

The effect of silica surface modification on the dielectric properties of silica-filled epoxy compounds

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Abstract

Crystalline silica was modified by annealing at temperatures ranging up to 1000 °C and by treating with a silane coupling agent (γ -glycidoxypropyltriethoxysilane) at concentrations up to 1 wt.%. The silica was dispersed in a matrix of diglycidyl ether of bisphenol-A epoxy resin. The dielectric properties of the composite samples were measured in the frequency range from 0.6–300 kHz. The results reveal that the dielectric loss index values of the samples are associated with water molecules adsorbed on the silica surface. An interpretation in terms of the cluster model of dielectric relaxation is provided. A relationship between the parameters pertaining to the silica modification and those describing the effects of the boiling water treatment on one hand and the dielectric loss index of the composites on the other has been determined.

Introduction

Silica-filled epoxy resin compounds are widely applied in the electrotechnical and electronic industries. Application of silica as a filler in the epoxy resin potting compounds and epoxy resin molding compounds results in a decrease of the thermal expansivity and an increase of the thermal conductivity [1] as well as in an improvement of mechanical and dielectric properties [2]. In a wide range of applications, e.g. under the effect of water or moisture, a stability of the dielectric properties of filled epoxy resins is required [2, 3, 4].

The mechanical and dielectrical properties of such epoxy resin systems are highly dependent on interactions between surfaces of the filler particles and the epoxy resin matrix [5]. Kisielew [6] and Skudelný [5] have shown that surfaces of silica particles contain layers of adsorbed water molecules. The adsorbed water facilitates the process of permeation of additional water molecules into the filled epoxy resin compound, resulting in a deterioration of its properties. For this reason, it is necessary to modify the surface of the silica particles to decrease the water absorption of epoxy compounds and to enhance adhesion between filler

particles and the epoxy resin matrix. We note that our materials are composites since the filler and the matrix perform different functions [7].

Modification of the silica is usually carried out by annealing it at high temperatures, up to 1000 °C and/or by application of silane coupling agents [5, 8]. Composition of the chemical surface functional groups of the silica changes and needs to be controlled by direct analytical methods. However, the type of ground crystalline silica used as a plastics filler usually has a very low specific surface area, about 2–4 m² g⁻¹. It is quite difficult to determine the number of the functional groups on the silica surface by means of analytical methods since the concentration of these groups is too low [8]. The other possibility is to study the effects of silica modification on the properties of the silica-filled plastics.

The dielectric properties of mineral-filled plastics are sensitive to the water adsorbed on the surface of such fillers. It has been shown by Banhegy and Karasz [9] who studied CaCO₃-filled polyethylene that the dielectric properties of such composites are sensitive to the water adsorption on the surface of the filler.

The cluster model of dielectric relaxation

Shahidi *et al.* [10] and Dissado and Hill [11] have pointed out that dielectric loss index and

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dielectric permittivity of sand are dependent on the percent of adsorbed moisture. It has been also shown that, for a low water adsorption, the dielectric loss index (ϵ'') and dielectric permittivity (ϵ') is non-Debye and are given by the following formula:

$$\epsilon(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_{\infty} + B(i\omega\tau)^{n-1} \quad (1)$$

where

$$B = K_1 \exp(K_2 W) \quad (2)$$

K_1 , K_2 and n are constants, W is the water content, and τ stands for a relaxation time.

If $\tau = \tau_0 \exp(E/RT)$, where E is the activation energy, R the gas constant and T the thermodynamic temperature, then the dielectric loss index is given by:

$$\epsilon''(W, T) = K_1 \exp(K_2 W) \exp\left(\frac{(n-1)E}{RT}\right) \omega^{n-1} \quad (3)$$

Similarly, the dielectric permittivity becomes:

$$\epsilon'(\omega) \sim \omega^{n-1} \quad (4)$$

A theoretical basis for these formulae has been given by Dissado and Hill [11] in terms of the cluster model of dielectric relaxation. They applied the model to heterogenous systems containing adsorbed water. According to them, water molecules adsorbed on the surface of a mineral filler form clusters due to hydrogen interactions. At high frequencies, an intracuster motion of protons takes place, as demonstrated by an increase in the value of the exponent n . At lower frequencies, however, the intercluster motions of protons dominate; the values of n vary in the range 0.3–0.007.

The n exponent values are related to the mean cluster order and are independent of temperature. Small values of n correspond to highly irregular clusters while higher values are ascribed to clusters of regular structure.

