On the Microhardness Testing of Electrically Stressed Poly(phenylene oxide): Polystyrene Blends

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ABSTRACT: Microhardness measurements have been performed on untreated (virgin) and electrically stressed, solvent-cast laboratory-prepared samples of pure poly(phenylene oxide) (PPO), pure polystyrene (PS), and PPO : PS polyblends with different weight proportions. Results of such measurement on untreated polyblend sample show that microhardness (H_v) increases with increase in the content of PS up to 10 wt %, which attributed to the existence of homogeneous phase morphology. However, this feature is not observable in samples containing higher content of PS. Electrical stress is found to modify considerably the mechanical property of polymer. The effect of electric field on the microhardness of such samples (PPO : PS :: 90 : 10) has been characterized by the existence of a peak. Trapping of charge carriers in electrically stressed samples imparts hardening to the polyblend up to an applied step field of 190 kV/cm. However, the excessive charging beyond this step field value destroys this characteristic. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 2535–2539, 2008

Key words: microhardness; hardening; electrically stress; polyblend; trapping of charge; homogeneous phase morphology

INTRODUCTION

The use of polymer in engineering as dielectrics is becoming increasingly important because of its permanent electrification effects, good charge storing capability, etc. Apart from these, choice of polymeric dielectric for each concrete case depends on its mechanical property like resistance to the local deformation (hardness) over a wide range of temperature and electric field strength. Polymer blending in recent years has therefore provided materials of the required electrical and mechanical properties depending on morphology and structure.[1–3]

The physical blends of poly (2,6-dimethyl-1,4 phenylene oxide) (PPO), a polyether, and polystyrene (PS) are well known and comprise a class of successful engineering materials. It is the first blend that was found to be miscible over a complete composition range and represents the commercial product with trade name NORYL.[4,5] The two polymers differ strongly in the glass transition temperature, i.e. in their dynamical properties as well as in their structural properties. Initial study of PPO and PS blends yielded inconclusive results in that two distinct phases—PS rich and PPO-rich—could be resolved from the dynamical mechanical loss peak measurements.[5,6] The same samples, however, exhibit only a single glass transition temperature (T_g) in calorimetric measurements.[5] Further studies involving dielectric relaxation showed noticeably broader relaxation than the relaxation for the pure polymers, but revealed only a single T_g intermediate between those observed for the blend components.[7] It was concluded that while certain level of miscibility occurred, compositional fluctuations were prevalent enough to yield data indicating definite level of microheterogeneity.[5]

This paper reports a noble study by correlating the mechanical and electrical properties of PPO : PS polymer blends. Further, it also indicates an interesting feature of plasticization and antiplasticization effect in electrically stressed polyblends of PPO : PS.

EXPERIMENTAL DETAILS

Material and preparation of samples

The materials used in the present investigation, for the preparation of blends, PPO and PS, were obtained from M/s Aldrich chemicals (St. Louis, MO) and were supplied by Redox, Jabalpur.

Various pure and polyblend samples which are in form of thick film of 60–90 μm in thickness, having different weight percent ratio of PPO and PS were prepared by the solvent cast technique. In this technique, PPO and PS were dissolved in a common

solvent chloroform (LR grade) and then casted on a plane glass substrate inside an oven at 60°C. In order to investigate the effect of electrical stress on the microhardness behavior, some of the samples were subjected to step fields of 100, 150, 190, and 210 kV/cm and at temperatures of 50, 70, 90, and 110°C. For this, the sample was sandwiched between two electrodes of the electrode assembly filled inside an oven. The assembly was heated and the desired temperature was maintained for half an hour. The step field was then applied and maintained for 45 min at the desired temperature. The samples were then cooled down to the room temperature, with the applied step field still on. The total time of application of electric field (which leads to polarization) was kept 1½ h in each case. The samples so treated were then removed for microhardness measurements.

Measurement of microhardness

Microhardness measurements on treated and untreated film samples (60–90 μm thickness) were carried out by means of mhp-160 microhardness tester. Indentation was made with a Vickers's diamond pyramidal indenter having a square base and pyramidal angle of 136° between the opposite faces attached to Carl Zeiss NU-2 microscope. A sample of dimension 0.25 cm² was cut and fixed firmly with a nonreactive adhesive on an optically plane glass plate in such a way that the surface to be indented was perfectly horizontal. The plate along with the sample was then mounted on the stage of microscope so as to avoid any displacement of samples during indentation. The load ranging from 10 to 100 g was applied gently at a steady rate. Care was taken to avoid any jerks and variation during indentation. The time of application of load was kept 30 s in each case. The length of the diagonal made by the indenter was measured by a micrometer eyepiece with an objective of sufficient magnification.

