Dielectric Relaxation Studies of Low Thermal Expansion Polymer Composites

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ABSTRACT: The results of temperature-dependent dielectric and rheological measurements are reported on polymer-ceramic composite films, poly(methyl methacrylate) (PMMA) : lead titanate (PbTiO$_3$). Analyses of relaxational processes of the PMMA host matrix have been investigated using temperature-dependent dielectric and rheological measurements. It is found that the α-relaxation is more significantly affected by the addition of filler in comparison to β-relaxation. The composite films are found to have much lower dielectric constants in comparison to the pure ceramic material. Suitable models have been used to explain the observed dielectric constant of the composite films. Using rheological measurements, occurrence of reinforcement in these composite films due to the addition of ceramic filler has also been observed and the results are discussed in the article. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Poly(methyl methacrylate) (PMMA) and its derivatives based composites have attracted significant research interest because of their potential applications in nonlinear optics, orthopedic and dental applications, energy storage, etc.[1–7] Some of these composites have shown capacity to act as thermally stable substrates with the added advantage of inbuilt flexibility and tunable thermal expansion.[8–12] The composite systems where relaxational processes play important role in determining the final property and industrial application are polymer-piezoelectric/ferroelectric composites. These composites are being extensively studied as they provide a route of making thin film capacitors with tunable dielectric constant and large piezoelectric constants.[13–18]

It is well known that polymers are characterized by a large number of dynamic processes involving various length scales that may extend over more than 15 decades in time or frequency.[19–21] In addition to vibrational or librational modes, these polymers may undergo motion which are fast as well as localized (e.g., methyl-group rotations).[21] Many different experimental techniques such as dielectric spectroscopy, NMR, dynamic mechanical analysis, and dilatometry have been employed to investigate these segmental relaxational processes.[19,21–25] These localized motions may involve the secondary β-relaxations and the segmental motions responsible for α-relax-ations (which are dominant in the glass transition). Such investigations in blended systems have shown that the faster relaxations and those related to the more local dynamics are less affected in comparison to structural relaxations which are strongly affected by blending.[21,26,27] One important polymer series in which studies of relaxational processes play an important role in deciding the final applicability is based on "poly(alkyl methacrylates)." Main focus of these studies are on the variation of dynamic glass transition (α) and secondary relaxations (β and γ). More recently, there have also been studies dealing with the crossover region in polymers where the relaxation times of the α- and β-relaxational processes approach each other.[28–32]

The present work deals with the characterization of one such polymer : ferroelectric ceramic composite system based on PMMA : PbTiO$_3$ (PT), for which it has been shown earlier that the thermal expansion coefficient can be suitably tuned by adjusting the filler concentration.[8,9] In this article, results of temperature-dependent dielectric and mechanical property measurements in these composite films are presented. The theoretical models (or mixing rules) to estimate the effective dielectric constant in such composite films are discussed. It is shown that the results obtained by dielectric measurements can be realistically compared to those obtained by rheological studies.

Figure 1. SEM of PT particles which are used as filler. The inset shows a typical nature of dispersion of PT particles in PMMA matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

PT ceramic particles were obtained from Aldrich (Germany). The particles have an average size distribution in the range of 1–5 μm as shown in Figure 1. PT has a tetragonal crystal structure with *P4mm* space group with a typical X-ray diffraction pattern as shown in Figure 2(c), while PMMA is amorphous at room temperature having a typical halo-type X-ray diffraction as shown in Figure 2(a). The PMMA : PT composites were prepared using the procedure described in earlier publications.[8,9] Also, the structural investigation of pure PT and similar systems have been reported earlier.[33–38] Composite formation was confirmed by carrying out the XRD and Raman studies. Figure 2(b) depicts one representative XRD pattern for a PMMA : PT composite film with a volume ratio of 60 : 40. The composites show partial crystallinity. All the diffraction peaks can be indexed to the tetragonal phase of the filler (PT) structure. The halo is due to the amorphous matrix of the PMMA polymer. Further, the intensity ratio of the diffraction resulting from the crystalline PT filler is not affected from the matrix which confirms a total separation of the filler and matrix phase in the composite films. Raman spectroscopic experiments also gave no evidence of any vibrational coupling between the PMMA host matrix and the PT filler as can be seen from Figure 3. Homogeneous dispersion of particles in the polymer matrix was confirmed by scanning electron microscopy (SEM) and results have already been reported elsewhere.[9] A typical micrograph showing the dispersion of particles is shown in the inset of Figure 1.

Figure 2. XRD pattern of PMMA : PT (60 : 40) composite films (b) as compared to the XRD of pure PT (c) and PMMA (a) respectively.