We present results pertaining to effects of silica surface modification on the dielectric loss index of silica-filled epoxy resin compounds as well as on changes on the dielectric loss index under the influence of water. The results are interpreted in terms of the cluster model of the dielectric relaxation.

Experimental

Samples of epoxy resin compounds filled with the same weight concentration of modified and unmodified silica were studied. The following compositions were prepared: diglycidyl ether of bis-

phenol-A (Epikote 828), 20 wt.%, hexahydrophthalate anhydride hardener, 13.5 wt.%, benzoildimethyleneamine accelerator, 0.5 wt.%, silica filler, 66 wt.%.

Two methods of silica surface modification were used:

– annealing for 2 hours in a muffle furnace at: 110, 400, 600, 700 and 1000°C;

– application of a silane coupling agent, γ -glycidoxypropyltriethoxysilane (NB-1115, Chemiekombinat, Nunchritz, Germany)

The silane coupling agent was hydrolyzed prior to surface treatment for 0.5 h in an aqueous alcoholic solution (ethyl alcohol and water, 4:1 by volume). The silica was treated with the solution and thoroughly mixed. The silane-modified silica samples were then heated in air at 110 °C for 2 hours. Two kinds of the silane-modified silica were thus prepared from solutions, containing respectively 0.3 wt.% and 1 wt.% of the silane.

Samples circular in shape and 2 mm thick were obtained from a mold after curing epoxy resin compound at 120 °C for 12 hours.

A low voltage Shering Bridge type VKB of Rhode & Schwartz, Munich, Germany, was used for the dielectric measurements. The dielectric loss index was calculated from measured values of dielectric permittivity and dissipation factor ($\tan \delta$) as

$$\epsilon'' = \tan \delta \epsilon' \quad (5)$$

The influence of water content was studied for samples filled with silica modified by annealing after boiling them in water for 24 hours and subsequently cooled in water to 24 °C. Samples containing silica modified with a silane coupling agent were autoclave-boiled at 121 °C for 24 hours and then cooled in water to 24 °C.

Results and discussion

Unmodified silica

Measured values of dielectric loss index as a function of frequency and temperature for the epoxy resin compounds filled with unmodified silica are presented in Fig. 1. It is seen that the dielectric loss index decreases with increasing frequency and increases with increasing temperature. It is also evident that the dielectric loss index is a linear function of frequency for a constant temperature. Similar dependence on frequency was measured for dielectric permittivity, Fig. 2. In this case, similarly as in the study of Banhegy and his colleagues [12], the frequency dependence of dielectric loss index may be described by formula

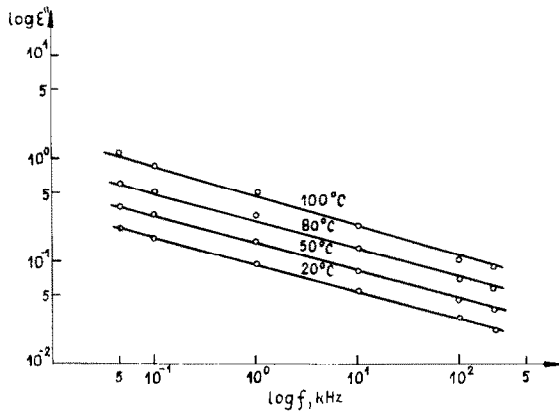


Fig. 1. The dielectric loss index (ϵ'') dependence on the frequency for epoxy resin compounds filled with unmodified silica.

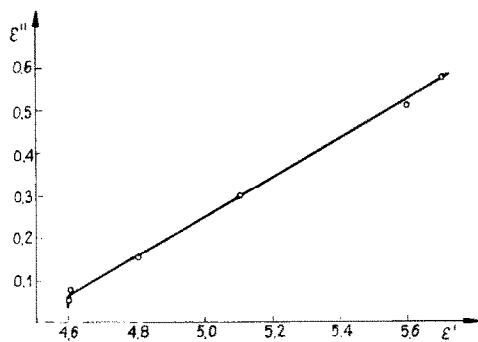


Fig. 2. The dielectric loss index (ϵ'') dependence on the dielectric permittivity (ϵ').

(3). Shahidi *et al.* [10] and Dissado and Hill [11] have pointed out that horizontal shifting of the curves such as in Fig. 1 makes a master curve possible. Such a curve gives the dielectric loss index dependence through a wider range of frequencies, applying essentially the time-temperature-frequency equivalence principle [13], since common features of mechanical and dielectric response of polymeric materials are well known to exist [14].

As is seen in Fig. 3, the master curve of the dielectric loss index is a linear function of the frequency; with the slope $n=0.73$, where n is equal to the exponent n of formula (3).

