Dielectric and Mechanical Properties of Polystyrene/Acrylonitrile–Butadiene Rubber Blends

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ABSTRACT: The dielectric and mechanical properties of polystyrene(PS)/acrylonitrile–butadiene rubber (NBR) blends were studied with the aim of improving the insulation properties of NBR. Compatibility investigations, performed with viscosity and dielectric methods and confirmed with the calculated heat of mixing, indicated that such blends were incompatible. To overcome the problem of phase separation between NBR and PS, we chose epoxidized soya bean oil to act as a compatibilizer and added 3% to the blends under investigation. This led to the conclusion that a sample containing 10% PS (either pure or scrap) possessed the most suitable electrical and mechanical properties. For this reason, the sample was chosen for studying the effect of the addition of three types of fillers (quartz, talc, and calcium carbonate) in increasing quantities (up to 80 phr) on the dielectric and mechanical properties. The variation of the dielectric properties with temperature (20–60°C) was also investigated. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 540–552, 2002

Key words: dielectric properties; mechanical properties; blends; fillers; compatibility

INTRODUCTION

In recent years, a number of polymer blends have been commercially exploited. Their importance arises from the new and desirable properties absent in the homopolymers. The production of such polymer blends makes it possible to improve the physical properties of the individual polymers and, consequently, offers an economical way of designing new polymeric materials with improved properties.

Electrical properties of various polymer blends[1–10] have been investigated. It has been shown that the dielectric properties of polymers and polymer blends depend in general on the structure, crystallinity, morphology, and presence of other additives. In heterogeneous polymer blends, the permittivities of the polymers are influenced by interfacial effects (i.e., due to the polarization arising from the differences in the conductivities of the two phases).[11]

Many authors have studied the compatibility of polymer blends with different methods. The calculation of the heat of mixing is considered one of these tools. Schneier[12] proposed an equation for calculating the heat of mixing for two-component blend systems and calculated the heat of mixing for a number of polymer pairs selected from Bohn's[13] list.

Viscosity techniques have been applied to investigate the compatibility of polymeric blends in dilute solutions.[14–16]

Phase separation in polymer blends can also be detected with the dielectric relaxation method.[9,17] This dynamic method requires intensive work to be carried out for the study of the compatibility of blends. A rapid dielectric method was proposed to study the compatibility of the blends.[18,19]

Fillers are generally incorporated into polymers to modify physical and electrical properties. The addition of a conductive filler such as carbon black into a polymer[20] or a polymer blend[21] leads to an end product that possesses conducting or semiconducting properties. However, the addition of white fillers to the same polymer[20] or polymer blend[21] leads to an end product that possesses good insulation properties.

Polystyrene (PS) is the fourth largest volume commodity thermoplastic, ranking behind polyethylene, polypropylene, and poly(vinyl chloride). Therefore, PS recycling is a good business, and there are growing indications that a sustainable industry is emerging.

PS is considered to be an excellent insulating material because it possesses very low dielectric loss (ϵ'') and very high resistivity.[22]

Acrylonitrile–butadiene rubber (NBR) is characterized by good mechanical properties and good oil resistance,[21] but it has moderate insulating properties and higher values of permittivity ($\epsilon' = 17$–14).[19] The considerably high ϵ'' values (1.33–2.00) cause NBR to lose to some extent its insulating properties. For this reason, we have sought to blend it with a nonpolar

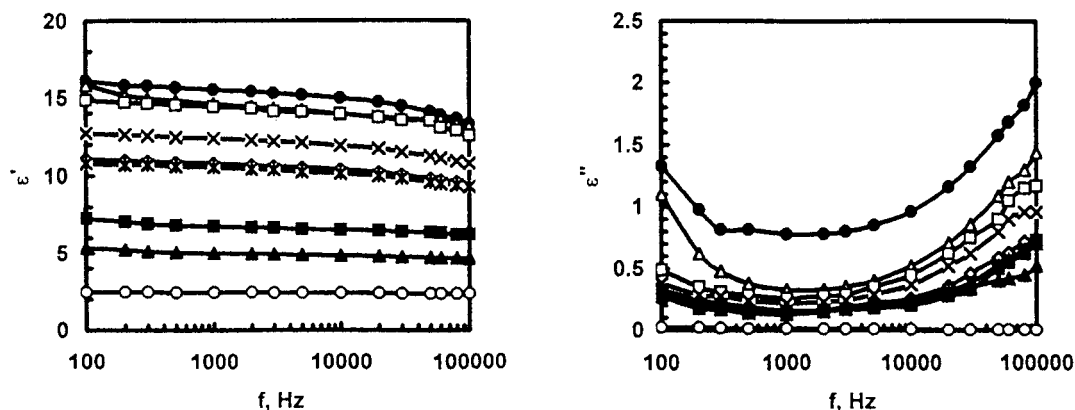*Correspondence to:* S. L. Abd-El-Messieh (salwalou@hotmail.com).

Figure 1 ϵ' and ϵ'' for pure PS/NBR blends: (○) PS, (△) 5 PS, (□) 10 PS, (×) 13 PS, (◇) 17 PS, (✳) 20 PS, (■) 33 PS, (▲) 43 PS, and (●) NBR at room temperature (≈25°C).

polymer such as PS to reduce these higher values of ϵ'' and make the changes in both ϵ' and the mechanical properties as minimal as possible. Also, we have aimed to replace pure PS with scrap PS in the blend to get a cheaper end product possessing promising electrical and mechanical properties and to solve the problems caused by the accumulation of waste polymers.

EXPERIMENTAL

Materials

Nitrile rubber (33% acrylonitrile and 0.5% ash) and peroxide [1,3-bis(isopropyl)butyl benzene peroxide on calcium carbonate; trade name, Perkadox 14/40; molecular weight = 338] were used in this work.

Pure PS was obtained from Hoechst, whereas PS scrap was obtained from National Plastics Co. (Egypt).

The fillers used in this work were quartz, talc, and calcium carbonate.

Epoxidized soya bean oil with an oxiran content of 6 was used.

Blend preparation

The melt mixing was carried out in a Brabender plasticorder at 150°C and at a rotator speed of 30 rpm. The mixing was continued for 5 min, and then peroxide was added to the mix on a laboratory two-roll mill (470-mm diameter and 300-mm working distance). The speed of the slow roll was 24 rpm with a gear ratio of 1:1.4. The compounded blends were left overnight before vulcanization.