Figure 3. Evolution of Raman spectra in PMMA:PT composite films as a function of PT content.

For dielectric measurements, a sample capacitor in sandwich geometry consisting of the polymer-film (~few 100 μm thick) with sputtered gold electrodes (60 μm thickness and 10 mm diameter) on both sides of the polymer-film was used. A broadband dielectric spectrometer Novocontrol BDS 4000 (based on the high resolution ALPHA Analyzer) was used to measure the dielectric function $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$ at 10 points per frequency decade in the frequency range of 10^{-1}–10^7 Hz and in the temperature range of –100 to +150°C under inert conditions (dry nitrogen gas). Temperature accuracy of ± 0.5°C was maintained during the measurement.

A dynamic mechanical spectrometer (GABO Eplexor 150N) was used to perform the temperature-dependent rheological measurements in tensile mode under oscillatory regime. The samples consisted of dumbbell shaped samples cut from dried films, with typical cross-sections of 0.35 × 2 mm². Contact forces around 3 N were used to keep the sample stretched during the measurements. The experiments were performed at a fixed frequency of 1 Hz and strain amplitude of 0.1%. Temperature control to within ±0.5°C was maintained over a temperature range from −100 to 150°C, at a heating rate of 1 K/min.

RESULTS AND DISCUSSIONS

Dielectric Measurements

It has been observed that most of the glass forming polymers have a loss peak in the β-relaxation which is very close to a symmetric shape (in log frequency) with the relaxation times following an Arrhenius temperature dependence (log $\tau \propto 1/T$). On the other hand, the α-relaxation is asymmetric with a high frequency broadening. The α-relaxation time follows a non-Arrhenius dependence that can normally be described by the Vogel Fulcher (VF) equation.[19] It has been found earlier that if the measurements are performed in the frequency domain, the response is normally well described by the phenomenological Havriliak–Negami (HN) equation given as[39]:

$$\varepsilon * (\omega) = \varepsilon_\infty + \sum_k \frac{\Delta\varepsilon_k}{(1 + (i\omega\,\tau_k)^{\alpha_k})^{\gamma_k}} \quad (1)$$

with $\omega = 2\pi\nu$, ε_∞ being the high frequency limit of $\varepsilon'(\omega)$ outside the dispersion zone, $\Delta\varepsilon$ are the respective intensities of each process, and α, γ are the shape parameters with the constraint $0 < \alpha \le 1$, $0 < \gamma \le 1$. However, in most of the cases, the β relaxation can be described by the special case of the HN equation where $\gamma = 1$. This symmetric HN function is known as the Cole–Cole (CC) equation.[40]

The maximum loss frequency ω_{max} for each process is given by[31]:

$$\omega_{max} = \frac{1}{\tau}\left(\frac{\sin[\pi\alpha/2]}{\tan[\pi\alpha/2(\gamma+1)]} - \cos[\pi\alpha/2]\right)^{-1/\alpha} \quad (2)$$

For $\omega << \omega_{max}$ and $\omega >> \omega_{max}$ the HN function for $\varepsilon''(\omega)$ respectively reduces to power laws with the exponents α and $\alpha\gamma$. In the present case, using the nonlinear least-squares Levenberg–Marquard minimization method, the relaxation processes were fitted by a superposition of two Havriliak–Negami (HN) functions ($k = 2$):

It should be noted that the ester group in the side chain of PMMA contributes to the electric dipole. The β-relaxation in PMMA arises from the hindered rotation of the —$COOCH_3$ group about the C—C bond which links it to the main chain.[31] Therefore, most of the polarization relaxes through the β-relaxation and only a smaller part relaxes through the main chain segmental dynamics as reflected in the α-relaxation. To fit the α-process, all parameters were free, while for the β-processes the asymmetry parameter γ was set to 1. The adjustment of the two HN functions on the continuous data points for each of the two regions produced two stable maximum frequencies although their intensities varied significantly with the temperature. Typical good fits were obtained at temperatures below T_g, near T_g, above T_g, and well above T_g for pure PMMA ($T_{g\ (PMMA)} = 100°C$) as shown in Figure 4. Similar good quality fits were also obtained at other intermediate temperatures. For the data analysis, the contributions from the conductivity of the sample (which become significant at high temperatures) have also been considered in the fitting procedure. The same strategy was also used to determine the relaxations in PMMA : PT composite samples.