Figure 4 depicts the values of dielectric loss index as a function of temperature for two frequencies. It is seen that these curves are linear. According to formula (3), the slope of these curves is given by $(n-1)E$. The value of n obtained from the data in Fig. 3 is equal to 0.73. The activation energy of relaxation processes calculated on this basis is equal to 52.3 kJ mol^{-1} .

Mangion and Johari [15] have shown that dielectric loss index measured above 0°C for unfilled epoxy resin compounds is an increasing function

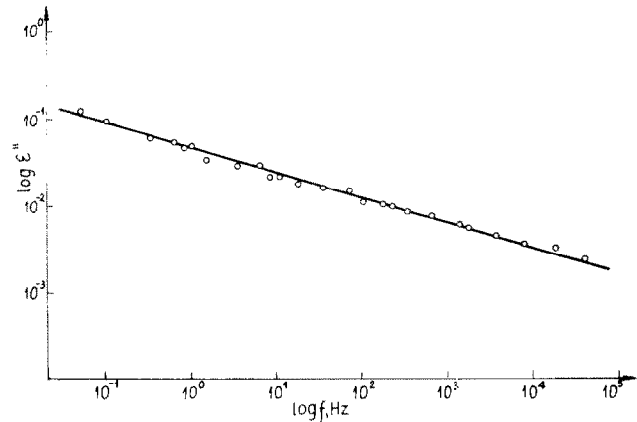


Fig. 3. Master curve for the epoxy resin compounds filled with unmodified silica.

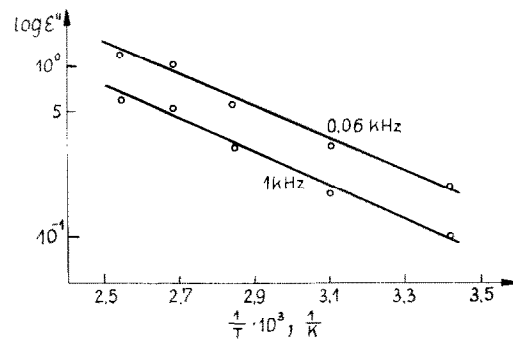


Fig. 4. The dielectric loss index dependence on temperature for epoxy resin samples filled with unmodified silica.

of frequency. The slope of the curves in Fig. 1 for filled epoxy resins is negative; that is, the dielectric loss index is a decreasing function of frequency. This change in the slope suggests that the low frequency relaxation processes in silica-filled epoxy resins are much more intense than in unfilled epoxy resin samples. We assign these relaxation processes to the presence of water molecules at the surface of filler particles. In fact Dissado and Hill [11] and Shahidi *et al.* [10] have shown that the dielectric properties of heterogeneous systems containing adsorbed water on the mineral filler surface can be explained by the cluster model discussed briefly earlier on. According to this model, the calculated value of the exponent n (0.73) suggests that the measured dielectric loss index data for our composites are associated with the intracluster motion of charge carriers on the surface of the filler.

Annealed silica

In turn, we studied similar composites but with the silica filler modified by annealing. The dielectric

loss index was measured as a function of frequency for epoxy resin samples containing a constant concentration of the silica-filler previously annealed at several temperatures. As can be seen in Fig. 5, the increase of annealing temperature to 1000 °C results in a decrease of measured dielectric loss index. It is also seen that annealing the silica at temperatures up to 400 °C results in a decrease of dielectric loss index, particularly pronounced at lower frequencies.

The dielectric loss index values for the samples containing silica annealed at the temperature above 400 °C are lower. There is no substantial change of the dielectric loss index as a function of frequency for these samples. However, for the samples containing silica annealed at 1000 °C there is an initial increase of the dielectric loss with increasing frequency.

The results demonstrate that the dielectric loss index values for our samples are associated with water molecules present on the silica surface. Annealing results in water desorption from the surface of the silica particles.

Literature data [6, 16, 17] show that there are water molecules adsorbed on the surface of silica particles and they are removed under the influence of a high temperature. The molecular water and the hydrogen-bonded hydroxy groups are removed from the surface by annealing at temperatures up to 500 °C. There are silanol groups (Si-OH) which remain on the surface of the silica particles annealed up to 500 °C. However, at temperatures of 1000 °C these silanol groups are destroyed and they form siloxane linkages (Si-O-Si) on the silica surface [5]. It should be noted that up to about 500 °C the dehydration of the surface water molecules is reversible [6, 16].