Vulcanization

The vulcanization was carried out in a heated platen press under a pressure of about 40 kg/cm^2 and at temperature of 162 ± 1°C

Techniques

The mechanical properties, the tensile strength and ultimate elongation (elongation at break), were determined at room temperature on a Zwick 1101 tensile
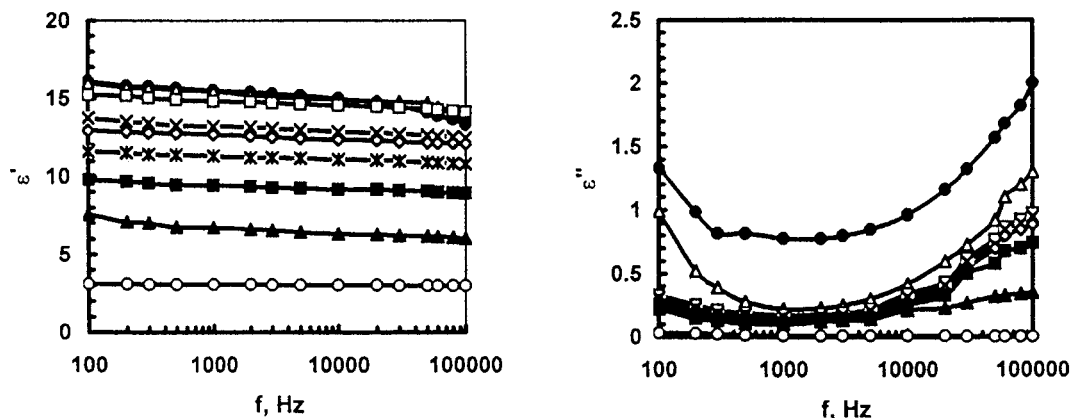

Figure 2 ϵ' and ϵ'' for scrap PS/NBR blends: (○) PS, (△) 5 PS, (□) 10 PS, (×) 13 PS, (◇) 17 PS, (✳) 20 PS, (■) 33 PS, (▲) 43 PS, and (●) NBR at room temperature (≈25°C).
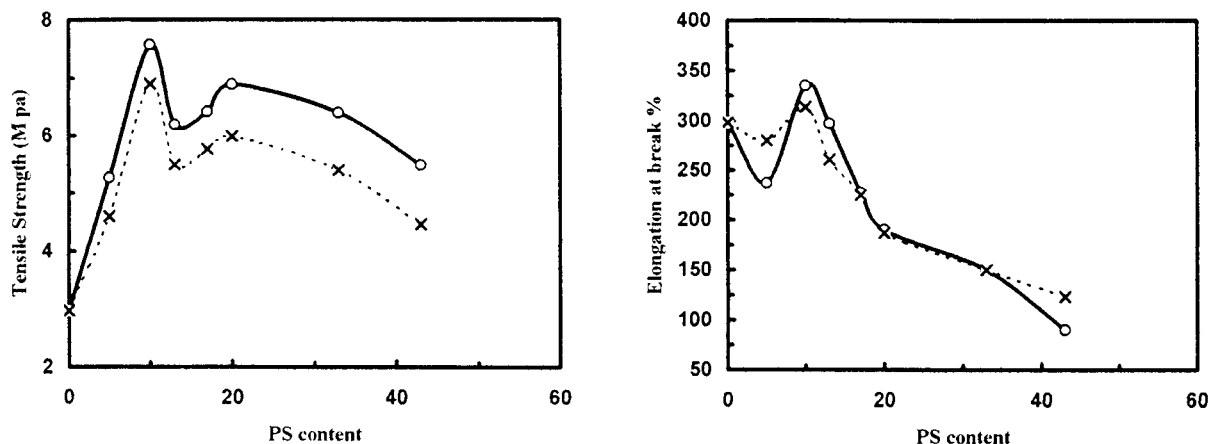
Figure 3 Variation of the tensile strength and elongation at break with the PS content in PS/NBR blends: (○) pure and (×) scrap PS.

testing machine according to ASTM Standard D 412 661.

Dielectric measurements were carried out from 100 Hz to 100 kHz with an AG-411 B LCR meter (Ando Electric, Ltd., Japan). The capacitance (C_M) and loss tangent tan δ were obtained directly from the bridge from which ϵ' and ϵ'' were calculated. An NFM/5T guard ring capacitor from Wiss Tech. Werkstatten GmbH (Germany) was used as a measuring cell. The cell was calibrated with standard materials (trolitul, glass, and air) with thicknesses ranging from 1 to 5 mm. For each sample, a relation between the thickness and C_M was plotted as a standard curve. C_M for the standard materials obtained from the standard curves is plotted against the known ϵ' values for trolitul, glass, and air (2.5, 7, and 1, respectively). The relation between C_M and ϵ' was linear, and so ϵ' corresponding to any measured C_M value could be deduced. To check the standard curve, we used two Teflon samples (ϵ' = 2.0)[23] of different thicknesses. The experimental errors in ϵ' and ϵ'' were ±3 and ±5%, respectively.

The viscosity (η) of the investigated solutions was measured with an AV 350 from Schott Gerate (Germany). In this case, the liquid meniscus was sensed optoelectrically at the measuring levels. These precision devices ensured the high accuracy of the capillary viscometer. The viscosity measuring unit was connected with a CK100 flow-through cooler to control the temperature to an uncertainty of ±0.1°C.

RESULTS AND DISCUSSION

ϵ' and ϵ'' for different PS/NBR (either pure or scrap PS) blends (0, 5, 10, 13, 17, 20, 33, 43, or 100% PS) were measured over a frequency range of 100 Hz to 100 kHz. The measurements were carried out at room temperature (≈25°C). The data obtained are illustrated graphically in Figures 1 and 2. It is clear that ϵ' decreases with the applied frequency (f) increasing, showing an anomalous dispersion. In such a range, ϵ' has contributions from orientation, atomic, and electronic polarization.[21] Also, it is clear that ϵ' increases

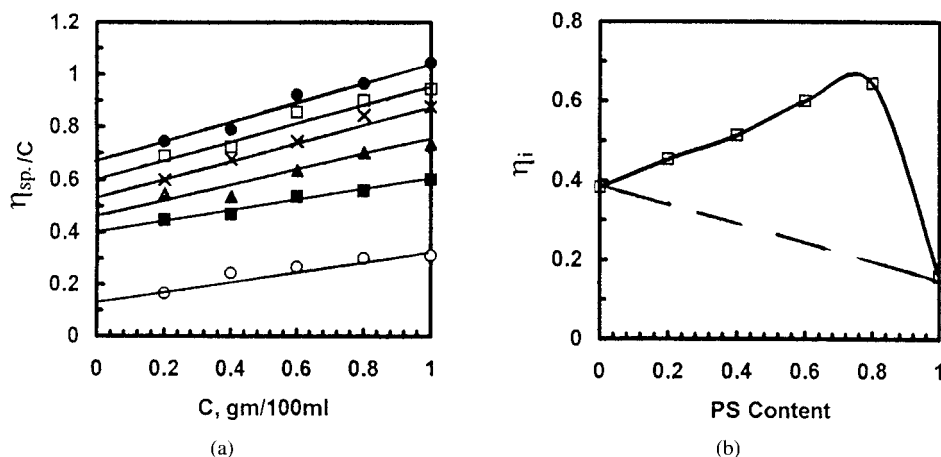**Figure 4** Relation between (a) η_{sp} and the concentration of (○) PS, (●) 0.8 PS, (□) 0.6 PS, (×) 0.4 PS, (▲) 0.2 PS, (■) NBR, and (b) η_i and the PS content.
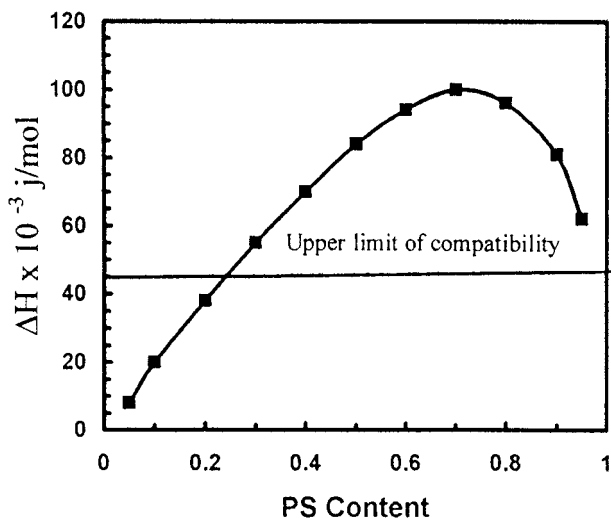
Figure 5 Relation between the heat of mixing and the weight fraction of PS.