Figure 5 shows the variation in the Arrhenius plots of the peak maximum frequencies from the HN fits obtained for the pure PMMA and the composite films. From this curve, we can mark two regions, namely Region A where the splitting of α and β processes is observed and a low temperature Region B where the β process is evidently dominant in the films. It is quite evident from Figure 5 that both, α- and β-relaxation processes are getting modified when a ceramic filler is added to the polymer matrix but the nature of the relaxation remains the same. The β-relaxation (related with the side chain rotational motion) is less affected in comparison to the α-relaxation (related with the main chain segmental motion). This can be understood because a motion which is more dependent on the local dynamics of the smaller side chains will feel little obstruction due to the addition of micron-sized filler inorganic particles. On the other hand, the α-relaxation experiences the obstruction due to the presence of filler and therefore expectedly shows significant modification in its relaxation frequency. Slight modification to the motion related to the β-process can be a result of the in situ polymerization method of sample preparation which may induce some coupling between the inorganic filler and the sample. Results of the dynamical measurements presented later in this article further strengthen this observation.

The arrows in Figure 5 indicate the glass transition temperatures determined from the DSC measurements. The variation of position of the α-peak obtained from the temperature-dependent dielectric spectroscopic measurements also clearly predicts the temperature at which we should see the glass transition temperatures. It may be noted that the temperatures of glass transition slightly shift as a function of filler concentration, possibly because of the presence of ceramic fillers during the polymerization process which may affect the molecular weight (and hence T_g) of the host polymer matrix and also the appearance of reinforcing effects on the basis of interactions along the phase boundaries (as shown later).

From Figure 5, we also see that as the temperature increases, the α- and β-relaxations are less separated in frequency and finally
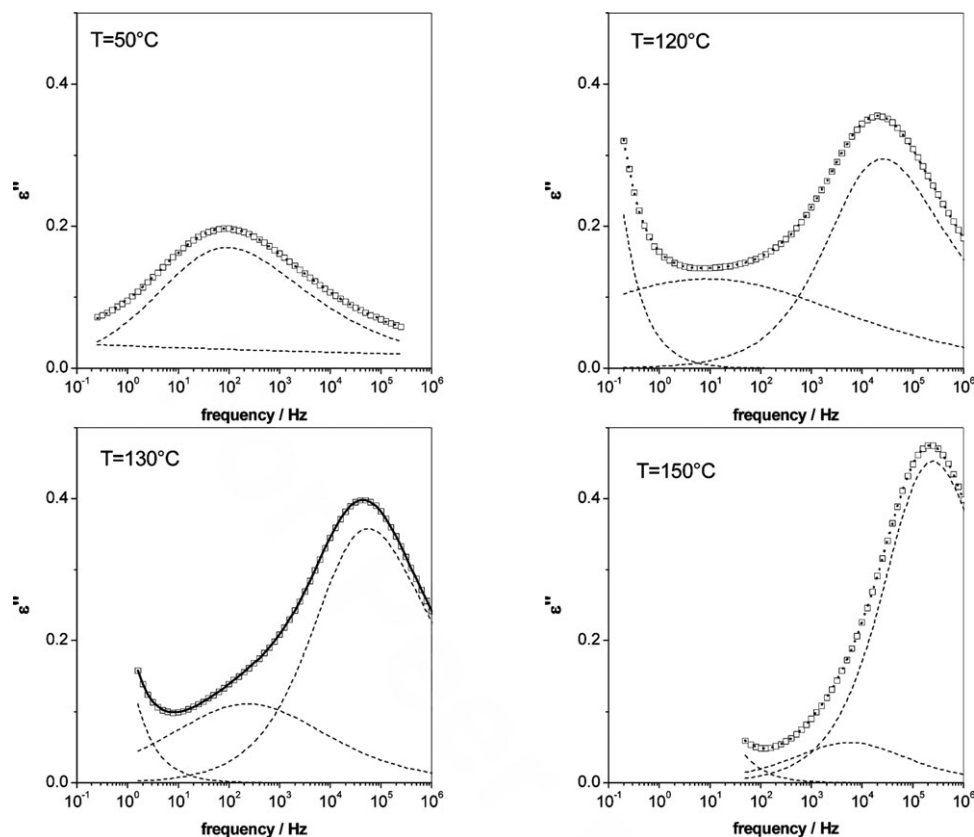
Figure 4. Imaginary part of dielectric constant (ε'') as a function of log frequency for pure PMMA at various temperatures. The isotherms have been fitted using the HN equations. The open symbols represent the observed data. The solid lines show the simulated data and the dashed line show the fitted functions.

they show a trend of merging into one apparent relaxation (Region A). This phenomenon has been named as crossover region in the literature and has also been discussed by many authors in relation to the fundamental understanding about the behavior of the "liquid–glass transition." It can also be important for understanding the complex dynamics of biopolymers, early stages of crystallization or in the theoretical field of nano-thermodynamics. However, all these aspects are not being dealt in detail in this article but the fact of the occurrence of such phenomena in the material discussed has been mentioned to direct the interested readers to other relevant literature.[27–29]

In the present composite system, the room temperature dielectric constant of the filler material and host polymer matrix is ~400 and ~3, respectively. But if we compare the room temperature dielectric values of the PMMA : PT composite films as a function of filler concentration, we observe that the values do not change significantly even for higher filler concentrations. There are mathematical models which deal with the prediction of the overall dielectric constant in composite systems as a function of filler concentration. The results of applying these theoretical models on the PMMA : PT composite films are discussed in the next section.