Effects of rehydration of the silica surface by boiling of the samples in water are presented in

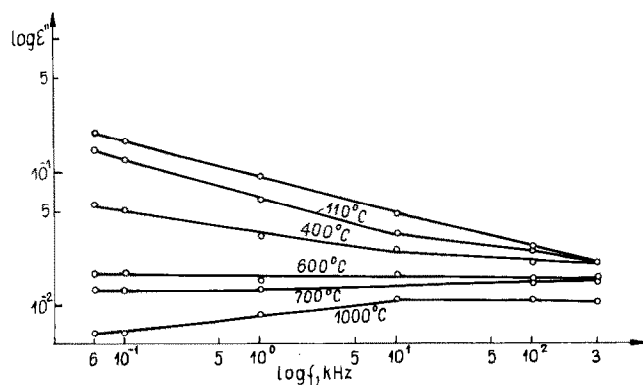


Fig. 5. The dielectric loss index dependence on frequency for the epoxy resin compounds filled with silica annealed at several temperatures.

Fig. 6. It is seen that the dielectric loss index for samples filled with the silica annealed up to 400 °C have similar values and higher than the other samples, especially for a low frequency range. The increase of the dielectric loss index for these samples is due to water adsorption on the silica surface during boiling.

Compare now results for the samples filled with the silica annealed at 600, 700 and 1000 °C. We find that increasing the annealing temperature lowers the dielectric loss index. This can be explained in terms of the already mentioned rehydration process. The higher the annealing temperature, the lower amount of rehydration is possible, and the higher the sample stability with respect to boiling water. Eventually, a smaller amount of reabsorbed water is reflected in the lowering of the dielectric loss index.

The master curve (obtained from the data presented in Figs. 5 and 6) for samples containing the silica filler annealed up to 400 °C is seen in Fig. 7. The master curve reveals a weak maximum of the loss index at frequency of about 10 Hz. This may be attributed to the dipolar relaxation

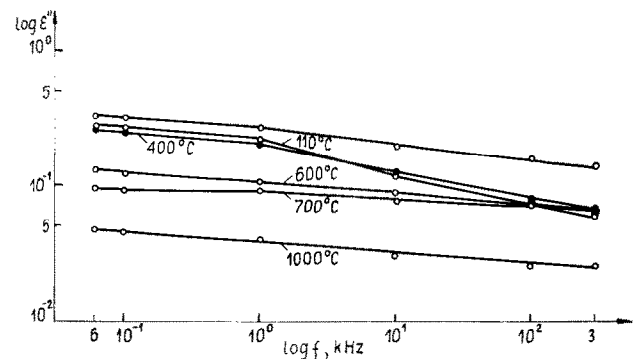


Fig. 6. The dielectric loss index dependence on frequency for epoxy resin compounds filled with silica annealed at several temperatures and boiled in water for 24 hours.

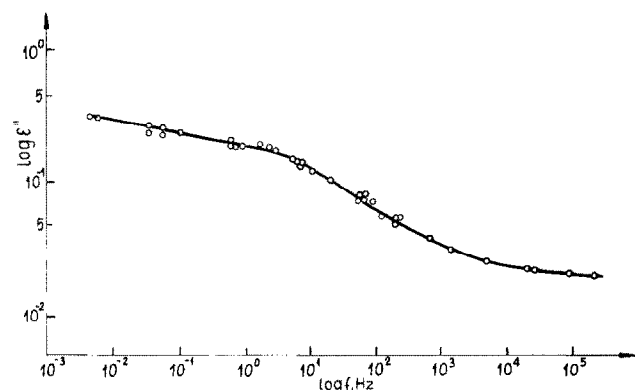


Fig. 7. Master curve for the epoxy resin compounds filled with silica annealed at 400 °C; results for boiled and unboiled samples.

process of the water molecules adsorbed at the filler surface [11, 18]. It is interesting to note that the slope of this curve at a higher frequency range is the same ($n=0.73$) as for the samples filled with the unannealed silica (Fig. 3). This indicates that the mechanism of the relaxation process is the same for both kinds of samples and might be described by the cluster model of charge carriers relaxation.

Silane-coupling-agent-modified silica

The results of the dielectric loss index measurement shown in Fig. 8 for samples filled with the silica surface modified with a silane coupling agent (NB-1115) suggest that silane influence on the dielectric loss index values is not very significant. Further, we find that the silane layer on the silica particles surface influences very little, the process of electric charge carriers relaxation taking place in adsorbed water layers on the silica surface.

