

Dielectric Behavior of PVDF/POMA Blends That Have a Low Doped POMA Content

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ABSTRACT: The real (ϵ') and imaginary (ϵ'') components of the complex permittivity of blends of PVDF [poly(vinylidene fluoride)] with POMA [poly(*o*-methoxyaniline)] doped with toluenosulfonic acid (TSA) containing 1, 2.5, and 5 wt % POMA-TSA were determined in the frequency interval between 10^2 and 3×10^6 Hz and in the temperature range from -120 up to 120°C . It was observed that the values of ϵ' and ϵ'' had a greater increase with the POMA-TSA content and with a temperature in the region of frequencies below 10 kHz. This effect decreased with frequency and it was attributed to interfacial polarization. This polarization was caused by the blend heterogeneity, formed by conductive POMA-TSA agglomerates dispersed in an insulating matrix of PVDF.

The equation of Maxwell-Garnett, modified by Cohen, was used to evaluate the permittivity and conductivity behavior of POMA-TSA in the blends. A strong decrease was observed in POMA-TSA conductivity in the blend, which was bigger the lower the POMA-TSA content in the blend. This decrease could have been caused either by the POMA dedoping during the blend preparation process or by its dispersion into the insulating matrix. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 752–758, 2003

Key words: PVDF; conducting polymer; polyaniline; blend; permittivity; interfacial polarization

INTRODUCTION

The purpose for developing blends of conventional polymers with conductive polymers is to increase the technological potential and versatility of the former. Such blends have the advantage of combining the excellent mechanical properties and processibility of conventional polymers with the high electric conductivity of conductive polymers. Polyaniline (PANI) and its derivatives play an important role in the development of new conductive blends^{1–9} because of their low cost, chemical stability in the doped state, solubility, processibility, and easy polymerization and doping. Previous studies² have shown that blends of PVDF [poly(vinylidene fluoride)] and PANI form an immiscible and incompatible system, leading to the formation of PANI agglomerates dispersed in the PVDF matrix. On the other hand, blends of PVDF with POMA [poly(*o*-methoxyaniline)] doped with toluene sulfonic acid (TSA) are perfectly compatible, allowing the processing of highly flexible and homogeneous films.⁹ Through the control of the percentage of POMA-TSA in the blend, it is possible to produce

films with conductivity varying between 10^{-11} and 10^{-2} S/cm,⁸ when measured by the standard four-probe method. Therefore, in addition to the preparation of conductive and semiconductive materials, it is possible to produce insulating blends that present dielectric properties depending on the blend composition. This article reports on a study on the real and imaginary components of the permittivity of PVDF and PVDF/POMA-TSA blends that have a low POMA-TSA content ($\leq 5\%$), in the frequency range of 10^2 to 3×10^6 Hz and the temperature range of -120 to 120°C . The equation of Maxwell-Garnett, modified by Cohen, was used to evaluate the permittivity and conductivity behavior of POMA-TSA in the blends.

THEORETICAL CONSIDERATIONS

The relationship between the permittivity and the conductivity of a dielectric material, in which an alternating electric field is applied, is given by:

$$i\omega\epsilon_0\epsilon^*(\omega) = \sigma^*(\omega) \quad (1)$$

where ϵ^* and σ^* are, respectively, the permittivity and conductivity complex; ϵ_0 is the vacuum permittivity; $\omega = 2\pi f$; and f is the frequency of the applied alternating voltage. We still have the following equations:

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (2)$$

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and

$$\sigma^*(\omega) = \sigma'(\omega) + \sigma_{DC} + i\sigma''(\omega) \quad (3)$$

where σ_{DC} is the direct component of the conductivity.

From eqs. (1), (2), and (3), it is possible to obtain the following equations:

$$\omega\varepsilon_0\varepsilon'(\omega) = \sigma''(\omega) \quad (4)$$

and

$$\omega\varepsilon_0\varepsilon''(\omega) = \sigma'(\omega) + \sigma_{DC} \quad (5)$$

If the dielectric material is a blend composed of particles of a dispersed conductive material in an insulating matrix, the complex permittivity of the heterogeneous medium, $\varepsilon^*(\omega)$, can be evaluated by using the Maxwell-Garnett equation, modified by Cohen,¹⁰ to take into account the shape effect of dispersed particles:

$$\frac{\varepsilon^*(\omega) - \varepsilon_1^*(\omega)}{L\varepsilon^*(\omega) + (1-L)\varepsilon_1^*(\omega)} = \eta \frac{\varepsilon_2^*(\omega) - \varepsilon_1^*(\omega)}{L\varepsilon_2^*(\omega) + (1-L)\varepsilon_1^*(\omega)} \quad (6)$$

where subscripts 1 and 2 are related, respectively, to the insulating and conductive materials, η is the volumetric fraction of the conductive material, and L is the characteristic depolarization factor of the conductive particles and its value ($0 \leq L \leq 1$) depends on the geometrical shape of such particles.