The mean value of diagonal was used for the calculation of hardness number. For every value of load, several indentations were made, and average hardness number was computed. Untreated and treated samples containing different wt % of PPO and PS were tested by the aforementioned method. All these measurements were carried out at room temperature.

The Vicker's hardness number, H_v, was calculated from the relation:

$$H_v = \frac{1.854L}{d^2} \, (\text{kg/mm}^2)$$

where L is the load in kilograms and d the length of diagonal of indentation in millimeters.
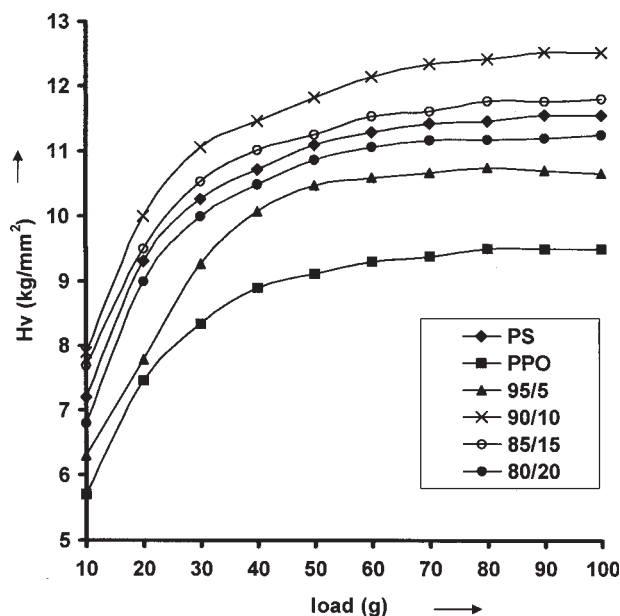
Figure 1 Variation of H_v with load for untreated pure PS, pure PPO, and different wt % ratios of PPO : PS blend samples.

RESULTS AND DISCUSSION

The result of variation of microhardness with varying wt % of PPO and PS with different load, composition, and field variations are discussed later.

Microhardness of untreated sample

Effect of load

Figure 1 shows the variation of H_v with the load of indentation ranging from 10 to 100 g for pure PPO, pure PS, and PPO : PS blend samples with varying weight percentages; 95 : 05, 90 : 10, 85 : 15, and 80 : 20. It is observed from the curves that initially the microhardness increases with increase in the load for all the samples. However, on approaching a certain load value, the rate of increase of hardness slows down. Finally, the value of H_v tends to saturate. This trend is found to be similar for all the samples. Pure PS is found to be harder than PPO. Pure PPO attains a saturation value of 9.39 kg/mm² beyond the load of 60 g, while in case of pure PS, the saturation value is 11.44 kg/mm². Similarly, the saturation values of H_v beyond the load of 60 g for blend samples with 5, 10, 15, and 20 wt % PS are 10.69, 12.37, 11.8, and 11.18 kg/mm², respectively. The different values of microhardness at saturation load for PPO, PS, and various PPO : PS polyblends indicate the changes in the macromolecular structure and morphology due to which the related values of microhardness exhibit the hardening or softening characteristic of the material.

The increase in H_v with load can be understood on the basis of strain hardening[8,9] phenomenon in the polymers. There is a spectrum of micromode of deformation in polymer chain. Each micromode is activated by its characteristic temperature and strain conditions. When sufficient number of micromodes becomes active, large-scale plastic deformation begins. On applying load, the blend sample is subjected to greater strain hardening and hence H_v increases. This phenomenon can also be explained with the help of theory given by Amontons.[10] According to him, the microhardness may be correlated with the frictional force. The coefficient of friction decreases with increase in the load, and the frictional force is found to increase linearly with increase in the load. Hence the variation of H_v with load is curvilinear. Thus, the microhardness initially increases with increase in the load. On applying load the polymer is subjected to some strain hardening. Finally, when H_v value tends to become constant the polymer is completely strain-hardened. The rate of strain hardening is greater at low loads and decreases at higher loads. The rate of strain hardening in different samples is related to weight percentage ratio of two polymers in the blend, which governs the degree of crosslinking in the blend. Hence the different saturation load values are observed for different samples. The saturation value of H_v beyond 60 g may be due to permanent deformation caused by chain–chain slipping in polymer system.

Blending effect

Figure 2 shows the variation of Vicker's hardness number, H_v, with various wt % of PS in PPO : PS polyblends (untreated), i.e. 95 : 05, 90 : 10, 85 : 15 and 80 : 20 at various loads ranging from 10 to 100 g. The H_v value of pure PPO (0 wt % of PS) and pure PS (100 wt % of PS) are also plotted at different loads.