with the NBR content increasing in the blend. The increase in ϵ' with the incorporation of rubber is due to the increase in C≡N dipoles, which leads to an increase in the orientation polarization and to the presence of interfacial polarization.[24]

From the same figures, it is clear that the curves relating ϵ'' and log f are broader than Debye curves,[25] indicating that more than one relaxation process is present. These processes could be attributed to mechanisms related to the main chain and its related motions.[18,19,26–29] One of the expected mechanisms is related to the Maxwell–Wagner effect, which usually occurs at a lower frequency region for heterogeneous systems. The origin of such a process is an alternating current that is in phase with the applied potential due to the differences in the permittivities and resistivities of the blends. This phenomenon has also been noticed for both individual polymers, NBR and PS, as a result of the presence of peroxide in NBR,[27] which is usually added for the curing of rubber, and other impurities

such as catalysts and antioxidants added to PS throughout the polymerization process, oxidation process, and so on.[30]

From Figures 1 and 2, it can also be observed that both ϵ' and ϵ'' decrease with the PS content increasing in the blend. The decrease in ϵ'' is pronounced in a sample containing 10% PS as its value changes from 1.33 to 0.49 at 100 Hz and from 2 to 1.17 at 100 kHz. This is accompanied by a slight decrease in ϵ' as its value changes from 16.1 to 14.9 at 100 Hz and from 13.37 to 12.68 at 100 kHz. With the PS content increasing more than 10%, there is a slight decrease in ϵ'' followed by a higher decrease in ϵ'. This means that the incorporation of 10% PS into NBR improves to some extent the insulating properties of NBR.

In a comparison of Figures 1 and 2, it is clear that the values of ϵ' for the blends containing scrap PS are slightly higher than those containing the pure PS. This slight increase in ϵ' is accompanied by a slight decrease in ϵ''. This may be due to the oxidation of the impurities added to PS because structural defects that lead to the formation of oxidized centers cause interfacial polarization.[31] This interesting result leads to the conclusion that scrap PS could be used instead of pure PS for blending with NBR because it has proper dielectric properties. Also, it could be concluded that a sample containing 10% PS possesses the most promising insulating properties.

Figure 3 represents the variation of both the tensile strength and elongation at break with PS content, either pure or scrap. There is a pronounced increase in the tensile strength with increasing PS content in the blend until 10%. This increase is followed by a pronounced decrease for samples containing 13% PS, and then there is an increase again until 20%. After that, there is a slight decrease in the tensile strength for samples containing higher concentrations of PS. It is also clear from this figure that there is a drop in the values of the elongation at break for a sample containing 5% PS. After that, there is a pronounced increase in
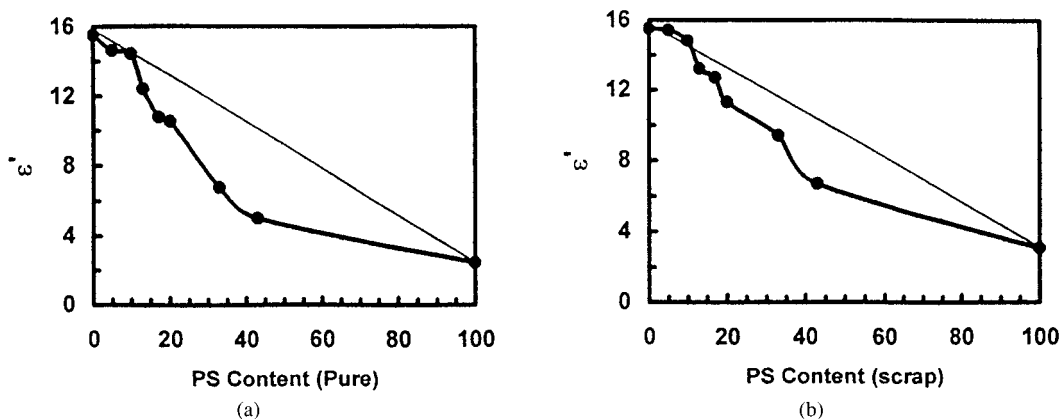

Figure 6 Relation between ϵ' at 1 kHz and the PS content: (a) pure and (b) scrap PS.
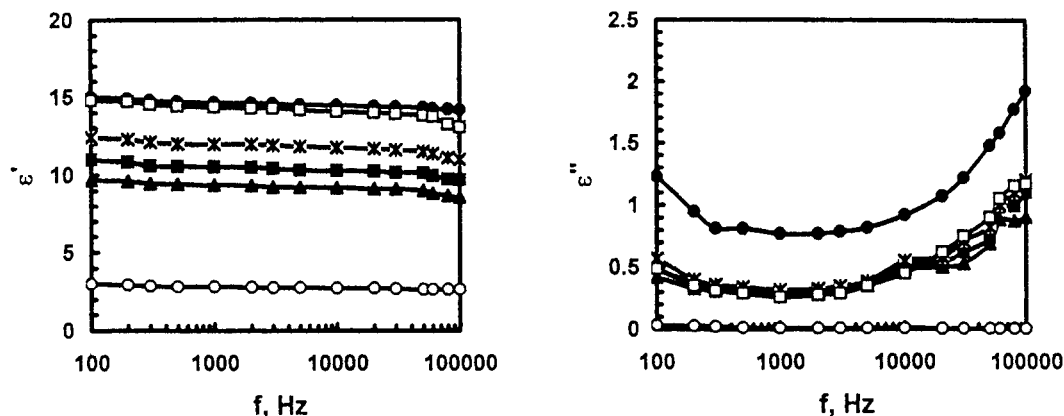
Figure 7 ϵ' and ϵ'' for pure PS/NBR blends with 3% epoxidized soya bean oil: (○) PS, (□) 10 PS, (✳) 20 PS, (■) 33 PS, (▲) 43 PS, and (●) NBR at room temperature ($\approx$25°C).

the elongation at break for a sample containing 10% PS. This abrupt increase is followed by a pronounced decrease for the higher PS content.

In both curves, the tensile strength and elongation at break detected for the blends containing scrap PS are lower than those detected for pure PS, but they have the same trend.

From previous investigations, it can be concluded that a PS/NBR blend containing 10% PS, either pure or scrap, possesses the most suitable electrical and mechanical properties.

Compatibility study

Viscosity measurements

Viscosity techniques have been applied to investigate the compatibility of NBR/PS blends in dilute solutions. The nature of the viscosity of dilute polymer solutions is based on the analysis of hydrodynamic properties related to the movement of macromolecules in solutions. The degree of compatibility of the polymer blends can be deduced from[14]

$$\eta_{\mathrm{sp}}/C) = [\eta_i] + K[\eta_i]^2C$$

where η_{sp} is the specific viscosity, C is the concentration (g/100 mL), η_i is the intrinsic viscosity, and K is a constant. A linear relation ship is obtained by the plotting of η_{sp}/C against C, as shown in Figure 4(a). From the intercepts of these lines with the y axes, η_i can be obtained. Plots of η_i versus the PS contents are illustrated graphically in Figure 4(b). It is clear that the values of η_i do not coincide with the line connecting the two individuals, indicating that the two blends are incompatible.

