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Dynamic mechanical, electrical and magnetic properties of ferrite filled styrene-isoprene-styrene

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The dynamic mechanical, electrical and magnetic properties of highly filled magnetic polymeric composites containing 75 to 85 wt % barium ferrite in a thermoplastic elastomer matrix styrene-isoprene-styrene (SIS), are reported. The dependence of the properties on the volume fraction of the filler has been investigated. It is shown that the toughness and shore hardness of the composite may be correlated to its dynamic mechanical parameters. The use of coupling agents for surface treatment of ferrites has been shown to improve the magnetic properties of the composite due to better filler dispersion.

1. Introduction

Recently, highly filled polymer composites have generated considerable interest in connection with their use as solid propellants in rocketry, polymer concrete, grinding wheels, piezo and pyro electric polymer components and polymeric magnets. In all these composite materials a high level of filler loading is required in order to achieve the desirable properties for specific end use application. The present study deals with polymeric magnets. The magnetic polymeric composites [1–6] represent a commercially important system due to their wide applications in computer line printers and memories, centring magnets for television, magnetic rolls of copying machines, magnetic chuck, bearing sleeves, timing motor rotors, refrigerator door latches, clamps, speedometers, tachographs, video tape recorders, etc. These composite materials contain barium or strontium ferrite or rare earth cobalt at up to 60 to 70 vol % or 87 to 92 wt % in appropriate polymer matrices. The present paper reports the dynamic mechanical, magnetic and electrical properties of ferrite filled styrene-isoprene-styrene composites, containing 75 to 85 wt % of the filler.

An attempt has been made to correlate the dynamic mechanical properties of the highly filled systems to static mechanical properties such as impact strength, hardness and toughness. The significance of this line of study is that it helps elucidate the mechanisms at the molecular level governing the observed trends in toughness and impact strength. However, such correlations have important practical implications, since the origins of loss phenomena in dynamic mechanical behaviour in molecular terms are reasonably well understood, thus in principle tough materials may be designed on a molecular level.

Magnetic properties are studied as they are eventually useful for the end use service performance of the material. The evaluation of dielectric properties and electrical conductivity of polymeric magnetic composites are of commercial relevance because of their increasing use in electrical applications, for which the material needs to possess high specific electrical resistivities [7] as well as magnetic properties.

2. Background

A number of investigators [8–11] have explored the relationship between the toughness of thermoplastics, as judged by their impact strength and their dynamic mechanical response. Vincent [12] has shown that there is an inverse correlation between impact strength and the dynamic storage modulus. The evidence for some relation between the toughness and the loss processes has been reviewed by Oberst [13], Boyer [14] and Heijboer [15]. Štefcovă and Schätz [16] have reported the values of the basic magnetic properties of permanent elastic magnets of silicone rubber in the form of coercive force, remanent induction and the maximum energy product, and their variation with volume percentage of ferrite. Most of the literature on the method of preparation of these composites and the techniques of improvement of magnetic properties is in the form of patents.

The dielectric behaviour of filled polymers has been reviewed by Van Beck [17]. Seymour [18] has recently reviewed the electrical conductivity in polymers. However, the majority of the filled systems investigated contain filler loadings up to 50 wt % only.

3. Experimental procedure

3.1. Materials

The barium ferrite powder of chemical composition

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$BaFe_{12}O_{19}$ and specific gravity of 4 was supplied by Morris Electronics, Pune. The average size of the platelet shaped particles was found to be about 3 μm by microscopic observations. The surface area of the filler, as determined by BET, was 1.07 $m^2 gm^{-1}$. Styrene-isoprene-styrene (SIS) Kraton 1107, supplied by Shell Chemie, Switzerland was used as the matrix. Titanate, KR-TTS (isopropyl trisostearyl titanate) of Kenrich Petrochemical was used as a coupling agent for surface treatment of the ferrite.