Theoretical Considerations

Calculations for dielectric systems consisting of two phase separated dielectrics (which can be connected in parallel or series) is generally done using the following equation[14]:
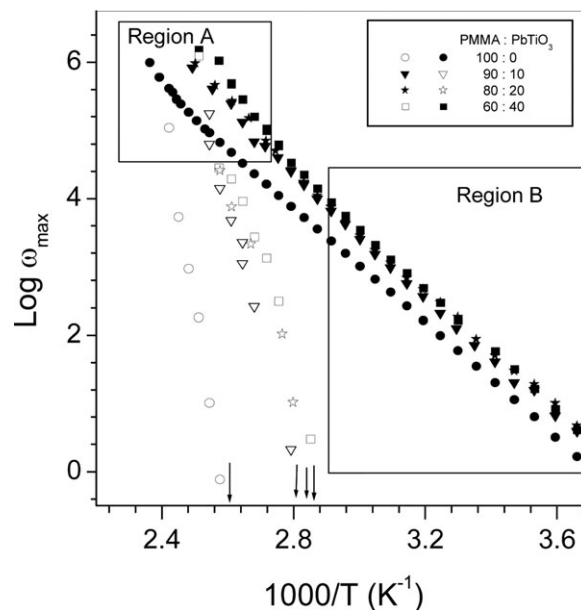

Figure 5. Arrhenius diagram for the ε'' peak maximum frequencies (ω_{max}) from the HN fits in PMMA:PT composite films. Open and closed symbols represent the α and β processes, respectively. The dashed line shows the region where the splitting of α and β processes starts. The arrows indicate the glass transition temperatures obtained from DSC measurements.
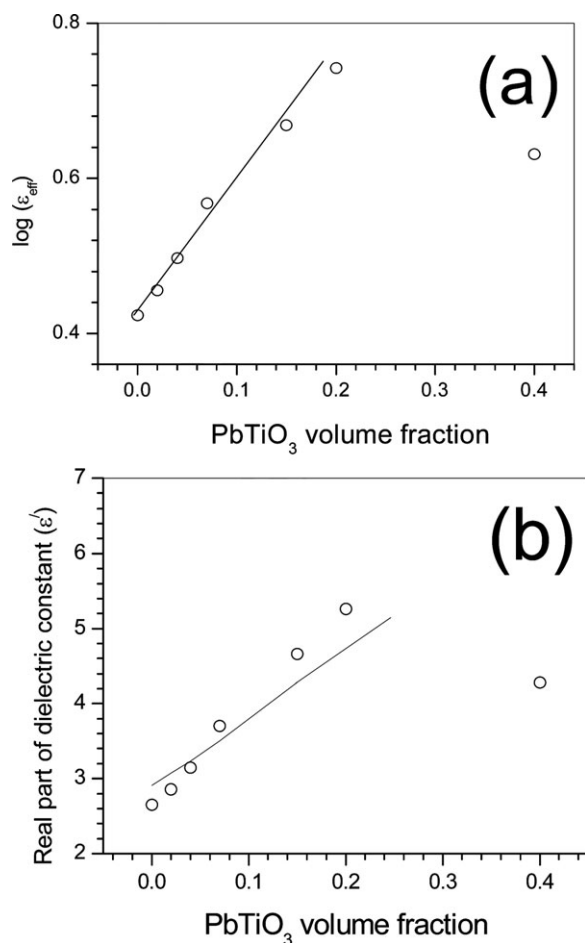
For a general multicomponent system, it can be written as

$$\log\varepsilon = \sum_{i=1}^{m} v_i \log\varepsilon_i \qquad (6)$$

Nevertheless, this equation can only be applied if ε_1 differs slightly from ε_2. On the other hand, the effective dielectric constant ε_{eff} for a composite having polymer of dielectric constant ε_p and dispersed ceramic particles of dielectric constant ε_c can be calculated from the Maxwell–Wagner mixing rule as written below[42]:

$$\varepsilon_{eff} = \varepsilon_p[(2\varepsilon_p + \varepsilon_c + 2v_c(\varepsilon_c - \varepsilon_p))/(2\varepsilon_p + \varepsilon_c - v_c(\varepsilon_c - \varepsilon_p))] \quad (7)$$