EXPERIMENTAL

Samples preparation

POMA was chemically synthesized with ammonium peroxydisulfate in a 1.0M HCl aqueous solution at 0°C, as previously described.¹¹ The PVDF (Forafilon F4000 HD) was purchased from Atochem and used as received. PVDF/POMA blends with different compositions were prepared by dissolving the constituents separately in *N,N*-dimethylacetamide (DMA) and mixing the solutions in various proportions. Next, the protonic doping of POMA into the blend was carried out by adding enough toluene sulfonic acid (TSA) to the solution to obtain a doping level of 50%. Films 15–30 μm thick were prepared by spreading the solution on a glass substrate previously heated to 65°C and maintaining them there for 60 min. This time interval was enough for the complete evaporation of the solvent. In this condition PVDF crystallized in the polar phase, β , as checked by infrared spectroscopy (Perkin Elmer Spectrum 1000 model, Shelton, CT). Disk-shaped samples 3 cm in diameter that had gold electrodes (1 cm^2 surface area) vacuum-evaporated on both sides were employed in the electrical measurements.

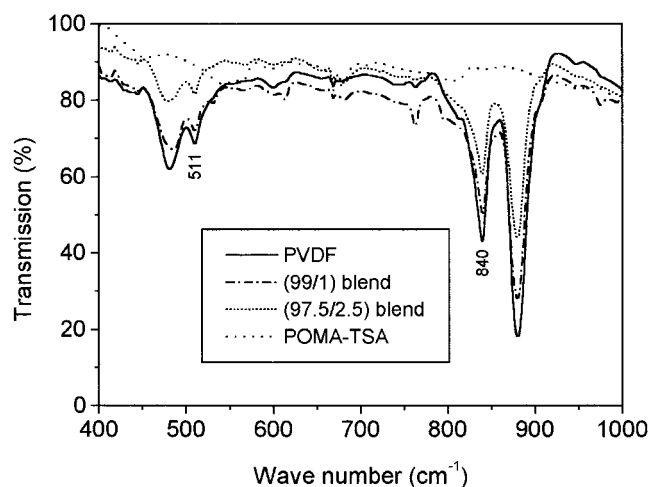


Figure 1 Infrared spectra of films of PVDF, POMA-TSA, and blends (99/1) and (97.5/2.5).

Samples containing 1, 2.5, and 5 wt % of POMA-TSA in the blend were prepared, designated as the (99/1), (97.5/2.5), and (95/5) blends, respectively. The PVDF and POMA densities, 1.78 and 1.20 g/cm^3 , respectively, were determined according to the ASTM D 792 standard.

Electrical measurements

The real (ε' = permittivity) and imaginary (ε'' = loss index) components of the complex permittivity were determined from the impedance and phase-angle values measured by a complex impedance analyzer (HP model LF 4192A, Englewood, CO), which was coupled in a TSC (Toyoseiki, Amagasaki, Hyogo, Japan) system. The measurements were done in a frequency range of 10^2 to 3×10^6 Hz and in a temperature range of -120 to 120°C (removal of POMA doping starts just above 120°C). The DC conductivity (σ_{DC}) was determined by employing an HP high-resistance meter, model 4338.

RESULTS AND DISCUSSION

Figure 1 shows the infrared spectrum of the PVDF and POMA-TSA, as well as for blends (99/1) and (97.5/2.5). Bands characteristic of the β phase, at 511 and 840 cm^{-1} , were found in PVDF and in its blends, as expected for a crystallization at 65°C , in which such a phase is known to predominate.¹²

Figure 2 shows the variation of the DC conductivity of the blends as a function of POMA-TSA wt % at room temperature (25°C) and at 47% relative humidity. It can be seen that the conductivity of the blend with the largest percentage of POMA-TSA (5%) increased to a value approximately 10^4 times the corresponding pure PVDF value, but it still remained in the electrical insulating range.