3.2. Sample preparation

1 wt % barium ferrite of the surface modifier in 2% xylene solution was added to a flask containing the required quantity of ferrite and the contents were stirred with a glass rod for 30 min. After standing overnight, the solvent was removed by heating in an oven at 130° C for 10 h. The compounding of the treated and untreated ferrite with SIS was done in a 70 cc roller type mixing chamber of a Brabender plasticorder PLE 330. The blending was done at a rotational speed of 125 r.p.m. at the temperature of 180° C until the recorded torque reached an equilibrium value, which in all cases took approximately 3 min. Three compositions, namely, 75, 80 and 85 wt % of the untreated ferrite were prepared. Only one composition, namely, 85 wt % was prepared by using the treated ferrite.

3.3. Test specimens

Sheets of the compound with a thickness of 0.028 cm were prepared on a roll mill. The required size test specimens 2.1 × 0.5 cm were cut from the calendered sheets by careful use of a sharp cutting tool. Circular discs 2.5 cm radius, 0.5 cm thick were compression moulded for magnetic properties at 180° C and 2000 kg cm^{-2} pressure.

3.4. Testing method

The dynamic mechanical behaviour of the composites was studied by using the Rheovibron Viscoelastomer DDV-II-C (Toyo Baldwin Ltd.). The variation of storage modulus, loss modulus and damping factor were studied over a range of temperatures at 11 Hz. An extensive treatment of dynamic mechanical testing and viscoelasticity can be found in the literature [19–22] and should be referred to for details.

The hardness of the composite materials was measured with a shore durometer. A quarter inch thick specimen was placed below the pointed indenter of a shore durometer instrument and the pressure facet was pressed into the plastic specimen so that the base rested on the plastic surface. This was in accordance with the testing specification mentioned in ASTM D2240. The reading was taken after holding the sample for one minute so as to allow for stress relaxation in the viscoelastic sample.

The magnetic properties in terms of the residual induction, Br, coercive force, H_c, and maximum energy product, BH_{max}, were obtained through the hysteresisgraph model MH-1020 from Walker magnometrics. The procedure for measurement is given in detail in [23].

The permittivity ε', dielectric loss ε'' and electrical conductivity were measured in the frequency range from 1 Hz to 100 Hz at 27° C temperature using a Schering bridge 1620, manufactured by General Radio Company. The film samples used were disc of 8 mm diameter and 0.02 to 0.04 mm thickness and were vacuum metallized.

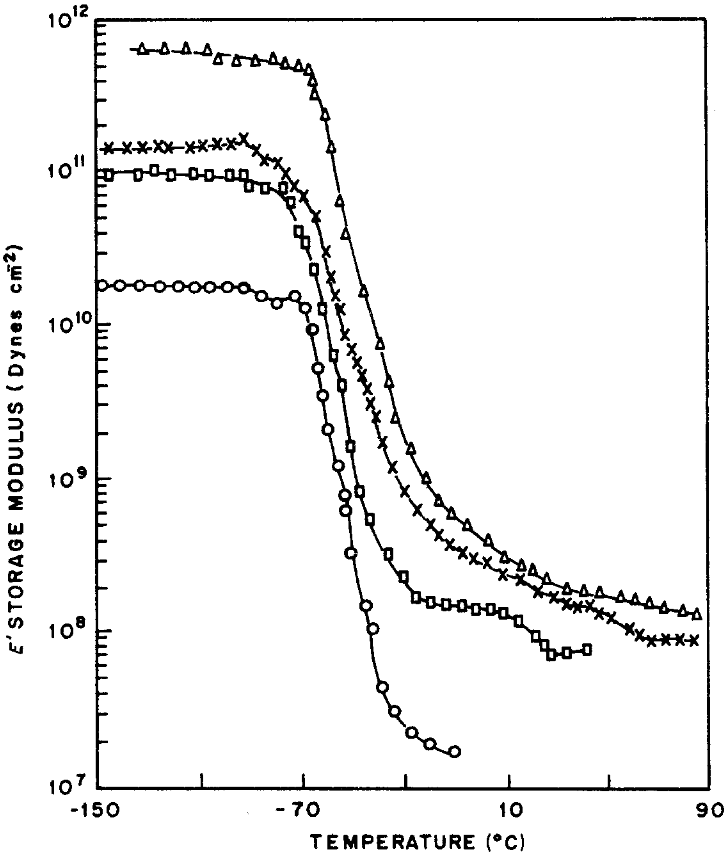

Figure 1 Variation of E' with temperature for filled and unfilled SIS block copolymer at 11 Hz. ○, without ferrite; □, 75 wt % ferrite; ×, 80 wt % ferrite; △, 85 wt % ferrite.

