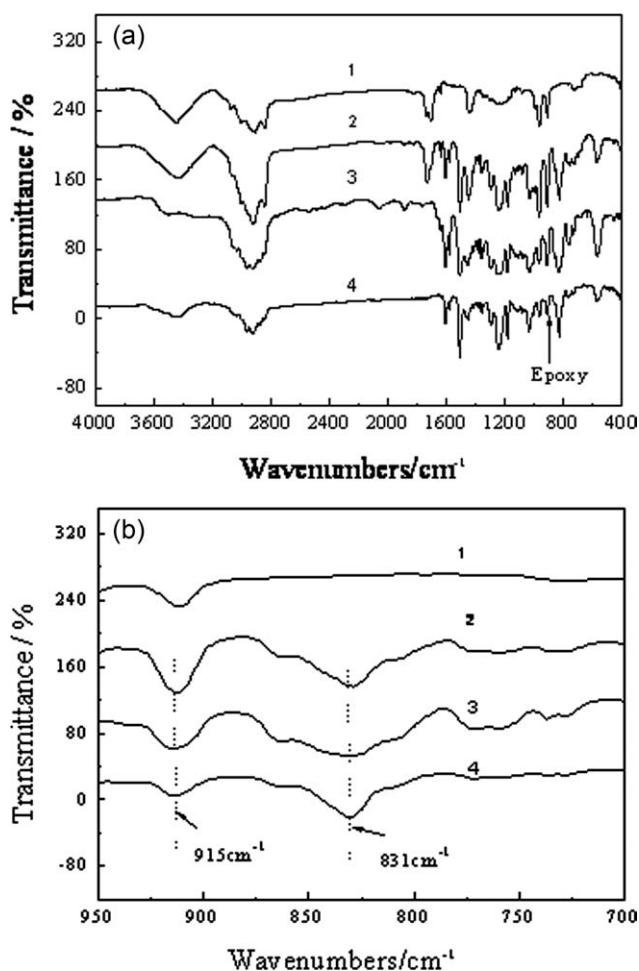
### Mechanical properties

The tensile and flexural properties and the impact strength of the cured epoxies containing various content of HTPB are summarized in Table I. All modified epoxy networks exhibited higher impact strength resistance than nonmodified epoxy. The best performance was achieved with 10 phr of rub-

ber. Above this optimum rubber concentration, a fall in the impact strength was observed. Similar behavior has been also reported in other rubber-modified epoxy systems and has been attributed to the agglomeration of rubber particles with the increase of rubber content because the presence of agglomerate acts as defects and initiates catastrophic failure.<sup>2,3,7,10</sup> The flexural strength is not markedly affected by the addition of 5–10 phr of HTPB when compared to the pure epoxy networks, also, the best tensile strength has been achieved with this system. A gradual fall in tensile modulus was noted as the concentration of HTPB increased. This may be due to the increase in the relative amount of dissolved rubber as HTPB content increases. Furthermore, the latter acts as plasticizer with an increase of free volume which conducts to a decrease of epoxy resin stiffness.

The elongation at break of the modified epoxy increases continuously with HTPB in the cured networks. The results indicates that the cured epoxy networks containing HTPB ranging from 5–10 phr exhibited the best balance of mechanical properties.

The impact behavior of the modified epoxy could be explained based on the two-phase nature of the system. According to Bucknall,<sup>5</sup> the HTPB particles were considered to bridge the crack as it propagated through the material. Thus, the rubber particles were able to prevent the crack growing to a catastrophic size. The increase in toughness was because of the amount of elastic energy stored in the rubber particles during stretching. Thus, the deformation of



**Figure 2** (a) FTIR spectra of (1) HTPB, (2) pure epoxy, (3) epoxy modified with 10 phr HTPB, (4) epoxy modified with 20 phr HTPB. (b) The magnified FTIR peaks of (1) HTPB, (2) pure epoxy, (3) epoxy modified with 10 phr HTPB, (4) epoxy modified with 20 phr HTPB.

the rubber particles in the matrix seemed to be responsible for the enhanced stress transfer and hence impact resistance.<sup>5,7</sup> Moreover, shear yielding of the matrix is another reasonable mechanism that might be operating.<sup>11</sup>