Figure 6(a) shows the logarithm of the room temperature dielectric constant in PMMA : PT composite films as a function of volume fraction of PT. The solid line shows the theoretical values predicted by the Lichtenecker logarithmic mixing law, showing acceptable fits between observed and calculated points. However, it should be remembered that this law only holds for cases where the dielectric constant of the polymer matrix differs only slightly from the dielectric constant of the filler particles.
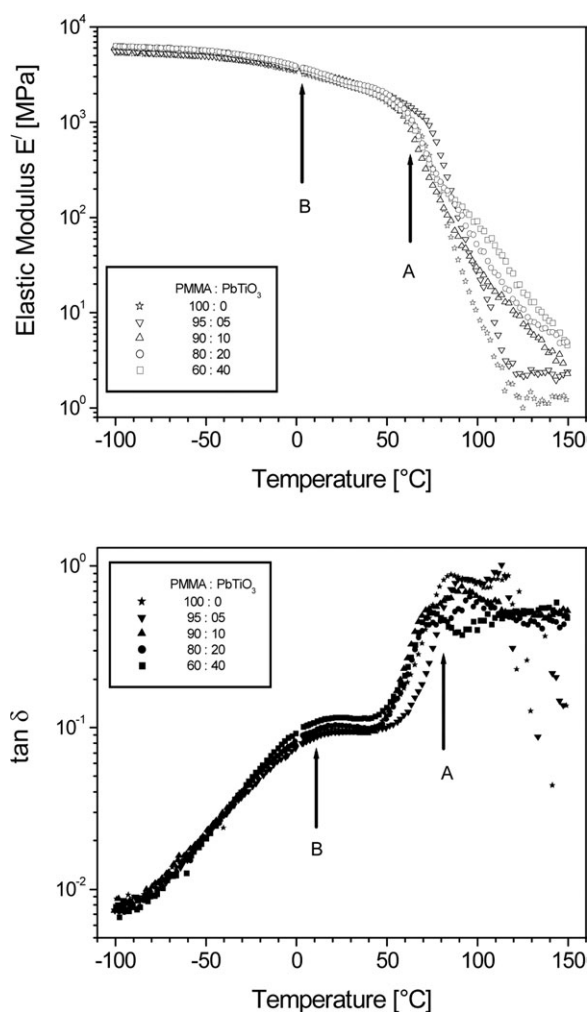

Figure 6. (a) Variation of the room temperature dielectric constant obtained experimentally and using the Lichtenecker equation. The open symbols represent the observed data and the solid line shows the simulated data. (b) Variation of the room temperature dielectric constant obtained experimentally and using the Maxwell–Wagner equation. The open symbols represent the observed data and the solid line shows the simulated data.

$$\varepsilon = v_1\varepsilon_1^n + v_2\varepsilon_2^n \qquad (3)$$

where, v_1 and v_2 are the volume fractions of phases 1 and 2. "n" is value of the exponent which determines the rate of any interaction effects (for a non-interactive system, $n = 1$). For a more general case of systems having m different dielectrics, eq. (3) transforms into

$$\varepsilon^n = \sum_{i=1}^{m} (v_i\varepsilon_i^n) \qquad (4)$$

However, in most cases the true values of the dielectric constant of several components is expected to lie between the values determined by eq. (4) for $n = 1$ and n = −1. Several equations have been proposed to calculate the dielectric constant of statistical composites. One equation frequently used is the Lichtenecker logarithmic law.[41] It can be written as:

$$\log\varepsilon = v_1\log\varepsilon_1 + v_2\log\varepsilon_2 \qquad (5)$$

Figure 7. Variation of elastic modulus (E') and damping factor (tan δ) of the PMMA:PT composite films as a function of PT content.
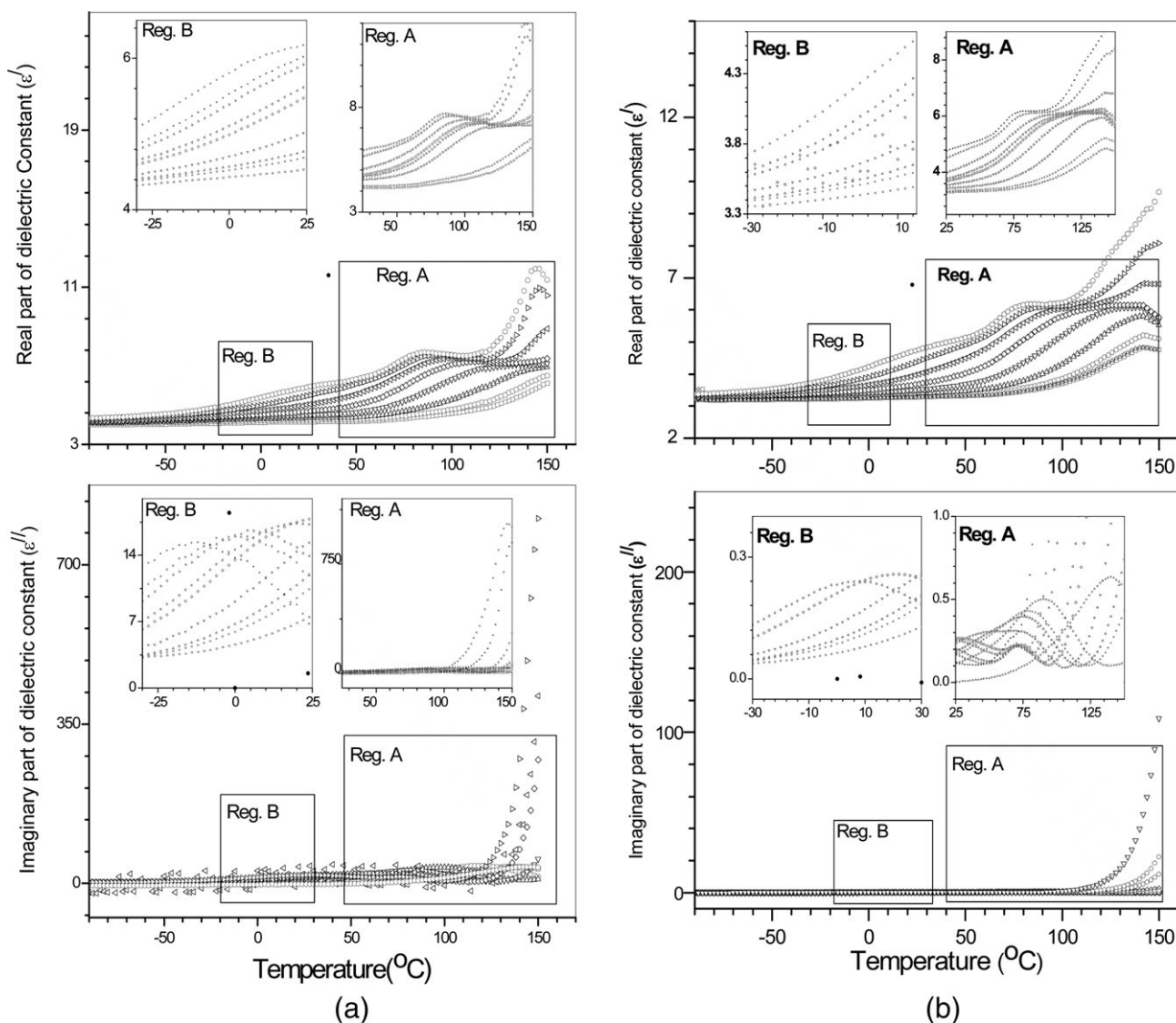
Figure 8. Variation of real and imaginary parts of dielectric constant in pure PMMA as a function of temperature and frequency in (a) pure PMMA and (b) 60 : 40 composite film. Data observed at frequencies namely 1 Hz, 10 Hz, 100 Hz, 500 Hz, 1 kHz, 10 kHz, 100 kHz, 500 kHz, and 1 MHz are shown in the figure.

Furthermore, it should also be mentioned that the fitting has only been done in the range where the increasing trend in dielectric constant is being seen. In films with PT > 50%, we see a decreasing trend in the dielectric constant. Such decreasing trend has been reported in few other systems consisting of polymer : ferroelectric filler composites.[14,43] But, satisfactory explanation for this observation remains elusive.

Figure 6(b) depicts the observed dielectric constant values in PMMA : PT composite films and its comparison with the values predicted by Maxwell–Wagner mixing rule. We can clearly see that there is a large difference between the observed and theoretically predicted values. The values being predicted by Maxwell–Wagner mixing rule are lower than the values which are being experimentally observed.

It is also important to mention that there are a few other mixing rules/models for studying binary systems which have been

recently proposed by Yamada et al. and Jayasundere and Smith.[44,45] But these models are not being applied to the present data since the Lichtenecker logarithmic law of mixing gives acceptable fits.