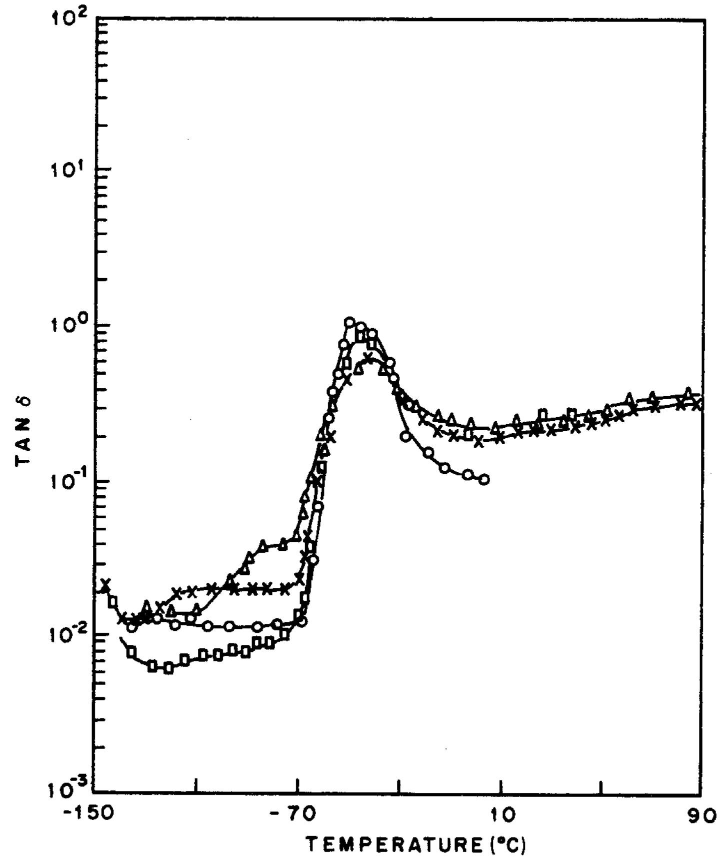

Figure 2 Variation of tan δ with temperature for filled and unfilled SIS block copolymer at 11 Hz. ○, without ferrite; □, 75 wt % ferrite; ×, 80 wt % ferrite; △, 85 wt % ferrite.

The dispersion of the ferrite particles in the matrix was examined by using a Cambridge scanning electron microscope.

4. Results and discussion

Figs 1 and 2 show the variation of the storage modulus, E', and tangent δ with temperature for filled and unfilled polymers, respectively. It is seen that the addition of ferrite raised the storage modulus considerably. It is also observed that even at the high filler loadings the damping characteristics of the matrix are not significantly affected, which is a desirable mechanical feature. It is seen that the percentage filling shifts the glass transition temperature of the composite towards higher values. Fig. 3 shows the effect of the volume fraction of filler as tensile storage modulus measured at 11 Hz and 30° C. The modulus is seen to increase with volume fraction of the filler.

Resilience has often been used as an inverse measure of damping:

$$R = \exp(-\pi \tan \delta) \qquad (1)$$

where R = resilience. The values of resilience at 30° C calculated by using Equation 1 are reported in Table I. It is seen that the addition of the filler concentration decreases the resilience considerably. This is because of the increased interval friction resulting from the interfacial surface area of the filler particles.