### Morphology

Figure 3 shows the SEM micrographs of the fractured surface of the unmodified and modified epoxy

matrix containing various concentration of HTPB. The morphology observed for the unmodified epoxy is characteristics of a brittle feature having smooth, glassy, and rivy fractured surfaces with ripples. The relative smoothness of the fractured surfaces indicates that no significant plastic deformation had occurred. The morphological development during cure can be correlated with the impact behavior. The ripples are due to the brittle fracture of the network, which accounts for its poor impact strength, as there is no energy dissipation mechanism operating here.<sup>3,6,11</sup>

SEM of the HTPB modified epoxy systems clearly show two distinct phases—a continuous epoxy matrix and the dispersed rubber phase. In epoxies with 5 and 10 phr of rubber, the particles were uniformly distributed throughout the matrix with a narrow particle size distribution, which is response for lower crack growth in these specimens. Furthermore, the fractured surfaces are rather rough, indicative of a ductile manner of fracture. Relatively distorted shape of rubber domains in these cured matrices is supposed to be attributed to higher amount of plastic deformation, promoting stress transfer between the particles and epoxy matrix. Thus, uniformly rubber particles act as stress concentrators<sup>5,12,13</sup> and exhibit highest impact strength than unmodified epoxy. In higher weight percentage (i.e., 20 phr) of rubber-modified sample, a heterogeneous particle size distribution was observed, which accounts for the declined mechanical performance.

### Dielectric properties

The signal propagation delay caused in an integrated circuit can be determined by eq. (1) as a means of the dielectric constant of the packaging material.

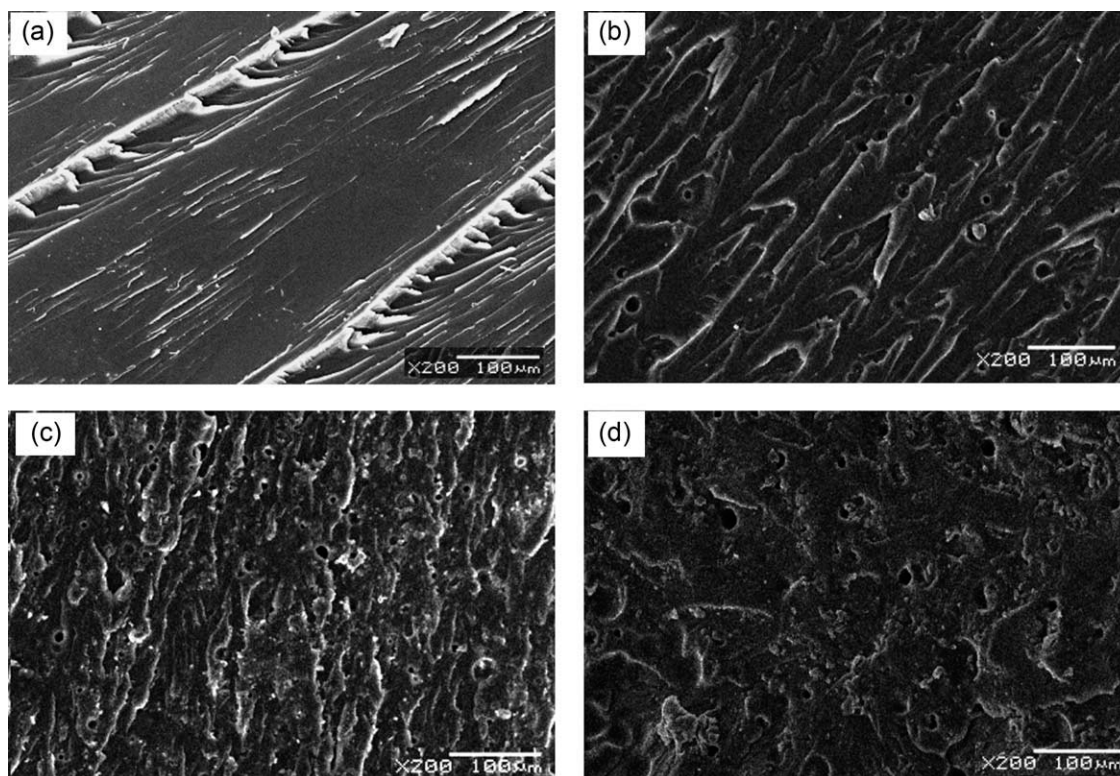
$$T_d = \frac{l}{c} \sqrt{\epsilon_r} \quad (1)$$

where  $c$  is the velocity of light,  $l$  the transmission distance of the singles, and  $\epsilon_r$  the relative dielectric constant.