Heat of mixing

The calculation of the heat of mixing is considered to be a tool for the determination of the degree of compatibility between polymer blends. Polymer compatibility in the solid state might occur if the heat of mixing is below 4.185×10^{-3} J/mol.[12] The heat of mixing, $\triangle H_m$, was calculated for the system under investigation with the following equation:[12]
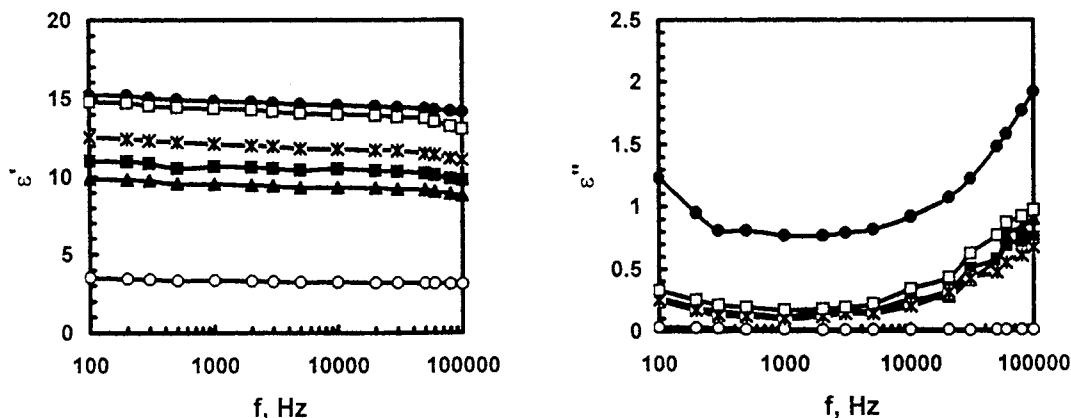

Figure 8 ϵ' and ϵ'' for scrap PS/NBR blends with 3% epoxidized soya bean oil: (○) PS, (□) 10 PS, (✳) 20 PS, (■) 33 PS, (▲) 43 PS, and (●) NBR at room temperature ($\approx$25°C).
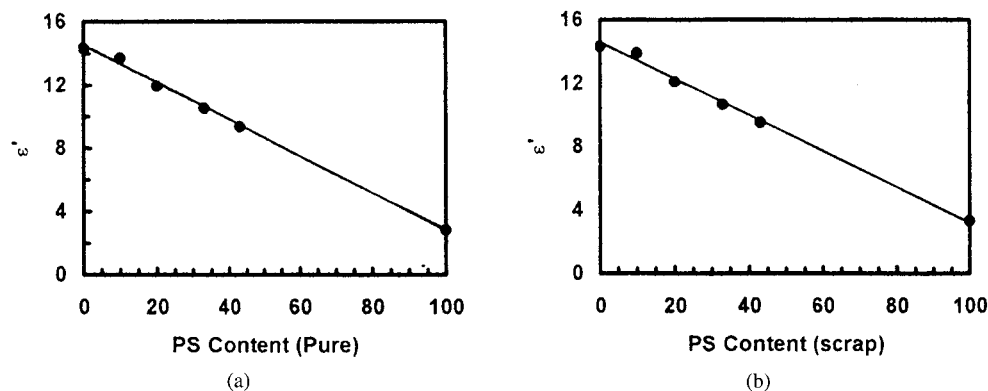
Figure 9 Relation between ϵ' at 1 kHz and the PS content with 3% epoxidized soya bean oil: (a) pure and (b) scrap PS.

$$\Delta H_m = \{X_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 [X_2/(1 - X_2) M_2 \rho_2$$
$$+ (1 - X_1) M_1 \rho_1)^2]\}^{1/2}$$

where X, ρ, and M are the weight fraction of the polymer, the density, and the monomer unit molecular weight, respectively, and δ is the solubility parameter of the polymers.

The obtained values are illustrated graphically in Figure 5. It is clear that the PS/NBR blends are expected to be thermodynamically incompatible because the calculated heat of mixing lies above the upper limit of compatibility, especially for blends that possess higher PS contents. However, it is clear that the calculated heat of mixing for lower PS contents (<20%) lies below the upper limit of compatibility, indicating some sort of compatibility for lower PS contents. This conclusion is considered to be good evidence for the results obtained from the viscosity measurements.

Dielectric measurements

ϵ' is plotted graphically versus the PS content, either pure or scrap, at $f = 1$ kHz in Figure 6. It is clear that

the values of ϵ' deviate from the line connecting the values of ϵ' for the two individuals. This deviation, which is much more pronounced for concentrations of PS higher than 10%, could indicate that PS/NBR blends are incompatible for values of PS higher than 10%.

From previous investigations, it can be concluded that PS/NBR blends are incompatible, especially at higher contents of PS.

To improve the compatibility between PS and NBR, we chose epoxidized soya bean oil as a compatibilizer and added 3% to PS/NBR blends containing either pure or scrap PS in various ratios (0, 10, 20, 33, 43, or 100). ϵ' and ϵ'' were measured in the same way as discussed previously, and the obtained data are illustrated graphically in Figures 7 and 8. From both figures, it is clear that the values of ϵ'' are slightly affected by the addition of oil, whereas the values of ϵ' for NBR decrease significantly all over the applied frequency range after the addition of oil. Even though the variation of ϵ' with the PS content in the blend decreases gradually after the addition of epoxidized soya bean oil, the nature of the relaxation spectra is not affected by the addition as the shape of curves relating ϵ'' and
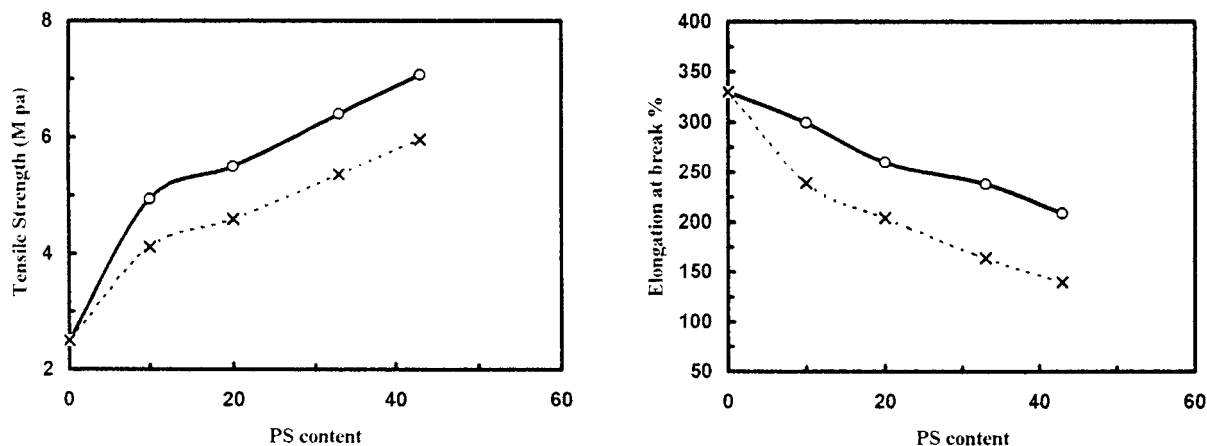