Rheological Studies

It is known that the dielectric and mechanical relaxation processes follow almost similar nature. Therefore, it is logical to investigate the variation of the mechanical properties for different composites. Figure 7 shows the variation of the elastic modulus (E') and damping factor (tan δ) of the PMMA : PT composite films, for different filler concentrations. The nature of the elastic modulus at low temperatures is not significantly affected with the concentration of the micron-sized fillers. Only the terminal modulus (seen at high temperatures) changes as a function of filler concentration; the maximum elastic moduli are rather independent from filler content and so is the glass

transition. This points toward the occurrence of reinforcement effects in the films because of the interactions between filler and the host polymer matrix. The presence of such interactions between the filler and the polymer chains was also obtained in the dielectric measurements (discussed in sections earlier). Further, the reinforcement has important consequences in terms of using the materials at higher temperatures, due to the increased mechanical stability. From the results of tan δ in Figure 7, it is also possible to see some change on the α-relaxation of the composites (in the range between 75°C and 115°C) in comparison to pure PMMA. The β-relaxation, however, does not change much in accordance with the previous dielectric data (see Figure 5).

Analyzing the frequency and temperature-dependent dielectric data in the composite films (shown in Figure 8), these differences can well be observed, marked on the figure as Regions A and B. These point toward the temperature regions where each of the relaxations α, β or their combination are dominant in deciding the overall relaxation in the polymer matrix. In the Region B, it is basically the β-relaxation which is dominant and in Region A, the α-relaxation (related to the glass transition temperature) starts coming to the picture.

From both, Figures 7 and 8 it is evident that only the α-relaxation gets markedly affected by the filler. In the region where the β-relaxation dominates, it is seen that this process is only slightly affected by the filler. This further confirms previous statements based on the dielectric studies (see previous sections) which stated that the addition of the filler particles significantly affects the α-relaxation (related to the motion of larger sized polymer main chain segments) but that the β-relaxation (related to the local rotational motion of the smaller side chains of the polymer) is not much affected. Another strategy which has been reported in the literature[19] to investigate the effect of molecular relaxation process is based on the analysis of dielectric strength of each process and on the shape of the response, in addition to the effects on the time scale.

CONCLUSIONS

The formation of PMMA : PT composite films have been confirmed using XRD and Raman measurements. Although some reinforcement has been seen from the rheological measurements, no clear signature indicating interaction of particles with the macromolecular chains was observed from Raman phonon mode analysis. The dielectric constant variation in these composite films shows interesting features. It is observed that the α-relaxation is more affected in comparison to the β-relaxation. This feature has also been confirmed with rheological measurements. It is shown that it is possible to decipher the regions where the α- β- or a combination of these two relaxation processes play the dominant role in deciding the overall nature of the composite films. It is also shown that the Lichtenecker mixing rule is quite successful in theoretically predicting the expected magnitude of the dielectric constant in the PMMA : PT composite films as a function of filler concentration.