The close relationship between dynamic loss characteristics and toughness have been indicated by many investigators [8–15]. Wada and Kasahara [8] have developed a simple theory to relate the ability of a

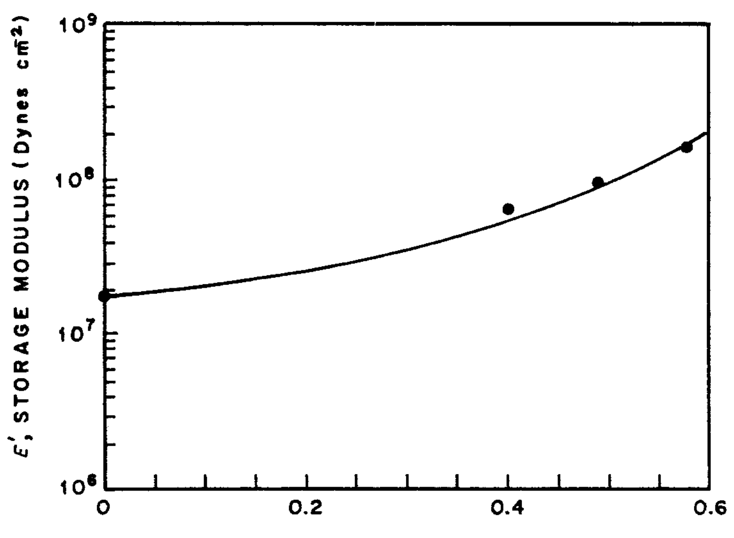

Figure 3 Variation of E' with ferrite volume fraction at 30° C.

TABLE I Impact strength and resilience estimates for the various systems

Matrix	Ferrite amount (wt %)	Impact strength (I)	Resilience (R)
SIS	–	3.0	0.75
SIS	75	2.9	0.45
SIS	80	2.75	0.44
SIS	85	2.7	0.42

material to dissipate the energy of impact (Izod impact strength, I) and the dynamic mechanical loss. The theory assumes the Maxwell element to represent the material. It is also assumed that the impact strength is proportional to fracture energy and that the fracture time is smaller than the relaxation time for the material. The fracture time, t_0, for the Izod test has been reported as several msec for common plastics material [24]. Wada and Kasahara [8] used data in the range of 0.1–1.0 cycles sec^{-1} because these frequencies do not deviate so much from $1/t_0$. In the present case the frequency used was 11 cycles sec^{-1} and this was assumed to be of the same order as $1/t_0$ for convenience of estimating the Izod impact strength. The fracture time would certainly be shorter than 0.1 sec, which is a necessary condition for the relationship between Izod impact strength and the integrated loss tangent as given by Wada and Kasahara:

$$I = \int_{0^\circ\mathrm{K}}^{300^\circ\mathrm{K}} \left(\frac{G''}{G'}\right) \mathrm{d}t \qquad (2)$$

where G' is shear storage modulus and G'' is shear loss modulus. It is known that the dynamic storage modulus in tension and dynamic storage modulus in shear are related by a constant relationship as follows for isotropic, elastic materials undergoing infinitesimal deformations in a homogeneous stress field

$$E' = 2(1 + \nu) G' \qquad (3)$$

where ν is Poisson's ratio. It should, however, be noted that for highly filled material [25] this equality does not hold. Nevertheless, E' would be proportional to G' because Poisson's ratio generally has a weak dependence on the level of filling [26] and temperature [27].

The relationship given by Wada and Kasahara [8] can be modified in terms of tensile dynamic storage modulus so that

$$I = \int_{0^\circ\mathrm{K}}^{300^\circ\mathrm{K}} \left(\frac{E''}{E'}\right) \mathrm{d}t \qquad (4)$$

In most polymers, values of loss tangent are known only above liquid nitrogen temperature. Since the data in the present case are not available below 133 K and the temperature dependence of tan δ below 203 K is not appreciable, the values are very small below this point. In this way impact strength has been estimated by the integration above 203 K as a first approximation. The value of impact strength calculated using Equation 4 is reported in Table I. It is seen that increasing filler concentration decreases the impact strength. This may be due to the filler particles acting as stress concentration points facilitating crack propagation.