Figure 10 Variation of the tensile strength and elongation at break with the PS content in PS/NBR blends with 3% epoxidized soya bean oil: (○) pure and (×) scrap PS.
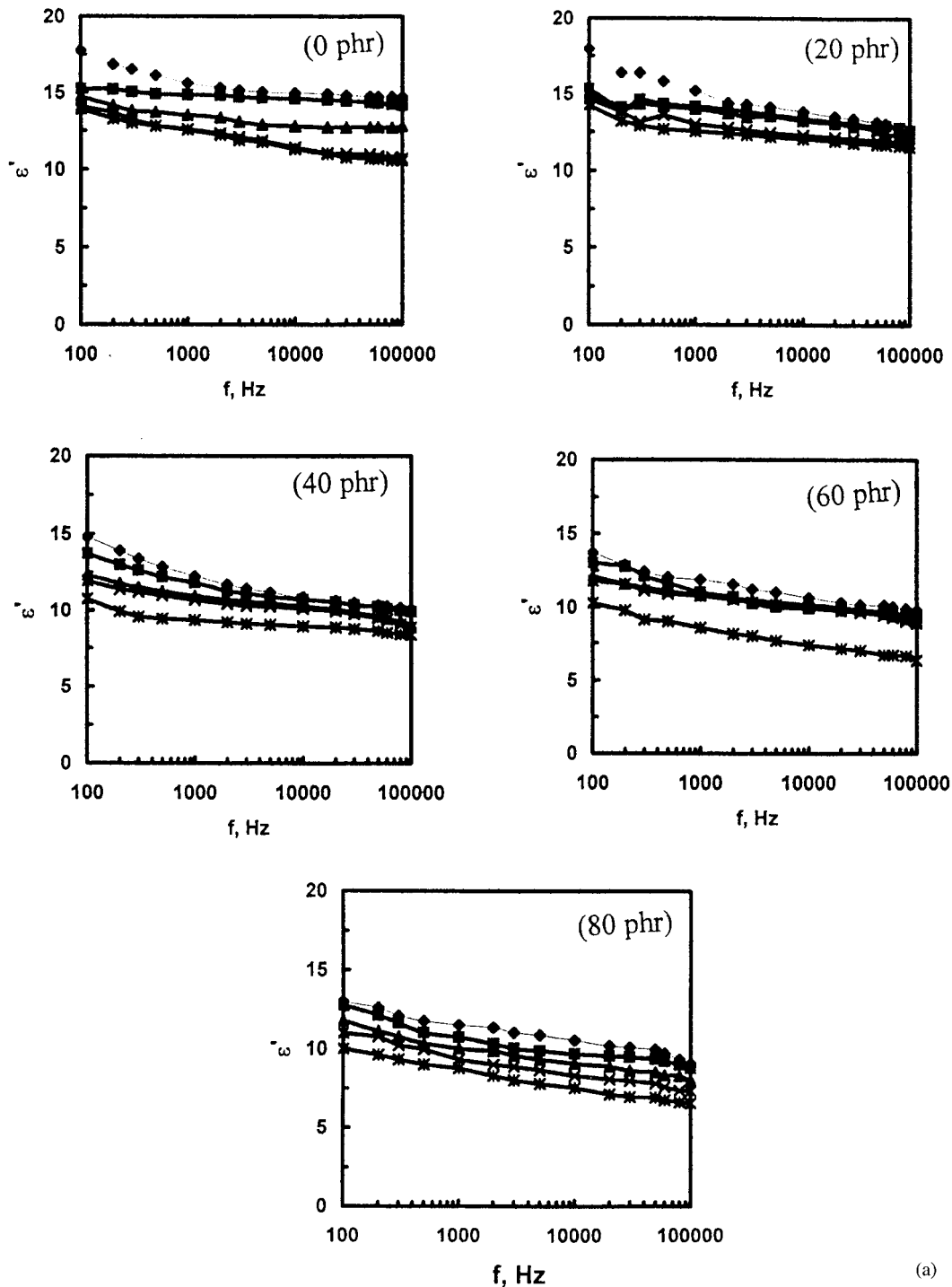
Figure 11 (a) ϵ' and (b) ϵ'' for 10/90 scrap PS/NBR with 3% epoxidized soya bean loaded with different contents of quartz at (♦) 20, (■) 30, (▲) 40, (×) 50, and (✳) 60°C.

f does not change in comparison with those before the addition of epoxidized soya bean oil (Figs. 1 and 2).

With ϵ' plotted against the PS content at $f = 1$ kHz, as shown in Figure 9, a fairly straight line, with an experimental error of less than 3%, is obtained for blends containing pure or scrap PS. This means that the addition of epoxidized soya bean oil to the inves-

tigated blends improves to some extent the degree of compatibility between PS/NBR blends.

The variation of both the tensile strength and elongation at break with the PS content, either pure or scrap, after the addition of 3% epoxidized soya bean oil is illustrated graphically in Figure 10. It is clear that the tensile strength increases with increasing PS con-
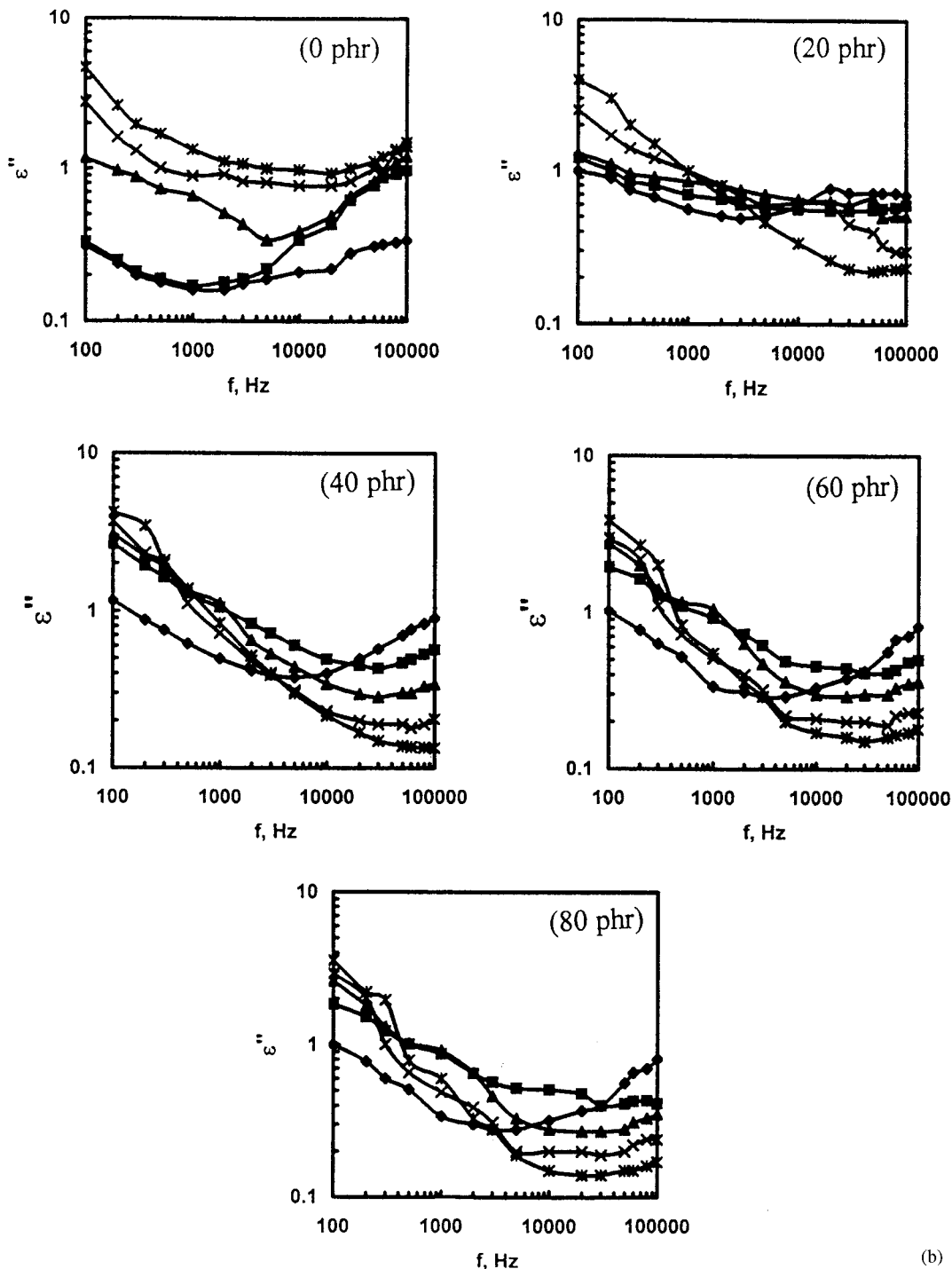
Figure 11 (*Continued from the previous page*).