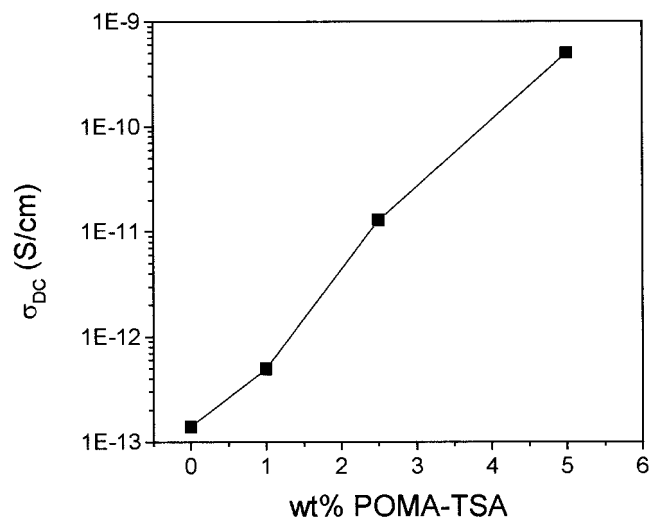


Figure 2 DC conductivity at 25°C of the blends as a function of weight percent of POMA-TSA.

Figure 3 shows the variation of the ϵ' and ϵ'' of the PVDF as a function of the temperature for four fixed frequencies. It is possible to distinguish three distinct regions of temperature. In the first, between -120 and the PVDF T_g ($\approx -40^\circ\text{C}$), no dipolar polarization occurred, and a smooth variation of ϵ' with the temperature and frequency can be observed. Dipolar polarization started around -40°C (frequency-dependent temperature) as a result of the dipoles' cooperative movement in the amorphous phase and the amorphous-crystalline interphase.¹³ This polarization, a dielectric manifestation of the PVDF glass transition, is responsible for the sudden increase of ϵ' , from 3.5 to 9. At this point a plateau was attained whose dependence on the frequency was very small. The temperature interval in which ϵ' varied between those two values increased with the frequency of the applied voltage, indicating an increase in the dispersion of the permittivity, which means an increase in the distribution of relaxation times. The maximum ϵ'' corresponding to that polarization was displaced to a higher temperature with the frequency; this is a characteristic behavior of a thermally activated process. This phenomenon led to an increase in the maximum value of ϵ'' with the frequency as a result of the increase in the electrical susceptibility with the temperature. The half height width of the ϵ'' peak increased with the frequency, which also indicates a larger dispersion of the permittivity. At higher temperatures (above $\approx 40^\circ\text{C}$ for $f = 1$ kHz), a sudden increase of ϵ' began with increasing temperature, probably because of polarization caused by dispersive currents. The temperature at which this polarization began increased with the frequency, and in practice no polarization occurred up to 100°C above 100 kHz. The large increase of ϵ'' associated with that polarization can be also observed in Figure 3.

Figure 4(a–c) shows the variation of ϵ' and ϵ'' as a function of temperature for four fixed frequencies for the blends (99/1), (97.5/2.5), and (95/5). It can be observed that even for temperatures below the T_g of PVDF, the values of ϵ' for the blends depended on the frequency and temperature, indicating polarization. At those temperatures the intensity of ϵ' increased with the amount of POMA. However, this increase was greatly reduced with an increase in frequency, as can be seen in Figure 5 at -78°C . That polarization was caused by the heterogeneity of the blend, which was formed by conductive POMA-TSA agglomerates dispersed in an insulating matrix of PVDF. In reality, this is an interfacial polarization¹⁴ (the Maxwell-Wagner-Sillars effect) that, as expected, decreases with the frequency and practically does not depend on the mobility of PVDF chains. An increase in the amount of POMA-TSA should result in a larger number of agglomerates and/or an increase in their size and, consequently, in greater polarization. The increase in temperature led to an increase in the POMA-TSA conductivity, which also led to greater polarization.

Between the T_g of PVDF and 40°C , two polarization processes coexisted in the blends: dipolar polarization, which took place in the PVDF, and interfacial polarization, which occurred because of the presence of