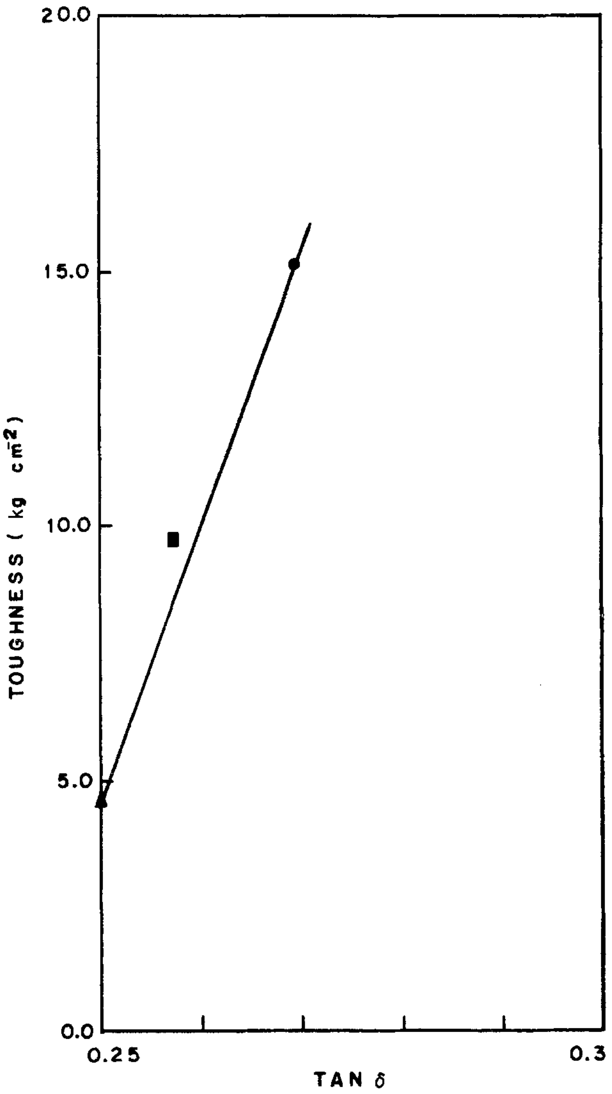

Figure 4 Variation of toughness of the material with tan δ at room temperature. SIS ferrite composites: ▲, 85 wt % ferrite; ■, 80 wt % ferrite; ●, 75 wt % ferrite.

For polymeric systems, Sachar [9] has shown that the toughness and the dissipation factor, tan δ, are related at room temperature. The value of tan δ at 30° C is taken from Fig. 2 while toughness values have been taken from [28], represented by the total area under the static stress–strain curve.

$$\text{Toughness} = \int_0^{\varepsilon_{\text{yield stress}}} \mathrm{d}\sigma + \int_{\varepsilon_{\text{yield stress}}}^{\varepsilon_{\max}} \sigma \, \mathrm{d}\varepsilon \qquad (5)$$

The relationship holds good in the present case as can be seen from Fig. 4.

A plot of tensile storage modulus at room temperature against the shore hardness on a semi-logarithmic scale for each of the systems studied shows a good linear correlation as given in Fig. 5. This has worked probably because shore hardness is a measure of the rebound energy. Fig. 5 also shows the increasing trend of hardness with percentage filling. This is because ferrites are much harder than the matrix used.

