P-V-T Measurements on PMMA : PbTiO$_3$ Polymer-Ceramic Composites with Tunable Thermal Expansion

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ABSTRACT: Results of Pressure-Volume-Temperature measurement on Poly(methyl methacrylate) : Lead Titanate, PMMA : PbTiO$_3$, composite system in the pressure and temperature range 0–200 MPa and 300–473 K, respectively, are presented. The thermal expansion coefficient in PMMA : PbTiO$_3$ composite is expected to be quite complex because the polymer has positive thermal expansion coefficient, whereas the filler has a negative thermal expansion coefficient. In this present article, the effect of pressure on the volumetric thermal expansion coefficient in PMMA : PbTiO$_3$ composite system is presented. It is shown that thermal expansion coefficient of the polymer can be tailored by adding filler which has negative thermal expansion coefficient. Theoretically, a simple additive rule is formulated which can predict the variation of expansion coefficient in the PMMA : PbTiO$_3$ composite system. The limitation of the additive rule is also discussed. It is also shown that the glass transition temperature depends on filler concentration and also has strong pressure dependence. The reasons for large pressure dependence are discussed. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2663–2667, 2010

Key words: PMMA; PbTiO$_3$; negative thermal expansion; composites; P-V-T

INTRODUCTION

Pressure dependent investigations have attracted tremendous focus in functional materials, ceramics, composites, etc.[1–5] Over the last few decades, pressure dependent studies in polymers and their composites have also started to come to the forefront of research. One of the major techniques used for these investigations in polymers is the Pressure-Volume-Temperature (P-V-T) measurement.[2] These studies not only help to understand the dynamics of polymers but also prove beneficial in increasing the applicability of polymer-based systems. P-V-T data are being used to calculate variation in physical parameters like specific volume, viscosity, compressibility (κ), thermal expansion coefficient (α), and free volume in polymer blends.[3–7] P-V-T method has also been used to investigate the pressure dependent glass transition in polymers.[8–12] More recent investigations show that even at elevated hydrostatic pressures, temperature continues to play an important role in deciding the relaxation characteristics near the glass temperature.[13–17] The affect of pressure on inducing dynamic homogeneity in polymer blends has also given interesting results.[18–21]

Thermal expansion coefficient is an important parameter both in the field of polymer engineering and composites; it even sometimes defines the application range of the material. Generally, polymers are considered to have a near constant thermal expansion over their entire usable temperature range. Therefore, within experimental limitations/error, single value expansion becomes a useful approximation for most calculations. Similar to solids, in polymers also the coefficient of volumetric thermal expansion is defined as sum of the coefficients of linear thermal expansion for the three principal directions. However, the coefficient of thermal expansion is always less for the glassy phase than it is for the rubbery/crystalline phase. Even though the values for coefficient of expansion for different types of polymers may vary, the difference between the coefficient for the glassy and rubbery phase in and around the glass transition temperature of any particular polymer is usually the consistent value for all polymers. This observation is widely used to support the free volume theory of glass transition. Over the last few decades, there have been studies which have reported procedure to modify the thermal expansivity of a material. These procedures are based on modification of the structure, use of dopants/substituents, or making blends. It has been recently shown that the thermal expansion of a polymer can be tailored by suitably choosing a filler, which has negative thermal expansion.[22,23] In this
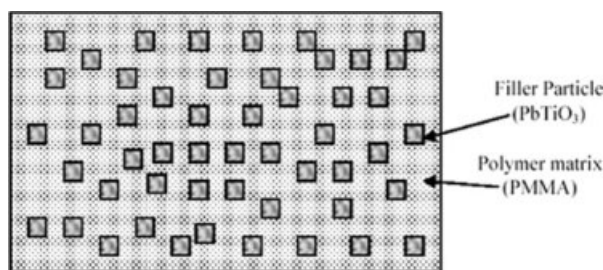
Figure 1 Schematic of composite system. The polymer (PMMA) matrix has a positive thermal expansion coefficient while the filler (PbTiO$_3$) particles have a negative thermal expansion coefficient.

article, the results of P-V-T measurement on one such composite system, namely PMMA : PbTiO$_3$ is reported. The variation of pressure dependent thermal expansion coefficient calculated using the change in specific volume is presented. It is observed that a simple additive rule can be used to estimate the variation of thermal expansion coefficient in samples with different filler concentration. Reasons which may cause slight variation between the theoretically and experimentally observed values are also discussed in the article. The effect of filler concentration on the glass transition temperature of the host polymer is also presented.