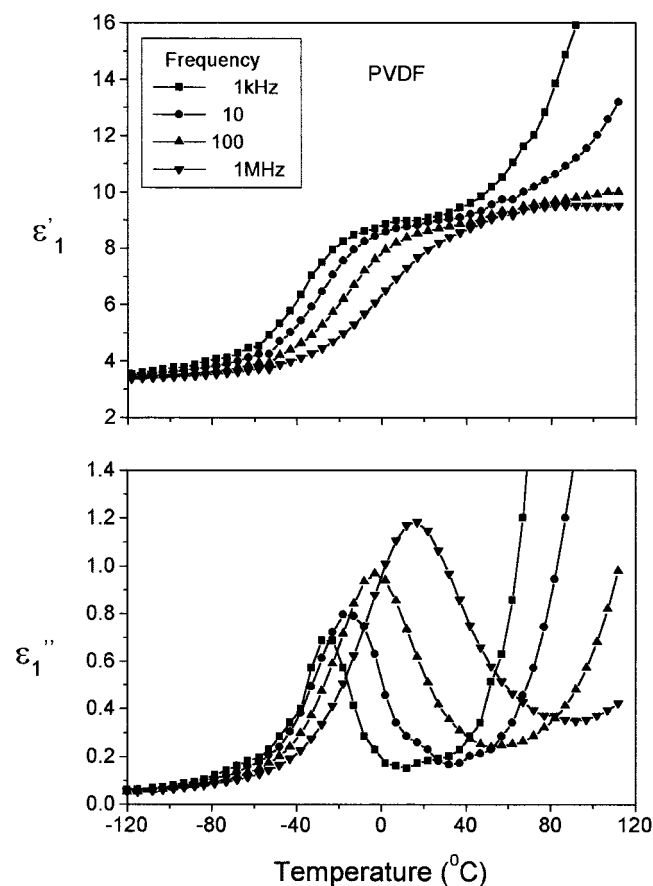


Figure 3 ϵ' and ϵ'' as a function of temperature at four fixed frequencies for PVDF.