In addition to the effect of filler loading on mechanical properties, the magnetic properties of the highly filled composites were also investigated. Fig. 6 shows

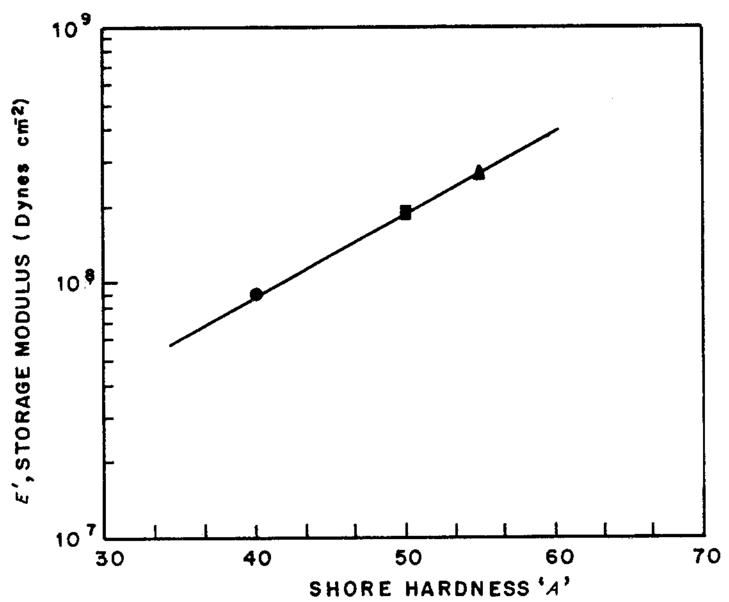

Figure 5 Variation of the storage modulus at room temperature with hardness of the material. SIS ferrite composites: ▲, 85 wt % ferrite; ■, 80 wt % ferrite; ●, 75 wt % ferrite.

the variation of magnetic properties with ferrite loading. Remanent induction, *Br*, which is a measure of magnetic flux density corresponding to zero magnetic forces in the magnetic material, increases linearly over the entire range of ferrite concentration. The coercive force H_c, is defined as the magnetizing force that must be applied to a magnetic material, in a direction opposite to the residual induction, to reduce the induction to zero. The coercive force is found to increase linearly with ferrite concentration. This also indicates that the permanence of the magnetic composite increases with percentage filling. The maximum energy product BH_{max} that a sample could supply to an external magnetic circuit (the strength of a magnet) is a nonlinear function of the magnetic filler concentration as shown in Fig. 6. The value of BH_{max} increases progressively with ferrite loading over the entire concentration range. The observed trend of increase of all the magnetic properties with percentage filling is due to all the magnetic properties being derived from the filler in case of polymeric magnets.

The surface treatment of the ferrite filler with titanate coupling agent was found considerably to improve the magnetic properties of the 85 wt % filled composite. The values of maximum energy product, BH_{max}, for the treated and untreated filler composites were 0.2125 kGs Oe and 0.1330 kGs Oe, respectively. This effect may be due to the improved dispersion and reduction of agglomerate formation because of surface treatment, as evidenced by the scanning electron micrographs (Fig. 7). The agglomeration of filler particles would reduce magnetic properties as a result of cancellation of the magnetic lines of forces within the system. Therefore, it may be concluded that the surface treatment of magnetic fillers is an effective means for improving the magnetic performance of magnetic polymeric composites.