ACKNOWLEDGMENTS

REFERENCES

1. Ellison, C. J.; Torkelson, J. M. *Nat. Mater.* **2003,** *2*, 695.
2. Floudas, G.; Stepanek, P. *Macromolecules* **1998,** *31*, 6951.
3. Jung, H. M.; Kay, J. H.; Yang, S. Y.; Wan, J. C.; Kim, Y. S. *Chem. Mater.* **2010,** *2*, 450.
4. Kim, G. H. *Eur. Polym. J.* **2005,** *41*, 1729.
5. Meyer, W. H. *Adv. Mater.* **1998,** *10*, 439.
6. Gladius, L. *J. Biomed. Mater. Res. B Appl. Biomater.* **2011,** *98*, 171.
7. Ulbricht, M. *Polymer* **2006,** *47*, 2217.
8. Chandra, A.; Best, A.; Meyer, W. H.; Wegner G. *J. Appl. Polym. Sci.* **2010,** *115*, 2663.
9. Chandra, A.; Meyer, W. H.; Best, A.; Hanewald, A.; Wegner, G. *Macromol. Mater. Eng.* **2006,** *292*, 295.
10. Miyazaki, T.; Nishida, K.; Kanaya, T. *Phys. Rev. E* **2004,** *69*, 061803.
11. Mukerjee, M.; Bhattacharya, M.; Sanyal, M. K.; Geue, T.; Grenzer, J.; Pietsch, U. *Phys. Rev. E* **2002,** *66*, 061801.
12. Papanicolaos, G. C.; Imielinska, K. *J. Macromol. Sci. Phys. B* **1998,** *37*, 201.
13. Bowen, C. R.; Gittings, J.; Turner, I. G.; Baxter, F.; Choudhuri, J. B. *Appl. Phys. Lett.* **2006,** *89*, 132906.
14. Cho, S. D.; Sang, Y. L.; Hyun, J. G.; Paik, K. W. *J. Mater. Sci. Mater. Electron.* **2005,** *16*, 77.
15. Nan, C.-W. *Phys. Rev. B* **2001,** *63*, 176201.
16. Ogitani, S.; Allen, S. A. B.; Kohl, P. A. *IEEE Trans. Adv. Packag.* **2000,** *23*, 313.
17. Shen, Y.; Yue, Z.; Li, M.; Nan, C.-W. *Adv. Funct. Mater.* **2005,** *15*, 1100.
18. Yao, J.; Xiong, C.; Dong, L.; Chen, C.; Lei, Y.; Chen, L.; Li, R.; Zhu, Q.; Liu, X. *J. Mater. Chem.* **2009,** *19*, 2817.
19. Kremer, F.; Schönhals, A. Broadband Dielectric Spectroscopy; Springer: Germany, **2002.**
20. Mazur, K. *J. Phys. D Appl. Phys.* **1997,** *30*, 1383.
21. McCrum, N. G.; Read, B. E.; Williams, G. An Elastic and Dielectric Effects in Polymeric Solids; Wiley: London, **1967.**
22. Fukao, K.; Uno, S.; Miyamoto, Y.; Hoshino, A.; Miyaji, H. *Phys. Rev. E* **2001,** *64*, 051807.
23. Sasabe, H. *J. Polym. Sci. A* **1968,** *6*, 1401.
24. Sharp, J. S.; Forrest, J. A. *Phys. Rev. E* **2003,** *67*, 031805.
25. Spiess, H. W. *J. Polym Sci Part A: Polym. Chem.* **2004,** *42*, 5031.
26. Farago, B.; Chen, C.; Maranas, J. K.; Kamath, S.; Colby, R. H.; Pasquale, A. J.; Long, T. E. *Phys. Rev. E* **2005,** *72*, 031809.
27. Narayanan, R. A.; Thiyagarajan, P.; Lewis, S.; Bansal, A.; Schadler, L. S.; Lurio, L. B. *Phys. Rev. Lett.* **2006,** *97*, 075505.
28. Beiner, M. *Macromol. Rapid Commun.* **2001,** *22*, 869.
29. Garwe, F.; Schöhhals, A.; Beiner, M.; Schröter, K.; Donth, E. *J. Phys. Condens. Matter* **1994,** *6*, 6941.

30. Kahle, S.; Korus, J.; Hempel, E.; Unger, R.; Höring, S.; Schröter, K.; Donth, E. *Macromolecules* **1997,** *30,* 7214.

31. Kahle, S.; Schröter, K.; Hempel, E.; Donth, E. *J. Chem. Phys.* **1999,** *111,* 6462.

32. Williams, G. *Trans. Farad. Soc.* **1966,** *62,* 2091.

33. Chandra, A.; Tyagi, A. K.; Vijaykumar, V.; Mukherjee, G. D.; Boehler, R. *J. Electroceram.* **2011,** *26,* 191.

34. Chandra, A. *Phys. Rev. B* **2008,** *77,* 017101.

35. Chandra, A.; Pandey, D.; Mathews, M. D.; Tyagi, A. K. *J. Mater. Res.* **2005,** *20,* 350.

36. Chandra, A.; Pandey, D. *J. Mater. Res.* **2003,** *18,* 407.

37. Chandra, A.; Pandey, D.; Tyagi, A. K.; Mukherjee, G. D.; Vijaykumar, V. *Appl. Phys. Lett.* **2007,** *90,* 142903.

38. Chandra, A.; Pandey, D.; Krishna, P. S. R.; Ramanadham, M. *Ferroelectrics,* **2005,** *324,* 37.

39. Havriliak, S.; Negami, S. *Polymer* **1967,** *8,* 161.

40. Bergman, R.; Alvarez, F.; Alegria, A.; Colmenero, J. *J. Chem. Phys.* **1998,** *109,* 7546.

41. Lichtenecker, K. *Phys. Z* **1936,** *31,* 906.

42. Mazur, K. *Plast. Eng.* **1995,** *28,* 539.

43. Starke, T. K. H.; Johnston, C.; Hill, S.; Dobson, P.; Grant, P.S. *J. Phys. D Appl. Phys.* **2006,** *39,* 1305.

44. Yamada, T.; Ueda, T.; Kitayama, T. *J. Appl. Phys.* **1982,** *53,* 4328.

45. Jayasundere, N.; Smith, B. V. *J. Appl. Phys.* **1993,** *73,* 2462.