From eq. (1), it can be seen that a high dielectric constant of the packaging material will cause a bad

**TABLE I**  
Mechanical Properties of HTPB Modified Epoxy Networks

Mechanical properties	HTPB concentration (phr)				
	0	5	10	20	30
Tensile strength (MPa)	65.2 ± 3.2	73.12 ± 3.6	67.31 ± 4.1	60.23 ± 3.4	52.36 ± 2.9
Tensile modulus (GPa)	2.98 ± 0.26	2.95 ± 0.21	2.83 ± 0.23	2.41 ± 0.18	1.91 ± 0.13
Elongation at break (%)	2.40 ± 0.21	5.46 ± 0.32	7.75 ± 0.43	8.42 ± 0.46	8.71 ± 0.52
Flexural strength (MPa)	100 ± 3	101 ± 4	98 ± 2	87 ± 3	81 ± 2
Impact strength (kJ/m <sup>2</sup> )	8.6 ± 1.7	12.5 ± 2.0	16.2 ± 2.3	14.1 ± 1.8	11.7 ± 1.4



**Figure 3** SEM micrographs of the fractured surfaces of epoxy networks containing HTPB at (a) 0, (b) 5 phr, (c) 10 phr, (d) 20 phr.

effect on the signal propagation by increasing the delay time,<sup>14</sup> and a low dielectric constant and loss is required for polymer packaging materials.

The dependence of dielectric properties of HTPB-modified-epoxy on the HTPB concentration and frequency are presented in Figure 4. As depicted in Figure 4(a) the dielectric constants slightly decreases with an increase in the HTPB concentration and frequency over the measured range from 1 to  $10^7$  Hz. In contrast, the dielectric constants of modified epoxy containing HTPB content at 10, 20, 40 phr are 4.24, 3.98, and 3.64 at  $10^3$  Hz, respectively, corresponding to 4.53 for pure epoxy. The decrease in the dielectric constant with an increase in the HTPB amount could be ascribed to the weak interfacial polarization effect because the HTPB lessens the space charge accumulation at the phase interface because of its nonpolar molecular structure, leading to a reduced dielectric constant.<sup>15</sup> Besides, the reduction in the dielectric permittivity may be explained by a simple diluting due to the low permittivity of HTPB rubber in relation to the neat epoxy.

The data in Figure 4(b) indicate that the dissipation factors are almost independent of the HTPB content in the measured range of 1– $10^6$  Hz. The dissipation factors of modified epoxy with various amount of HTPB all exhibit initial decrease with

increasing frequency, followed by an increase to a high frequency. As the frequency increases further, the dipole polarization effects reduce, and the value of the dissipation factor decline accordingly. The dielectric loss tangent tends to increase again when the frequency is above  $10^4$  Hz, which is associated with the matrix. In generally, they remain at a rather low level, i.e., less than 0.023 at wide frequency range.

Therefore, the dielectric analysis demonstrate that the HTPB modified epoxy possessed rather low dielectric constant and dissipation factor in the measured frequency range. Generally, a low dielectric constant and a low dissipation factor are very important for the modified epoxy used as plastic packaging and electronic substrate applications because both dielectric constant and dissipation factor greatly influence the signal-carrying capacity and the speed of the device to pass signals, and make a high accumulation of the device itself and a high clock rate possible.<sup>15</sup>