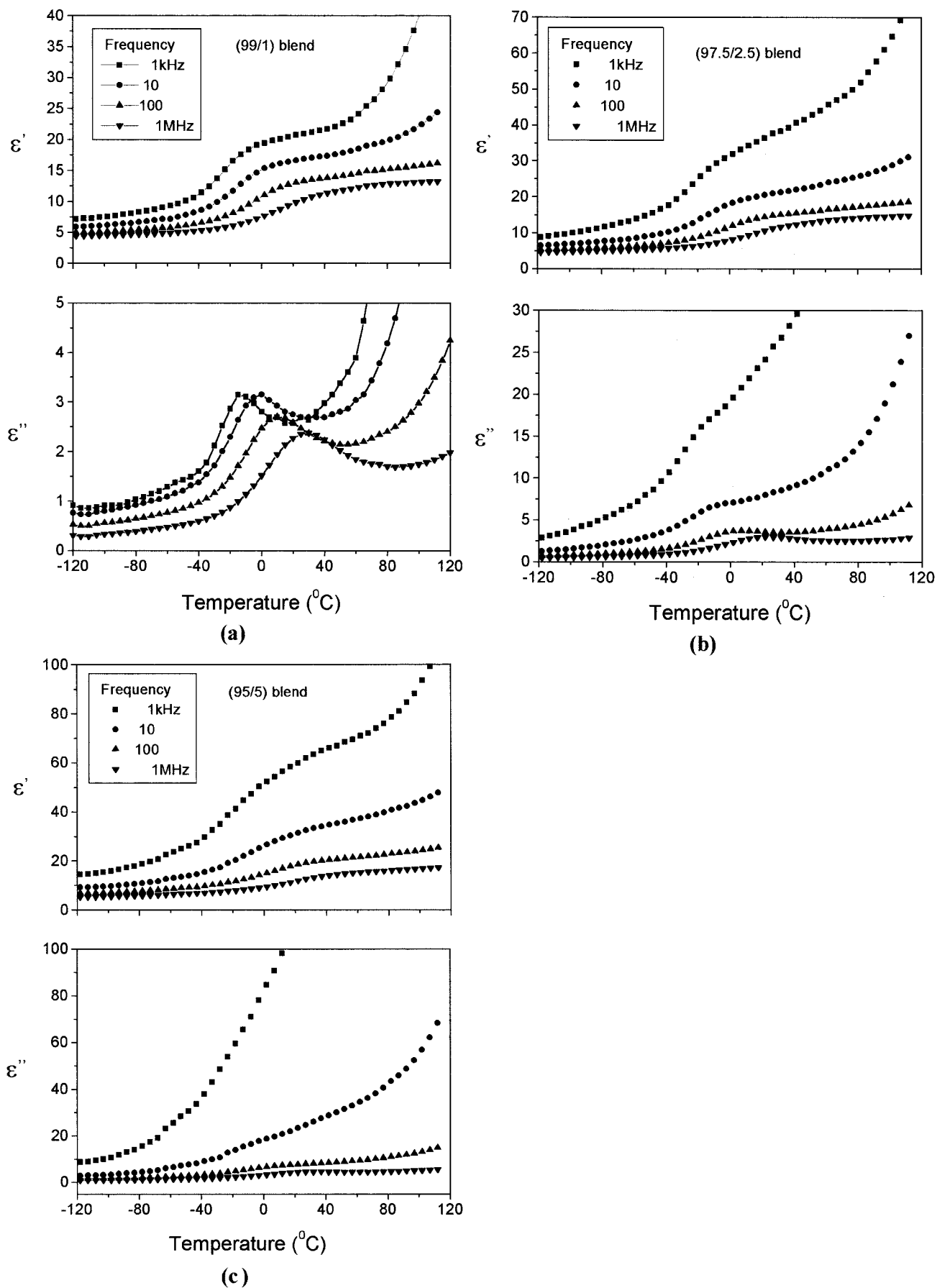


Figure 4 ϵ' and ϵ'' as a function of temperature for: (a) (99/1) blend, (b) (97.5/2.5) blend, and (c) (95/5) blend at four fixed frequencies.

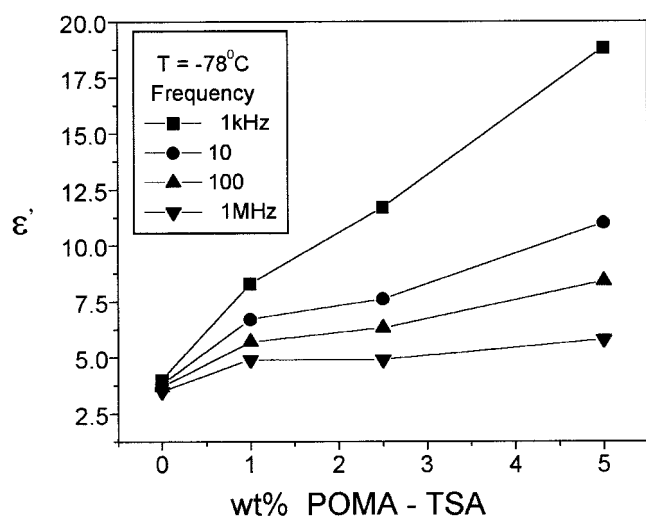


Figure 5 ϵ' as a function of weight percent of POMA-TSA at four fixed frequencies for the blends at -78°C .

POMA-TSA. As can be observed in Figure 3, the PVDF ϵ' value increased with the temperature (because of dipolar polarization) until reaching a plateau, which depended very little on the frequency. For the (99/1) blend the value of ϵ' attained in the plateau was strongly frequency dependent [Fig. 4(a)], decreasing with the frequency because of the interfacial polarization component. The dependence of ϵ' with the amount of POMA-TSA for different frequencies at 40°C is shown in Figure 6. The decrease in interfacial polarization with the frequency explains the reduction of the intensity of the peak of ϵ'' with the frequency for the blend with 1 wt % of POMA-TSA [Fig. 4(a)]. For the blends with 2.5 and 5 wt % of POMA-TSA, the ϵ'' peaks as well as the plateaus attained by ϵ' were not precisely determined for $f \leq 10$ kHz because of interference from the polarization, probably caused by dispersive currents, which began at a lower temperature with a decrease in frequency. Such a polarization phenomenon will be studied in greater details in another work.

The Maxwell-Garnett equation, modified by Cohen, was used to evaluate the permittivity and conductivity behavior of the POMA-TSA in the blends. Eqs. (2) and (6) may be combined to get:

$$\frac{[\epsilon'(\omega) - i\epsilon''(\omega)] - [\epsilon'_1(\omega) - i\epsilon''_1(\omega)]}{L[\epsilon'(\omega) - i\epsilon''(\omega)] + (1-L)[\epsilon'_1(\omega) - i\epsilon''_1(\omega)]} = \eta \frac{[\epsilon'_2(\omega) - i\epsilon''_2(\omega)] - [\epsilon'_1(\omega) - i\epsilon''_1(\omega)]}{L[\epsilon'_2(\omega) - i\epsilon''_2(\omega)] + (1-L)[\epsilon'_1(\omega) - i\epsilon''_1(\omega)]} \quad (7)$$

where subscripts 1 and 2 refer to PVDF and POMA-TSA, respectively. The real and imaginary components of the complex permittivity of PVDF and blends obtained experimentally were replaced in eq. (7), and

by using L as fitting parameter, the values of $\epsilon'_2(\omega)$ and $\epsilon''_2(\omega)$ could be determined for blends (99/1), (97.5/2.5), and (95/5). The best fitting was obtained for $L = 0$ (particles in the shape of long cylinders with their axes parallel to the applied electric field). In this case there were no fields of induced polarization outside each individual particle and therefore no modification of the applied electric field. The eq. (7) was reduced to:

$$\epsilon'(\omega) - i\epsilon''(\omega) = \eta[\epsilon'_2(\omega) - i\epsilon''_2(\omega)] + (1-\eta)[\epsilon'_1 - i\epsilon''_1(\omega)] \quad (8)$$

In practice this means that the complex permittivity of the blend is simply the weight-average of the components' complex permittivity.