EXPERIMENTAL

In this study, PMMA : PbTiO$_3$ composites were prepared by dispersing the filler during the conventional *in situ* bulk polymerization of PMMA in the following manner. The monomer MMA was distilled in vacuum and placed into a reaction tube. 2,2′-azoisobutyronitrile (AIBN) used as polymerization initiator was mixed with the MMA. The required amount of PbTiO$_3$ powder (supplied by Aldrich) was also added. The temperature of polymerization was maintained at 60°C for 3 h to complete the polymerization.[22] Pressure-Volume-Temperature (PVT) measurements were performed using a fully automated high-pressure dilatometer (GNOMIX, Gnomix, Boulder, Colorado). The measurement was carried out using the confining fluid technique.[2] Mercury was used as the confining fluid. The advantage of this technique is that the sample is under hydrostatic pressure at all times and there are neither friction nor leakage problems. Further, using this technique, the change in specific volume can be determined both as a function of pressure and temperature.[2] In the present case, the runs were performed by changing pressure from 0 to 200 MPa in steps of 10 MPa at constant temperatures. The "isothermal" measurements were performed in the range of 25–200°C in steps of 5°C.

It is worthwhile to mention here that the proof of composite formation has already been reported earlier.[22]

RESULTS AND DISCUSSION

The present polymer-particle composite system can be viewed as shown in Figure 1. As the components in the current system, PMMA and PbTiO$_3$, have opposite sign of expansion coefficient, the overall expansion coefficient of the composite is expected to show complex variation of thermal expansion coefficient. Even though the sign of expansion coefficients of the constituents of the composites are opposite, no appearance of pores was observed on heating the sample.[22] Therefore, the contribution of pores in determining the final expansion coefficient of the composites has not been considered in this article.

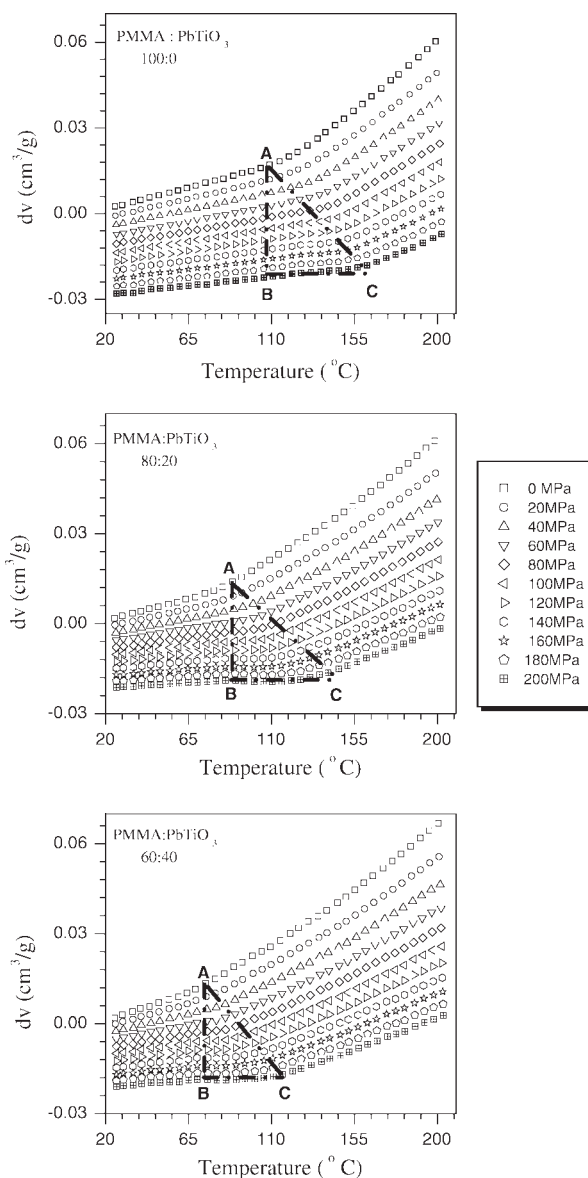Figure 2 shows the variation of specific volume with temperature in three representative compositions

Figure 2 Variation of specific volume as a function of pressure and temperature in three representative samples of PMMA : PbTiO$_3$ composite system.