tent in the blend, whereas the elongation at break slightly decreases. Also, the tensile strength and elongation at break are higher for blends containing pure PS than for those containing scrap PS.

Fillers are generally incorporated into polymers to modify physical and electrical properties and to reduce the cost of the end product. For this reason, a sample containing 10% scrap PS, having promising electrical and mechanical properties, was chosen for the same measurements after loading with three different types of fillers—quartz, talc, and calcium carbonate—in increasing quantities (0, 20, 40, 60, and 80 phr).

Figures 11–13 show the frequency dependence of ϵ' and ϵ'' for a 10/90 scrap PS/NBR blend loaded with quartz, talc, and calcium carbonate, respectively, in
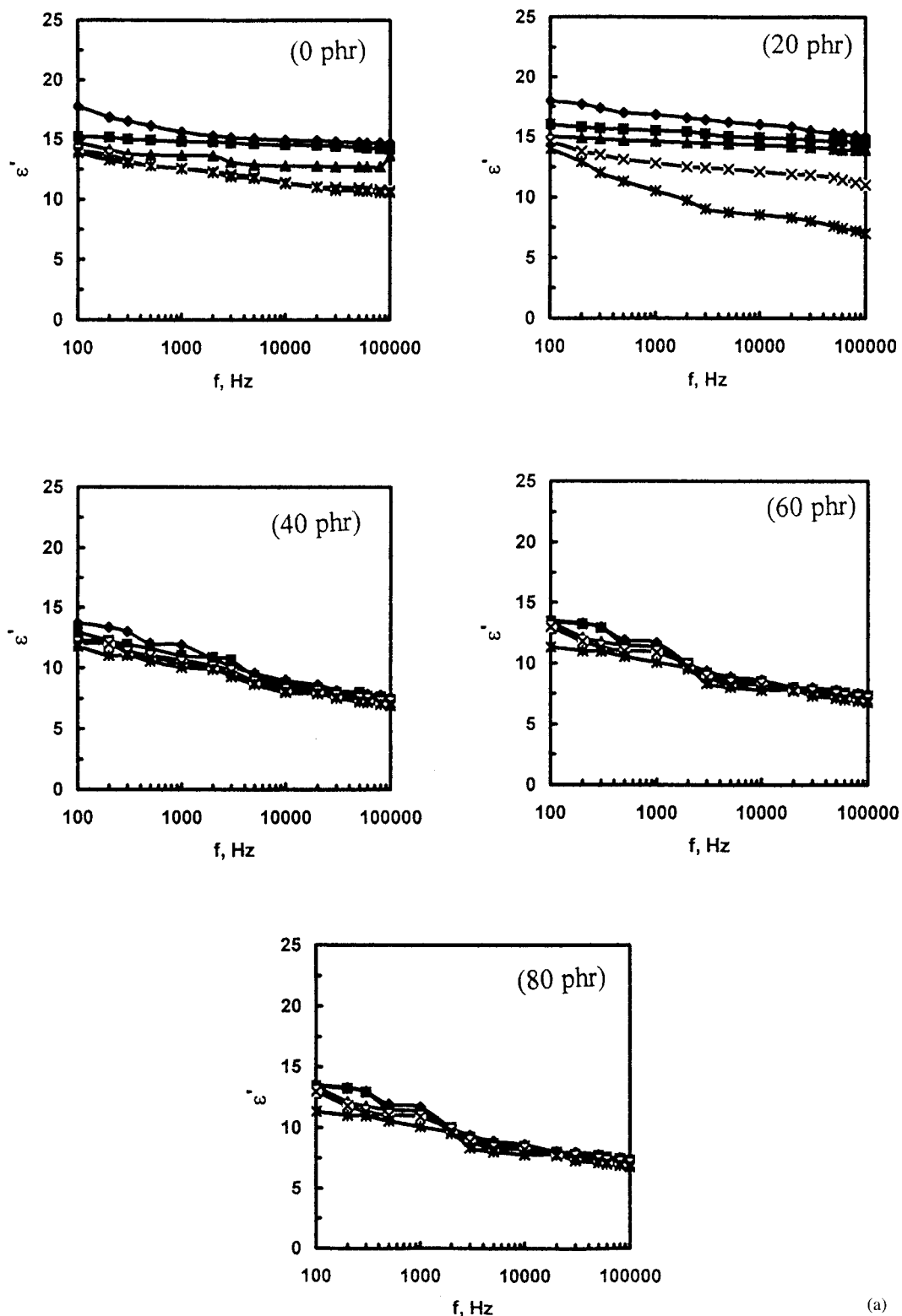
Figure 12 (a) ϵ' and (b) ϵ'' for 10/90 scrap PS/NBR with 3% epoxidized soya bean loaded with different contents of talc at ($\blacklozenge$) 20, ($\blacksquare$) 30, ($\blacktriangle$) 40, ($\times$) 50, and ($*$) 60°C.

quantities increasing up to 80 phr. The measurements were carried out at different temperatures, from 20 to 60°C. It is clear that ϵ' decreases with increasing frequency, showing anomalous dispersion. Also, ϵ' de-