Initially, with the increase in PS up to 5 wt % the value of H_v increases as compared to pure PPO. However, this value is less than pure PS. Further, when mixing PS upto 10 wt % in the blend, the value of H_v increases remarkably attaining maximum. However, with the increase of PS beyond 10 wt% and upto 15 wt %, the microhardness of PPO : PS polyblends starts increasing. Moreover, the H_v value of these samples is still higher than those of pure PS. The increase in the content of PS upto 20 wt % in the polyblends further decreases the level of microhardness, and the H_v values are less than that of pure PS sample. The microhardness of all the polyblend samples are higher than pure PPO. Thus, in general, the hardened polyblends are obtained with blending of PS in PPO upto 20 wt %. However, the level of microhardness of PPO : PS polyblend
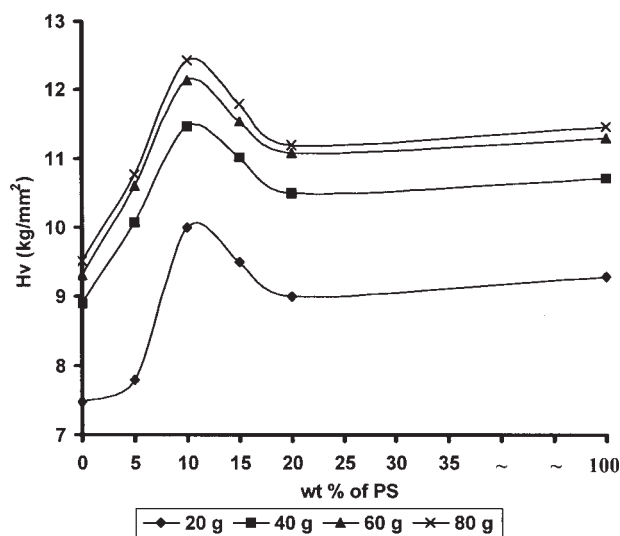

Figure 2 Variation of H_v with untreated samples of varying wt % of PS at different loads.

increases as well as decreases with varying content of PS in comparison to pure PS. The sample with 10 wt % of PS can be considered as optimum for producing hardened polyblend, since a maximum value of H_v is obtained for these polyblend samples.

The increase in the content of PS causes an increase in stiffness in the blend samples. Since PS is relatively harder than PPO, hence the increase in concentration of PS increases the level of microhardness upto 10 wt%, beyond which H_v decreases with increase in concentration of PS. The blend samples beyond 10 wt % of PS does not exhibit homogeneous phase morphology as compared to the phase homogeneity of pure PPO and blends with 5 wt % of PS. This indicates that the miscibility of the two polymers get restricted to 10% of PS, which limits the compatibility of two polymers, and blending beyond this composition yields a phase-separated system. However, the values of H_v at the ratio of 85 : 15, 80 : 20 and for pure PS are still higher than the value of H_v for pure PPO. This further suggests that the microhardness of PPO : PS blends is greater than that of pure PPO upto some concentration of PS in PPO.

Thus, loss of homogeneity and compatibility in blend samples is compensated with the increase in microhardness. This property could be suitable for application from strength considerations.

Microhardness of electrically treated samples

Effect of load

Figure 3 depicts the variation of H_v, with load of indentation ranging from 10 to 100 g for PPO : PS (90 : 10) samples which are electrically stressed and polarized at 110°C. It is observed from the various figures
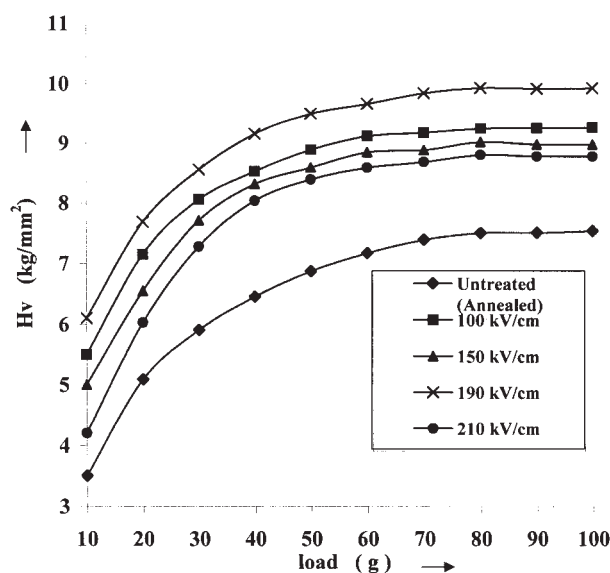
Figure 3 Variation of H_v with load for electrically stressed specimen of PPO : PS :: 90 : 10 blend polarized at 110°C with different fields.

that initially as the load increases, microhardness of the sample increases, and tends to saturate or become constant beyond the load of 60 g. The variation of H_v with load is similar to that explained for untreated samples, discussed in Effect of Load in the Microhardness of Untreated Sample section. The saturation values of H_v for the blend samples (90 : 10) polarized with the electric field at 100, 150, 190, and 210 kV/cm are 9.27, 9, 9.93, and 8.8 kg/mm², respectively.