The influence of HTPB rubber on the electrical insulation properties of modified epoxy with various HTPB content are summarized in Table II. As shown in Table II, both the volume resistivity ( $\rho_v$ ) and surface resistivity ( $\rho_s$ ) of the blend obviously increase with increasing the HTPB concentration. The volume resistivity values of the anhydride cured epoxy

containing 10, 20, and 40 phr HTPB rubber are  $7.16 \times 10^{16}$ ,  $2.11 \times 10^{17}$ , and  $8.27 \times 10^{17}$ , respectively, corresponding to  $3.72 \times 10^{16}$  for the pure epoxy. A similar trend to increase surface resistivity was observed also for the modified networks. The increase in surface and volume resistivity with the addition of HTPB could be ascribed to the excellent electrical insulation property of HTPB, which could inhibit and lessen the space charge accumulation at the phase interface and the formation of electric current inside the blend at applied high electric voltage because of its nonpolar molecular structure.<sup>14</sup> The results demonstrate that the HTPB modified epoxy has higher surface and volume resistivity as compared to the unmodified epoxy. Generally, the high surface and volume resistivity properties are very important for the modified epoxy used as plastic packaging and electronic substrate materials because they greatly prolongs the lifespan of electronic devices working under high electric field.<sup>14</sup>

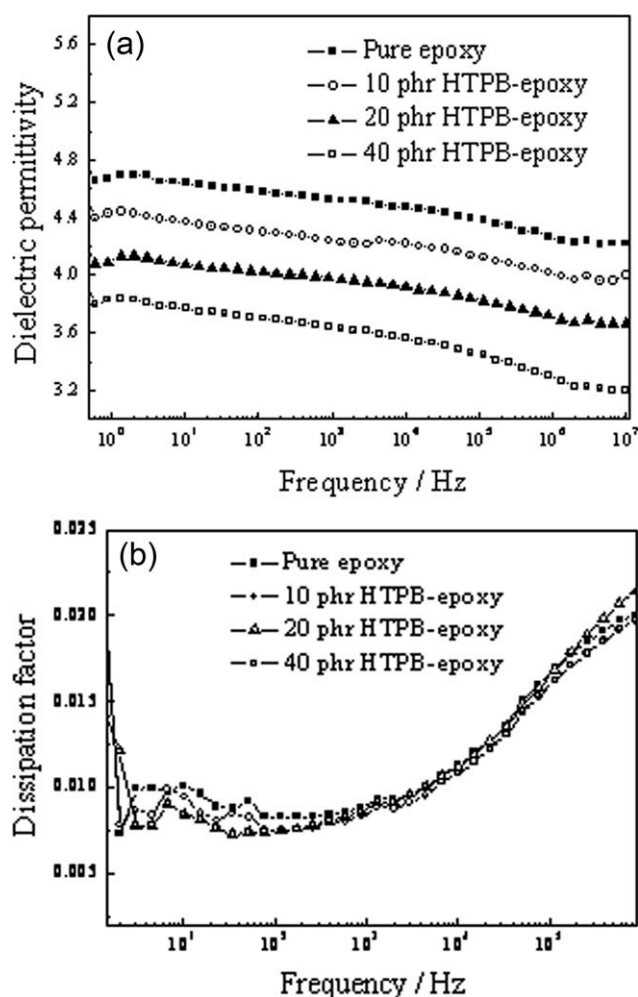


Figure 4 Dielectric properties of HTPB rubber modified epoxy networks (a) dielectric constant (b) loss factor.

TABLE II  
Surface and Volume Resistivity of Cured Neat and HTPB Modified Epoxies

HTPB concentration (phr)	$\rho_v/\Omega$ cm	$\rho_s/\Omega$
0	$3.72 \times 10^{16}$	$1.77 \times 10^{10}$
10	$7.12 \times 10^{16}$	$1.05 \times 10^{11}$
20	$2.11 \times 10^{17}$	$7.12 \times 10^{11}$
40	$8.27 \times 10^{17}$	$6.02 \times 10^{12}$

## CONCLUSION

In this study, epoxy was modified with HTPB liquid rubber using the MeHHPA anhydride as a hardener. The FTIR results confirmed the occurrence of a chemical reaction between the epoxy and HTPB in the presence of DMP-30 as a catalyst, which enhanced the compatibility between the two components.

The impact strength and the elongation at break of HTPB-modified epoxy were obviously superior to that of pure epoxy. The incorporation of 10 phr HTPB into epoxy showed best balance mechanical performance in terms of tensile and flexural properties. A further increase in the concentration of HTPB led to larger rubber particles which weakened the mechanical properties of the modified epoxy.

The dielectric constant and dissipation factor of HTPB-modified-epoxy decreased with increasing the HTPB concentration over a wide frequency range from 1 to  $10^6$  Hz, whereas, the electrical resistivity including surface and volume resistivity increased obviously.

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