creases with either the temperature or the filler content increasing. The increase in ϵ' with the addition of a filler by 20% may be due to the presence of polar groups in the filler. As the filler loading increases, the
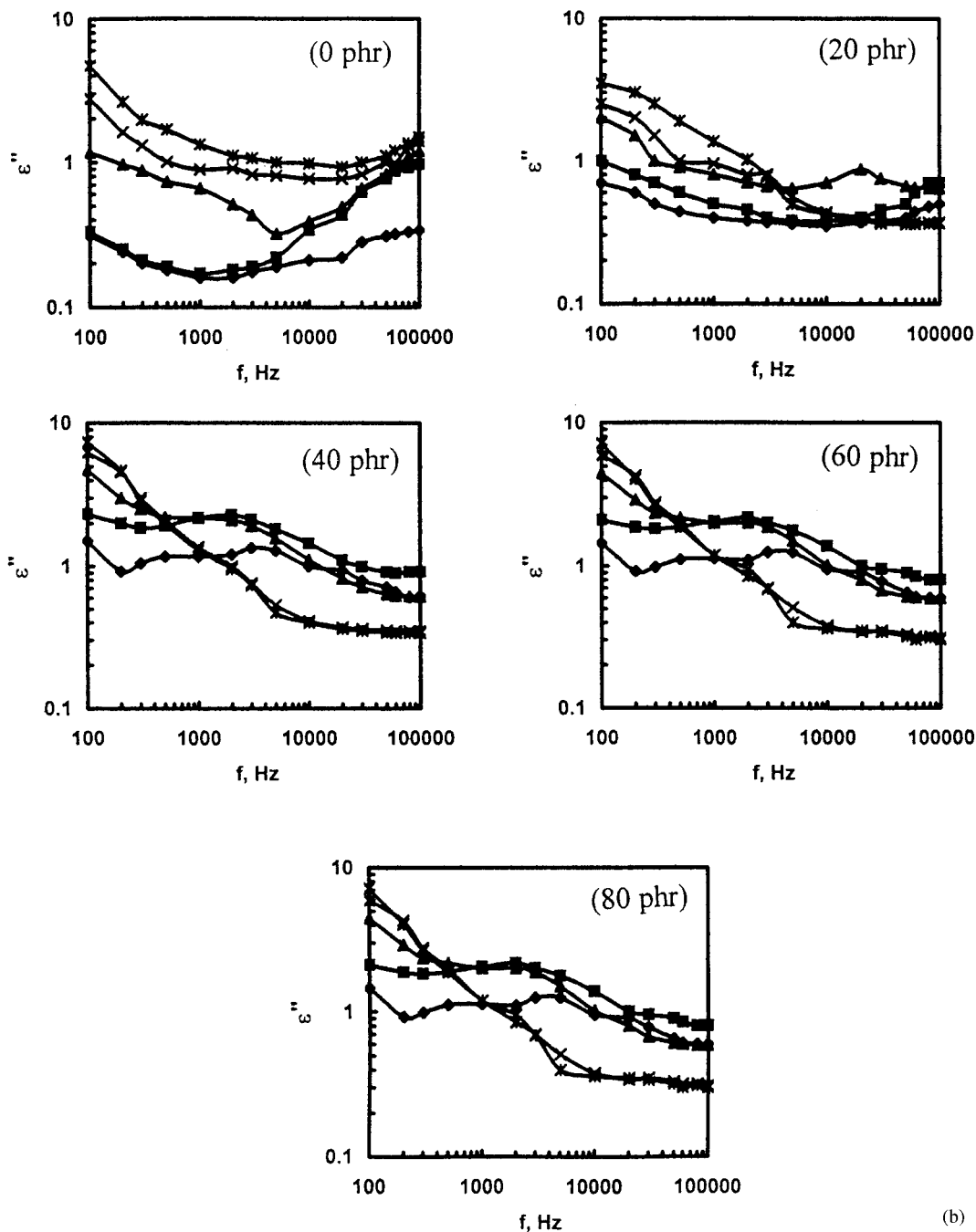
Figure 12 (*Continued from the previous page*).

density of the system also increases, and the extent of the orientation of dipoles is reduced; therefore, ϵ' shows a decrease at higher loadings. This finding is in good agreement with what was found for PP/NBR blends loaded with silica.[21] The decrease in ϵ' with increasing temperature may be due to the increase in the density of the blend.[21]

In a comparison of Figures 11–13, it is clear that the values of ϵ' after the addition of a filler show an increase in the order calcium carbonate > quartz > talc and decrease with increasing temperature for all types of fillers.

The curves relating ϵ'' and f in Figures 11–13 indicate that ϵ'' increases with increasing temperature for the three investigated types of fillers. Also, these values are much higher at the lower frequency range than those detected at higher frequencies. In addition, these curves are broad, indicating more than one relaxation mechanism. The Maxwell–Wagner effect at lower frequency ranges is one of these mechanisms.
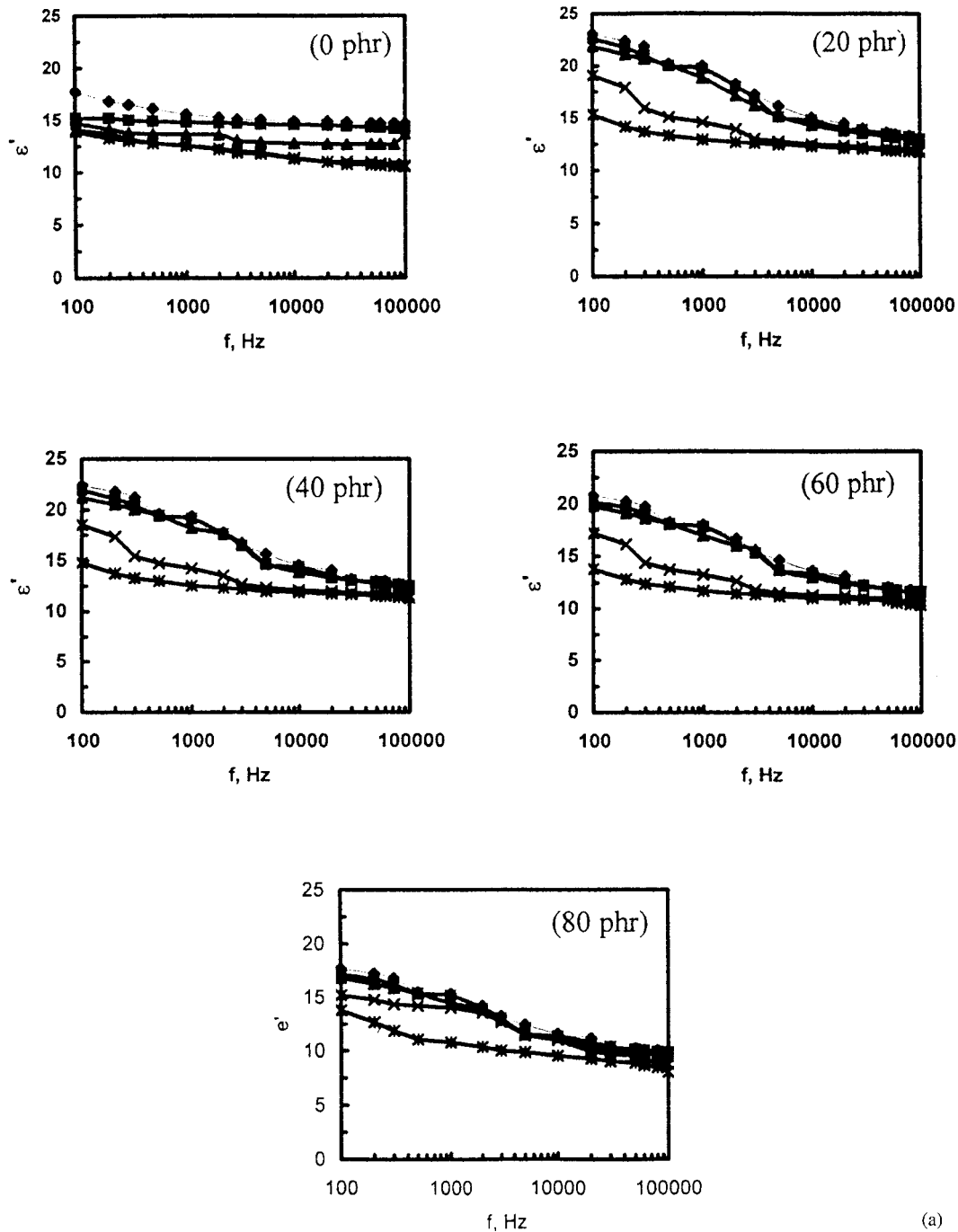
Figure 13 (a) ϵ' and (b) ϵ'' for 10/90 scrap PS/NBR with 3% epoxidized soya bean loaded with different contents of calcium carbonate at (♦) 20, (■) 30, (▲) 40, (×) 50, and (✳) 60°C.