In a recent work,⁸ the morphology of blends of PVDF/POMA-TSA with several compositions was investigated by scanning electron microscopy (SEM). For the (95/5) blend, fibrils formed by the POMA-TSA component were observed as straight rods about $7 \mu\text{m}$ long and about 350 nm in diameter located preferentially in the boundaries of the spherulites, which are the characteristic structures of PVDF. This result partly justifies the null value of the L parameter obtained in the fitting process of eq. (7).

The variation of real [$\epsilon'_2(\omega)$] and imaginary [$\epsilon''_2(\omega)$] components of POMA-TSA permittivity as a function of frequency at six fixed temperatures, determined with aid of eq. (8) for blends (99/1) ($\eta = 0.015$), (97.5/2.5) ($\eta = 0.037$), and (95/5) ($\eta = 0.074$), are shown in Figure 7(a-c), respectively. The variation of those components with frequency is presented to show how they can be strongly affected at low frequencies by the amount of POMA-TSA in the blend.

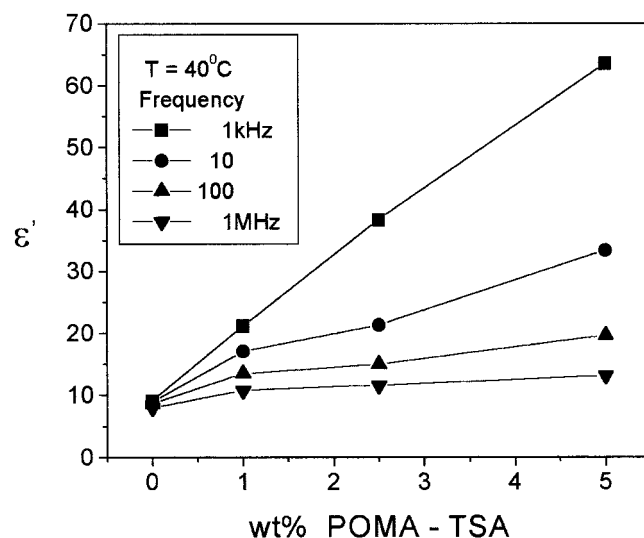


Figure 6 ϵ' as a function of weight percent of POMA-TSA at four fixed frequencies for the blends at 40°C .