of PMMA : PbTiO$_3$ system. The data can be divided into three sections, namely (a) region below the AB line, (b) region formed by ABC, and (c) the region above the AC line. The vertical line AB denotes the temperature at which the glass transition should occur if the glass transition temperature is pressure independent. Similar inflection point is also observed in thermal analysis data which is a direct indication of occurrence of glass transition. But with increasing pressure, the glass transition temperature shifts to higher temperatures and this shift is denoted by the AC line. This shift happens mainly due to the glasses which are formed *in situ* during compression (i.e., cooling) from the melt region attained for the previous pressure of the measurement cycle. These glasses carry significant formation history dealing with pressure and temperature at which they were formed and thus show higher formation pressure than the formation pressure of the initial glass. Correspondingly, the glass temperature shifts to higher values with increasing pressures. The situation marked by the triangle ABC is bit more complicated. This is the region where the data will be a composite function of PVT relationships of a series of glasses. As mentioned earlier, these series of glasses are formed because of the dynamic mode of measurements which results in glasses formed *in situ* during compression from the pressure at the previous measurement cycle. The presence of nonequilibrium states belonging to series of glasses formed *in situ* during measurement cycles prevents any attempts to carry out justifiable data analysis being carried out within this region. Therefore, values of parameters like compressibility, expansion coefficient, etc. can be meaningfully calculated only in the region below the AB line and region above the AC line.

One of the most important parameter which can be calculated using the P-V-T data is the thermal expansion coefficient. If we analyze the data shown in Figure 2 and calculate the expansion coefficient directly (i.e., without considering the density of the sample) then it is observed that with increasing filler concentration the overall expansion coefficient decreases. This clearly suggests that if we tailor the filler and polymer ratio carefully, then it may be possible to achieve a composite system with near zero thermal expansion. But P-V-T measures the change of the specific volume Δv (where $v = V/m$; V is the volume of the sample and m is the mass of the sample). Knowing the density of the sample, the volumetric thermal expansion coefficient "β" can be calculated from P-V-T data as:

$$\beta = \rho \left(\Delta v / \Delta T \right)$$

where ρ is the density of the sample, Δv is the change of specific volume for the temperature change ΔT.

Taking the density of polymer (PMMA) matrix ($\sim$ 1.2 g cm^{-3}) and filler (PbTiO$_3$) particle ($\sim$ 7.5 g cm^{-3}), the approximate density of the composite system was calculated. Following this, using the equation given above, the volumetric thermal expansion coefficient can be easily calculated. Figure 3 shows the variation of thermal expansion coefficient at various pressures below AB and above AC line, respectively. This figure depicts that for all the samples, the overall expansion coefficient decreases with increasing pressure. This suggests that depending upon the application, different compositions and pressure values can be chosen to give the desired results.

Until now, all the results discussed above are based on the experimental data. If variation of the volumetric expansion coefficient has to be a direct consequence of different sign of expansion coefficient of matrix and filler then an additive rule must be able to estimate the expansion coefficient of the composite system. A simple additive rule for the thermal expansion coefficient of the composite system can be written as:

$$\alpha = \alpha_m . V_m + \alpha_p (1 - V_m)$$

where α is the observed expansion coefficient, α_m and α_p are the expansion coefficient of polymer matrix and filler particle, respectively; V_m is the volume ratio of the polymer. For the sake of calculations, the effect of pressure on the thermal expansion coefficient of ceramic filler (PbTiO$_3$) in the temperature and pressure range under consideration can be taken as $\sim -1.6 \times 10^{-5}$ K^{-1} [Ref. 1]. The expansion coefficient of the polymer is taken as those obtained experimentally in the present study.