From Figures 11–13, it is clear that ϵ'' after the addition of fillers increases in the order calcium carbonate > talc > quartz.

In Figures 11–13, ϵ'' increases with increasing temperature in the lower frequency range, whereas it behaves in the opposite way in the higher frequency range. At the lower frequency range, some sort of electrical conductivity could be the reason for the increase. However, the decrease in ϵ'' with increasing

temperature in the higher frequency range may be due to the shift of the maximum loss to higher frequencies. This result, which is expected to be at higher temperatures, is logical because the relaxation time (τ) describing the molecular rotation ($\tau = 1/2\pi f_m$) decreases with increasing temperature; f_m is the frequency corresponding to the maximum loss.

Figure 14 depicts the variation of both the tensile strength and elongation at break with the filler con-
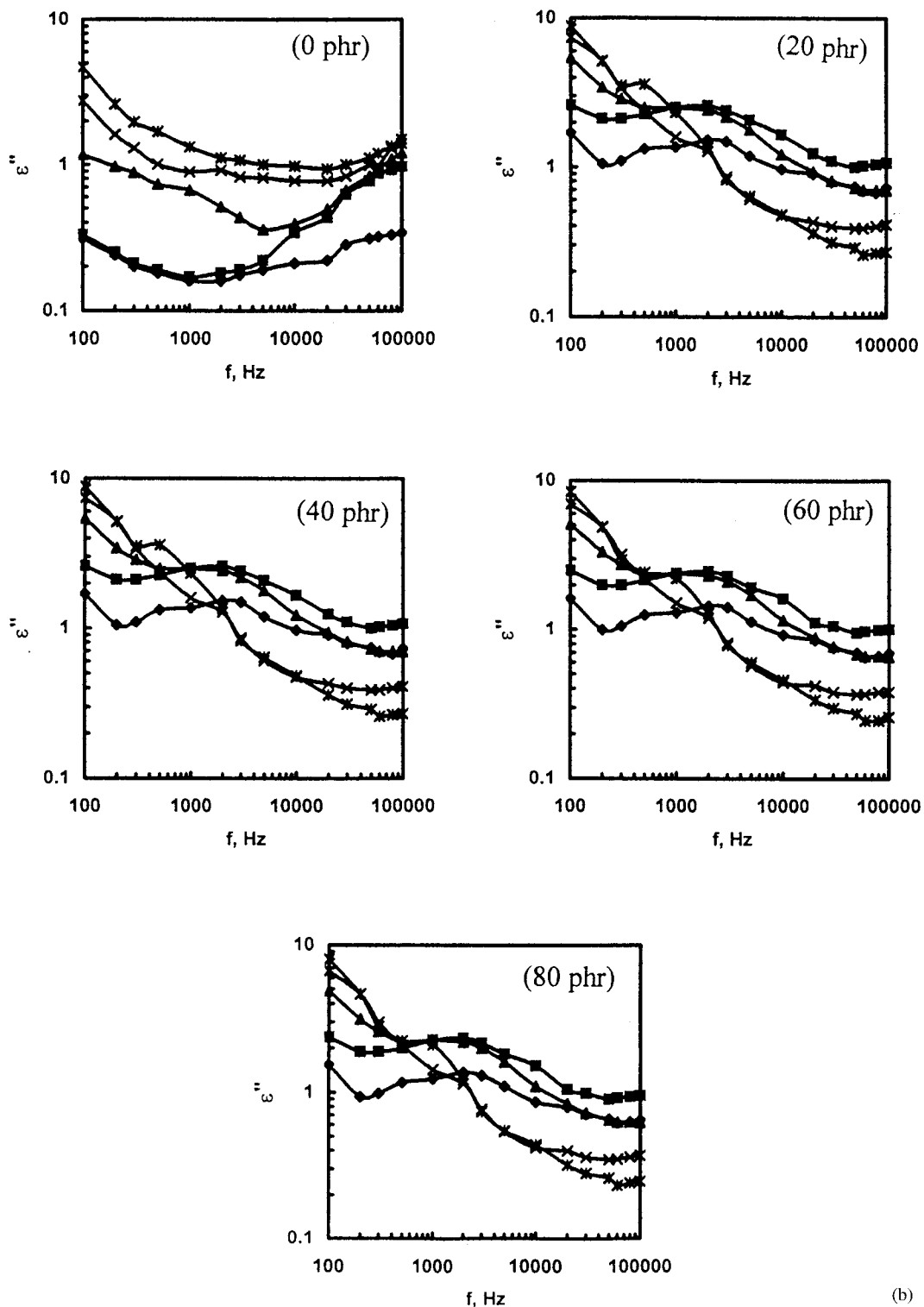
Figure 13 (*Continued from the previous page*).

tent. Up to 20%, the tensile strength shows a pronounced increase, after which there is a slight change with increasing filler content in the blend, especially in for talc and calcium carbonate. However, the elongation at break is slightly affected by increasing filler. Generally, both the tensile strength and elongation at break are increased in the order talc > calcium carbonate > quartz.
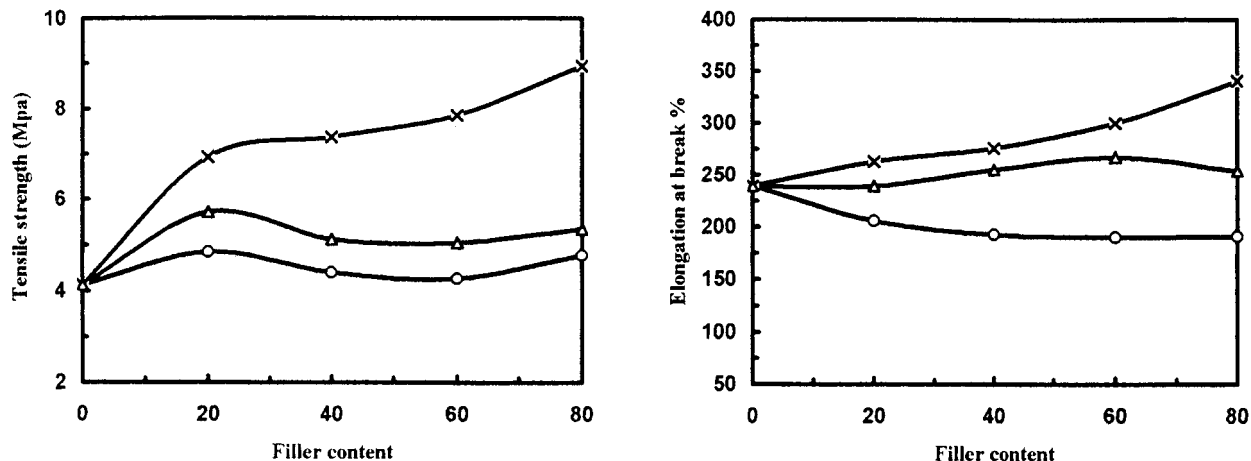
Figure 14 Variation of the tensile strength and elongation at break for 10/90 scrap PS/NBR with 3% epoxidized soya bean oil with the filler content: (○) quartz, (×) talc, and (△) calcium carbonate.

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