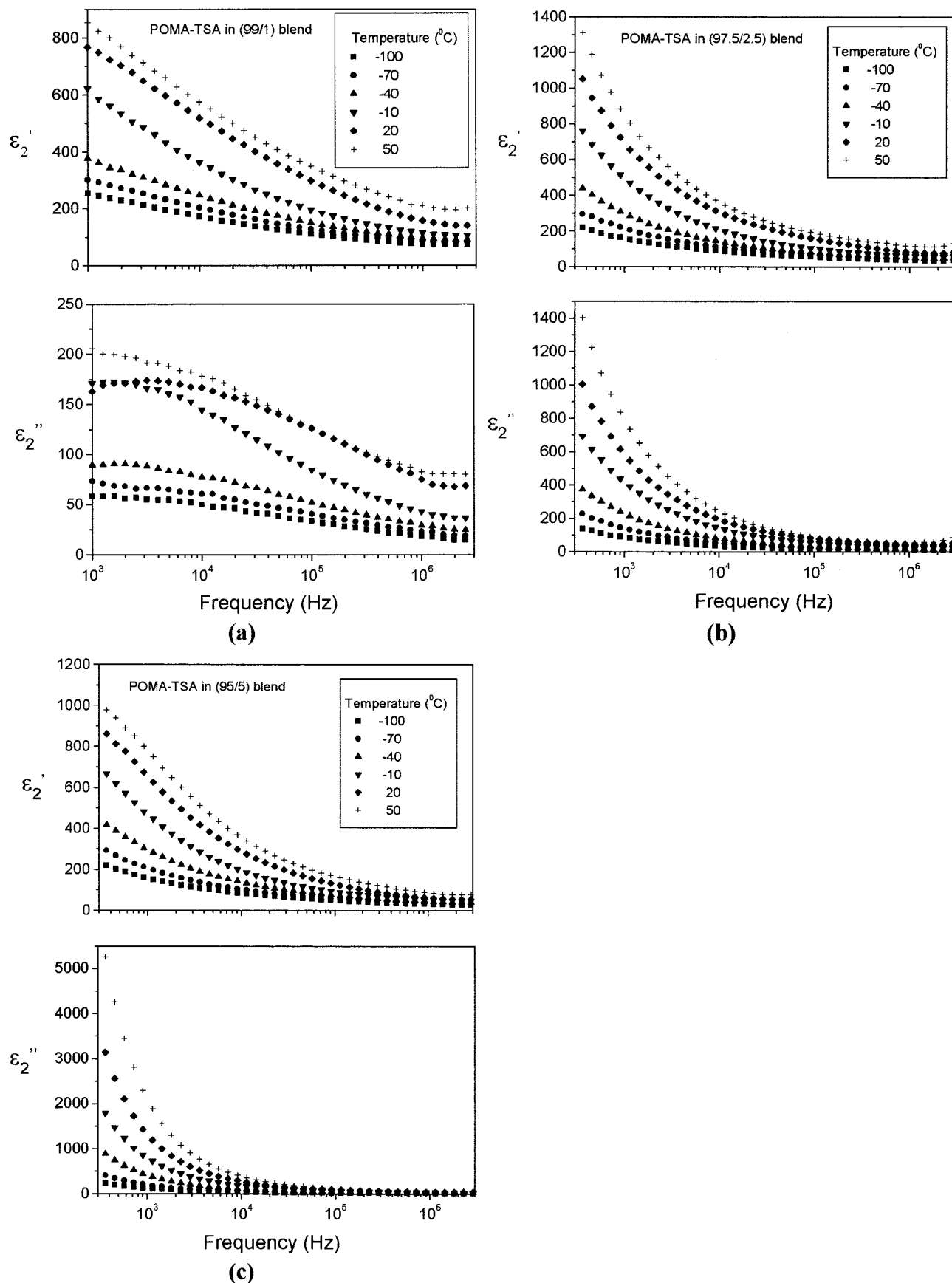


Figure 7 ϵ' and ϵ'' of POMA-TSA as a function of frequency for: (a) (99/1) blend, (b) (97.5/2.5) blend, and (c) (95/5) blend at six fixed temperatures.

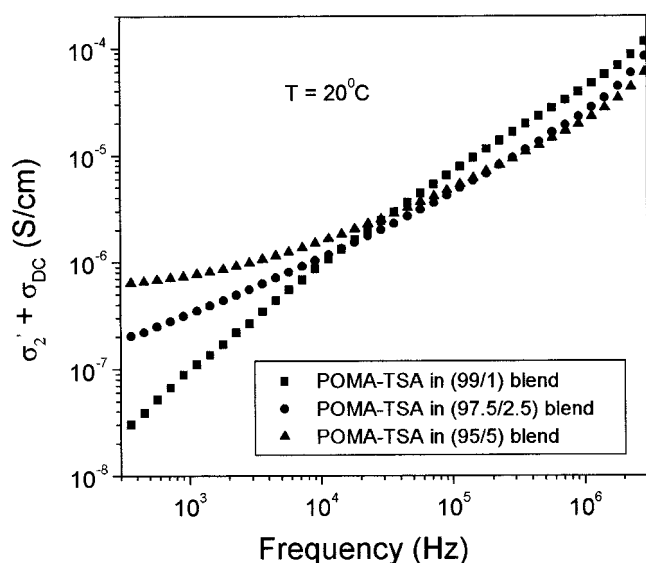


Figure 8 Variation of the real part of POMA-TSA conductivity in the blends with different compositions, as a function of frequency.

Variation of $\varepsilon_2'(\omega)$ as a function of frequency for the (97.5/2.5) and (95/5) blends were quite similar, except for $f \leq 2$ kHz, where a slight variation was observed. This variation increased with temperature. For the (99/1) blend the values of $\varepsilon_2'(\omega)$ were quite different from those obtained with the 2.5 and 5 wt % of POMA-TSA in the entire frequency interval studied, indicating that at low percentages POMA-TSA permittivity is more strongly affected by the environment.