Open symbols in Figure 3 give the theoretically estimated values of expansion coefficients at different pressures in three different samples of the PMMA : PbTiO$_3$ composite system. The values are calculated below the glass transition temperature [given in Fig. 3(a1–a3)] and above the glass transition temperature [given in Fig. 3 (b1–b3)]. Although there are some differences between the experimentally and theoretically calculated values, the difference is within $\sim \pm 15\%$. This difference is quite acceptable for current investigation because the present theoretical model represents an over simplified case. The formula gives no weightage to other properties which will also play and important role in deciding the bulk expansion coefficient of the composite, namely (a) porosity, (b) series of glasses which are formed during measurement cycles, (c) change in density of composite with changing pressures, (d) interactions between polymer matrix and filler particles, (e) temperature gradient inside the sample, etc. Therefore, if the expansion coefficient of
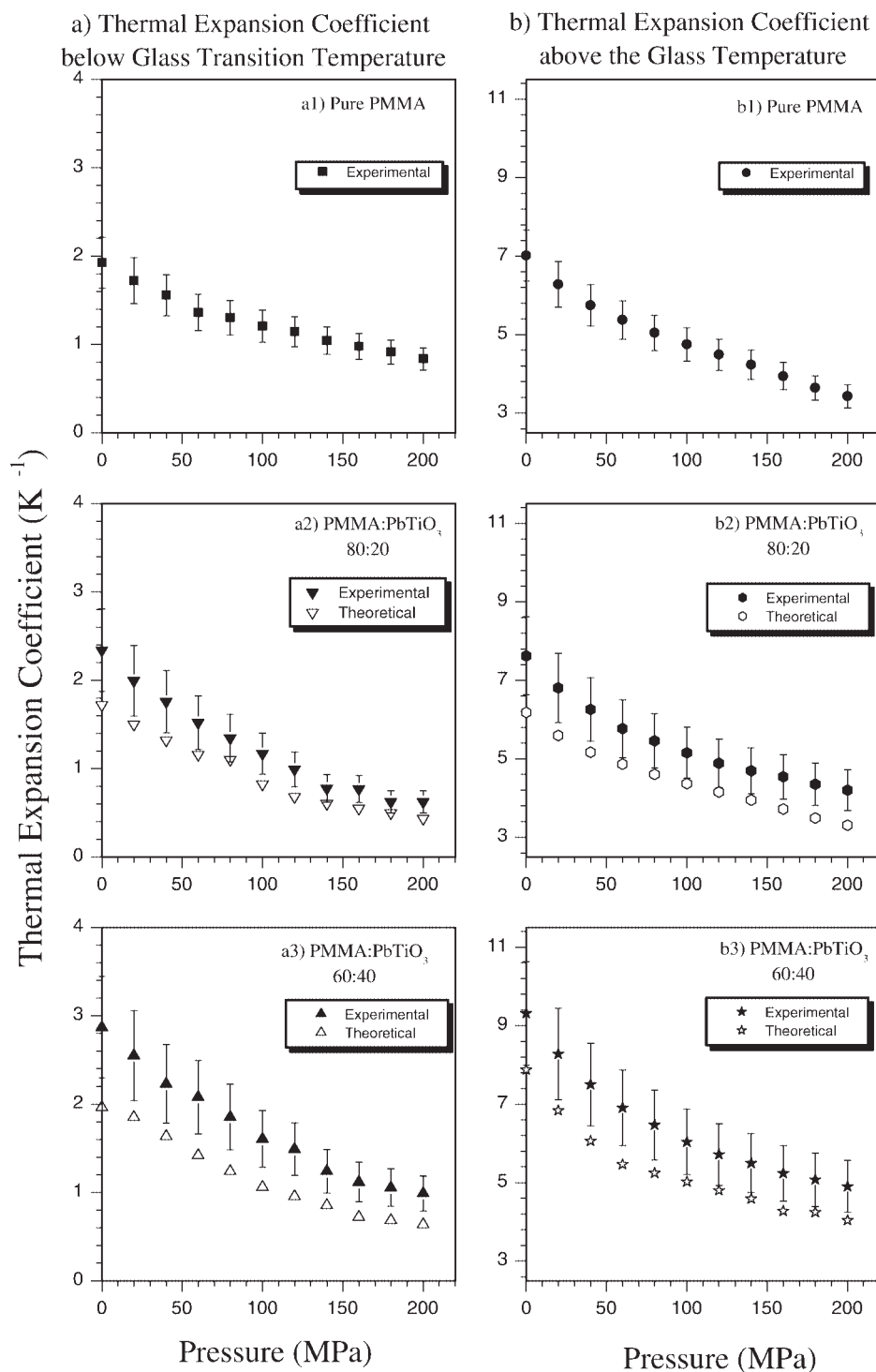
a) Thermal Expansion Coefficient
below Glass Transition Temperature

b) Thermal Expansion Coefficient
above the Glass Temperature

Figure 3 Variation of volumetric thermal expansion coefficient in three representative samples of PMMA : $PbTiO_3$ composite system. Filled symbols represent the experimentally observed value and open symbols represent the theoretically estimated values.

such composite systems is to be theoretically estimated then a very detailed formulation will be required.

As observed above, the thermal expansion of the polymer matrix is getting modified by the addition of the filler particle. The next properties which are

expected to get modified because of the presence of high dielectric constant filler are the relaxational parameters and dielectric constant of the polymer composite. Detailed temperature-dependent dielectric and rheological studies have been carried out and the results have been communicated elsewhere.[24]

CONCLUSIONS

Analysis of P-V-T data for PMMA : PbTiO$_3$ composite system in the pressure and temperature range 0–200 MPa and 300–473 K, show interesting results. It is also shown that the pressure-volume-temperature data can be divided into three distinct regions namely; (a) region below the glass transition temperature, (b) region where a composite function of P-V-T relationship of a series of glasses formed *in situ* during compression is observed, and (c) linear region above the glass transition temperature. It is shown that the glass transition temperature depends on filler concentration and also has strong pressure dependence. With increasing the pressure, the glass transition temperature shifts to higher temperatures. Variation of specific volume has been used to calculate the volumetric thermal expansion coefficient of the composite system. It is shown that a simple additive rule, within experimental limitation and theoretical approximations, is able to predict the variation of expansion coefficient in the PMMA : PbTiO$_3$ composite system.

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