The composites were also characterized for electrical

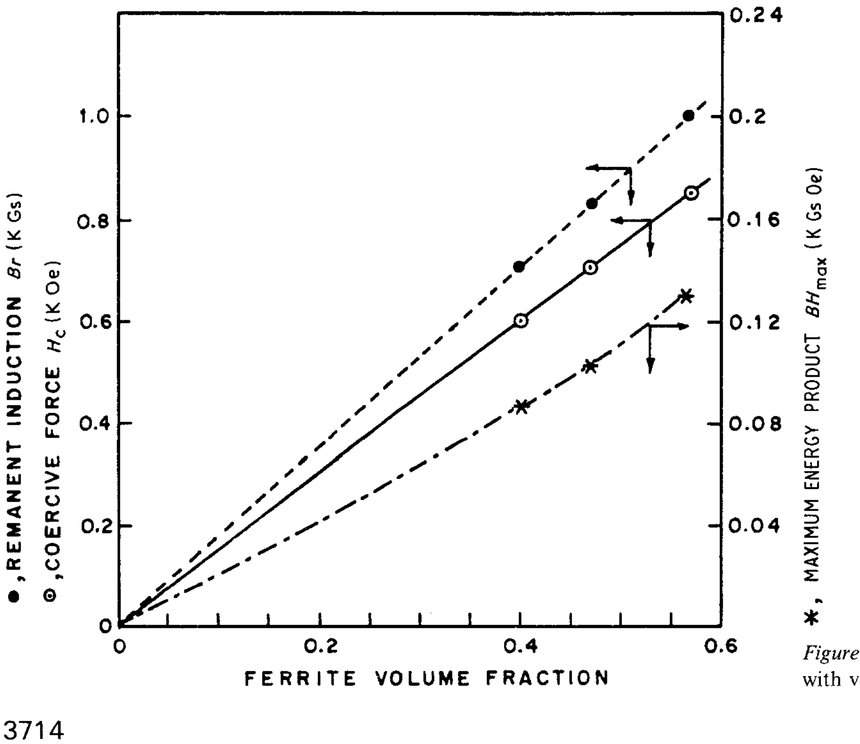

Figure 6 Variation of ●, *Br*; ⊙, H_c and $*$, BH_{max} with volume percentage ferrite.

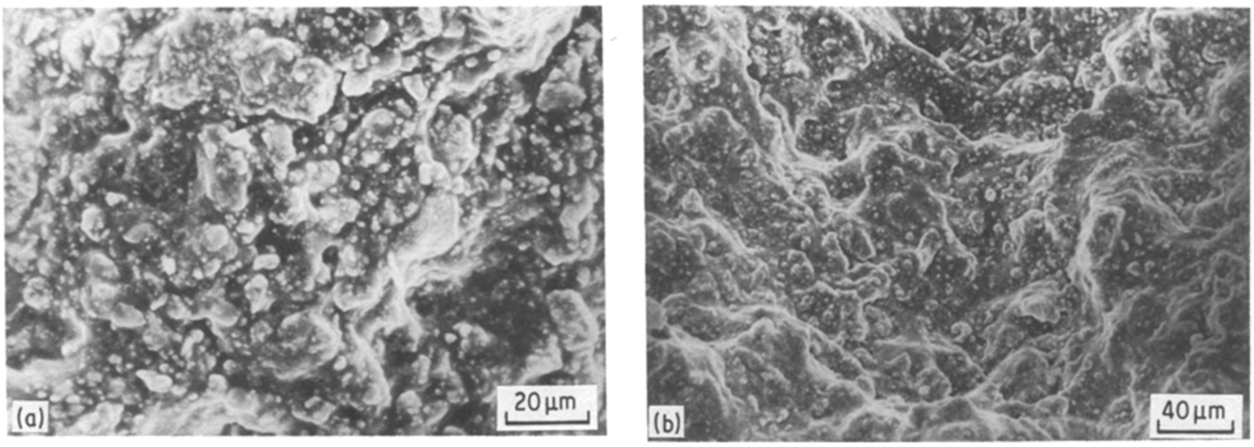

Figure 7 (a) Scanning electron micrograph of SIS filled 85 wt % ferrite. (b) Scanning electron micrograph of SIS filled 85 wt % treated ferrite.