The values of $\varepsilon_2''(\omega)$ for $f \leq 10$ kHz were strongly influenced by the percentage of POMA-TSA in the blend. At low frequencies the values of $\varepsilon_2''(\omega)$ increased with POMA-TSA content, indicating higher conductivity. POMA-TSA probably loses part of its conductive property into the blend, and the bigger that loss is, the lower is its content in the blend. This result can be clearly observed in Figure 8, where shows the variation of the real part of the conductivity [$\sigma_2'(\omega) + \sigma_{DC}$] of POMA-TSA, as a function of frequency, which was calculated using eq. (5) and the values of $\varepsilon_2''(\omega)$ evaluated for each blend composition. As the content of POMA-TSA increased, its conductivity also increased in the low-frequency region, indicating a probable increase in the component σ_{DC} .

The 50% TSA doped POMA, as used in the present work, is a conductive material, that is, the real component of the conductivity is practically independent of the frequency [$\sigma_{DC} \gg \sigma_2''(\omega)$]. The value of σ_{DC} ranged between 10^{-2} and 10^{-1} S/cm for a temperature variation ranging between -100°C and 25°C .¹⁵ However, when mixed with PVDF in order to form the blend, that conductivity should be strongly influenced by the environment, and this influence is the bigger the lower is the content of POMA-TSA in the blend.

The largest reduction was detected for the component σ_{DC} , either because of POMA-TSA dedoping during the blending process or its dispersion in the matrix. Therefore, the strong influence of the amount of POMA-TSA on the real and imaginary components of the blend permittivity should be caused not only by the increase in the amount of POMA-TSA but also by the variation of its conductivity, which itself depends on the blend composition.

CONCLUSIONS

PVDF/POMA-TSA blends with a low POMA-TSA content have high values of real and imaginary permittivity components in the low-frequency region. Those values increase with the temperature and amount of POMA-TSA in the blend. This effect might be related to interfacial polarization, which in turn is caused by material heterogeneity. The variation of ε' and of ε'' with the frequency for the POMA-TSA in the blends can be determined by the Cohen-modified Maxwell-Garnett equation. It was also found that when POMA-TSA is in the blend, the real component of its conductivity is strongly reduced. The DC conductivity of POMA-TSA is strongly decreased by the environment, either by the partial loss of the dopant or by the dispersion of POMA-TSA in the matrix. This decrease becomes greater the lower is the content of POMA-TSA in the blend.

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References

- Malmonge, L. F.; Mattoso, L. H. C. *Synth Met* 1995, 69, 123.
- Malmonge, L. F.; Mattoso, L. H. C. *Polymer* 1995, 36(2), 45.
- Yang, C. Y.; Reghu, M.; Heeger, A. J.; Cao, Y. *Synth Met* 1996, 79, 27.
- Virtaen, E.; Laakso, J.; Ruohonen, H.; Jarvinen, H.; Jussila, M.; Passiniemi, P.; Osterholm, J.-E. *Synth Met* 1997, 84, 113.
- Laska, J.; Zak, K.; Pron, A. *Synth Met* 1997, 84, 117.
- Mantovani, G. L.; MacDiarmid, A. G.; Mattoso, L. H. C. *Synth Met* 1997, 84, 73.
- Fu, Y.; Weiss, R. A. *Synth Met* 1997, 84, 103.
- Mattoso, L. H. C.; Malmonge, L. F.; Montovani, G. L.; MacDiarmid, A. G. *Curr Trends Polym Sci* 1998, 3, 99.
- Rocha, I. S.; Mattoso, L. H. C.; Malmonge, L. F.; Gregorio Jr., R. *J Polym Sci, Part B: Polym Phys* 1999, 37, 1219.
- Cohen, R. W.; Cody, G. D.; Coutts, M. D.; Abeles, B. *Phys Rev B: Solid State* 1973, 8, 3689.
- Mattoso, L. H. C.; Faria, R. M.; Bulhões, L. O. S.; MacDiarmid, A. G. *J Polym Sci, Polym Chem Ed* 1994, 32, 2147.
- Gregorio Jr., R.; Cestari, M. *J Polym Sci, Part B: Polym Phys* 1994, 32, 859.
- Gregorio Jr., R.; Ueno, E. M. *J Mater Sci* 1999, 34, 4489.
- Ku, C. C.; Liepins, R. *Electrical Properties of Polymers*; Hanser Publishers: Munich, 1987.
- Nogueira, J. S.; Mattoso, L. H. C.; Faria, R. M. In *Proceedings of the 9th International Symposium on Electrets*, Shanghai, China, September 25-27, 1996; p 145.