It is also seen from Fig. 8 that the silane coupling agent covering the silica surface protects this surface from the adsorption of water molecules during autoclave boiling of the samples. The dielectric loss index values for the samples with a modified filler are lower than for the samples containing unmodified silica. The content of the silane coupling agent used for the silica surface modification influences the dielectric properties of the autoclave-boiled samples. This may be explained by a higher water adsorption during boiling of the samples containing 1% silane coupling agent, as compared to the other silane containing samples.

The dielectric loss index increase for the silane-modified silica-containing samples reveals that the silica surface is not protected enough from the water molecules adsorption. This may be related

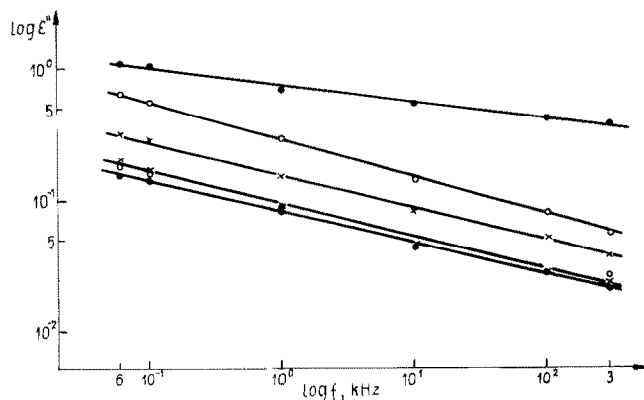


Fig. 8. The dielectric loss index dependence on frequency for the epoxy resin compounds filled with silane modified silica: ●, without silane; ×, 0.3% of silane; ○, 1% of silane, before and (a) after autoclave boiling at 121 °C for 24 hours.

to the fact that only one of the three hydroxyl groups reacts with the silica surface hydroxyl groups [19]. In turn this implies that the unreacted hydroxyl silane groups may enhance the water adsorption during boiling of the samples. For a higher silane coupling agent samples content such as 1%, the dielectric loss index increase may be also due to a different kind of interaction between the silane layers and the silica surface. Ishida and Miller [20] have shown that for such a high silane content, a great number of silane molecules are only physically bounded to the silica surface. This results in the increase of water diffusion at the epoxy resin-filler interface.

The results presented in Fig. 8 also show that the frequency dependence of the dielectric loss index is linear for all measured samples, with the slope being virtually the same as that for the unboiled samples ($n=0.75$). The slope values for the boiled samples are shown in Table 1. It is seen that the values of the slope depend on the content of the silane coupling agent on the silica surface.

It is interesting to note how these values change in relation to the slope of the unboiled samples. For the samples containing 0.3% of the silane, there are no changes in the slope values for both kinds of the samples; $n=0.75$. There is an increase of slope for samples containing unmodified filler ($n=0.87$) and a decrease for samples containing 1% of the silane coupling agent ($n=0.69$).

According to the cluster model, the values of the exponent n are attributed to the degree of structure regularity of the clusters [11]. Thus, there is no influence of boiling water on the clusters structure for samples containing 0.3% of the silane. The silane layer protects the silica surface from water adsorption. For the other kinds of samples, an increase of the dielectric loss index under the influence of the boiling water is larger. The clusters regularity decreases as the value of the exponent n is lower for samples containing 1% of the silane. It seems that this may be due to the enhanced water absorption during autoclave boiling of these

TABLE 1. Values of the exponent n for epoxy resin compounds filled with the silane modified silica of varying silane contents after autoclave boiling at 121 °C for 24 hours

Silane content (%)	n
0.0	0.87
0.3	0.75
1.0	0.69

samples as well as may be associated with the high content of the silane molecules on the filler surface.

It is interesting to note that, contrary to the other samples, there is an increase of the clusters regularity in the samples with unmodified silica after their autoclave boiling. Our results suggest that the silane layers covering the silica surface decrease water adsorption on that surface as well as affect the regularity of the clusters during autoclave boiling of the samples.

Conclusions

The dielectric loss index measurements for the epoxy resin compounds filled with modified and unmodified silica show that the results depend on the presence of water molecules adsorbed on the silica particles surface. The cluster model theory of dielectric relaxation may be used to describe the mechanism of the processes in question. According to the model, the dielectric relaxation processes taking place in our composites are related to the intracluster motion of charge carriers. The results reveal also that the surface silica modification by annealing at temperatures above 500 °C or covering it with a silane coupling agent at concentrations below 1% decreases the water absorption during boiling of the silica-filled epoxy resin compounds. This results in an increase of the stability of dielectric properties of the samples with respect to the presence of water.

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