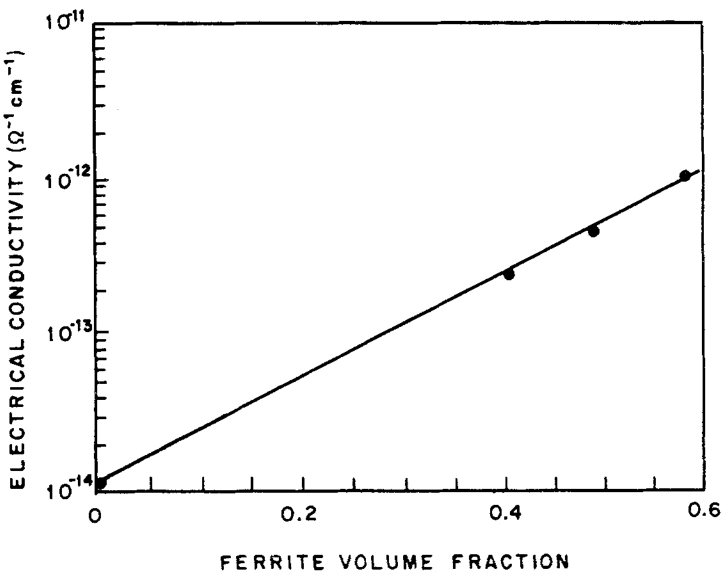

Figure 8 Variation of electrical conductivity with vol % of ferrite for SIS composite.

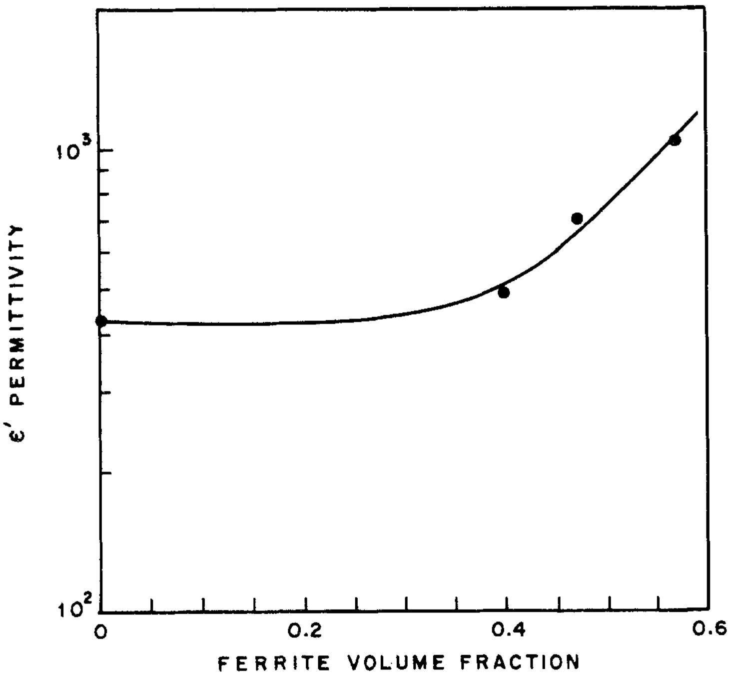

Figure 9 Variation of permittivity ε' with vol % of ferrite for SIS composite at 100 kHz.

conductivity and permittivity using a dielectric bridge. Fig. 8 shows a linear increase in electrical conductivity with percentage filling. It is observed that the magnetic composites have retained their electrical insulation characteristics even at high loadings of inorganic filler.

The variation of the electrical permittivity, ε', with filler loading is shown in Fig. 9. The permittivity of a material signifies its capacity to store electrical energy. Therefore, it is to be expected that the permittivity would increase with an increasing amount of inorganic filler. The surface treatment of the filler with titanate coupling agent was found to decrease the permittivity of the composite at 85% filler loading. The values of the electrical permittivity of the composites containing treated and untreated ferrites were found to be 7.5×10^2 and 10.2×10^2, respectively. The drop in permittivity due to surface treatment may be attributed to greater damping occurring at the matrix–filler interfaces due to better dispersion. The measurement of dielectric behaviour may thus be used as an effective tool for determining the level of filler dispersion.

5. Conclusions

In summary, the high filler loadings required for achieving desirable magnetic characteristics in polymeric composites do affect their dynamic mechanical behaviour. The storage modulus increases considerably. However, the damping characteristics of the thermoplastic elastomeric matrix were not significantly altered even at 75 to 85 wt % ferrite loading. Similarly, the electrical insulation characteristics of the composite were retained even at the high filler loading. It was found that the static properties such as toughness and hardness could be correlated to tan δ and storage modulus, E', respectively. The use of titanate coupling agents for surface treatment of ferrites improved the magnetic properties, possibly due to improved filler dispersion.

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