A comparison of untreated samples, however, reveals that the microhardness value of electrically stressed samples are greater than those of the untreated annealed samples (zero field). Thus, electrical stress causes hardening of polyblend samples. Prior to the application of the electrical step voltage, samples were maintained at a constant desired high temperature; this thermal stress leads to increase in mobility of polymer chains and chain segments. The directing action of applied electric stress then facilitates movement of mobile segments and chain in the field direction depending upon the intrinsic and extrinsic charges. On cooling the samples in the presence of applied stress, the chains and chain segments are frozen, with the new modified conformation depending upon the effective acting internal field. This leads to hardening of the samples. The degree of hardening increases both with the increase in the load and the applied electric field strength.

Effect of field

Figure 4 clearly shows the variation of H_v with the strength of applied electric field for the sample

polarized at 110°C. In case of blend samples with 90 : 10 composition (Fig. 4), for the load of 80 g, the value of H_v first increases from 7.52 to 9.27 kg/mm² as the field strength is increased from 0 to 100 kV/ cm. Thus on increasing the field value from 0 to 190 kV/cm, there is an increase in the microhardness of the blend samples. A dip in the value of H_v is observed at 150 kV/cm, where the value of H_v becomes 9 kg/mm². However, H_v again shows an increase up to the field strength of 190 kV/cm which is the optimum value, and thereafter at the field of 210 kV/cm, the value of H_v decreases to a value of 8.8 kg/mm². The application of electrical stress causes bulk charging, and these charges are trapped and frozen in. The trapped charges cause hindrance to the polymer chain mobility, thus causing stiffness to the otherwise flexible chain, which ultimately leads to hardening of polyblend samples. The degree of hardening increases linearly with the increase in the electrical field strength up to the value of 150 kV/cm, and thereafter an abrupt increase at 190 kV/cm is observed.

We know that the polymers have flexible chains and internal rotations of part of chains are possible thermally. Owing to thermal motion, the arrangement of atoms keeps continuously changing leading to different conformations. Each position of atom corresponds to a definite value of potential energy of the molecule, which is determined by all the interaction between atoms, electron, nuclei, etc. The energy required by the molecule to move from the position with minimum potential energy is called hindrance potential or rotation barrier.[11–13] If the supply of kinetic energy is small the group of molecule does not
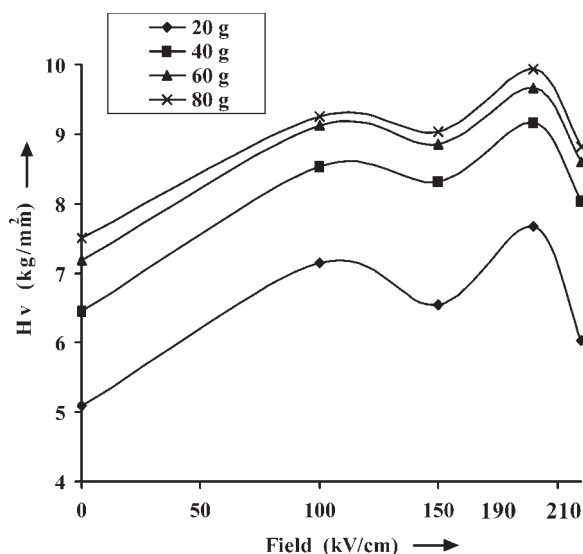

Figure 4 Variation of H_v with electrical field strength for PPO : PS :: 90 : 10 blend polarized at 110°C with different loads.

vibrate about the position of minimum potential energy, executing only restricted or retarded internal rotation. Bresler and Frenkel[14] showed that internal rotation is retarded by interaction between atoms not bonded chemically to each other. There may be interactions between atoms of the same chain (intramolecular) or between atoms belonging to unit of neighboring chains (intermolecular), ionic interaction, orientation interaction, deformational interaction, and dispersional interaction. Besides, intramolecular hydrogen bond formation is also possible. Under the influence of an external force field, the chain exhibits kinetic flexibility, which refer to rate of transition from one position of energy to another. The rate of conformational transformation depends on the ratio of potential energy barrier and energy of external influence. Thus, rotation of units and their passage from one position of potential energy minimum to another can occur only when there is ample supply of energy. Further, polymer links can assume only those positions in space allowed by the presence of an interaction. Thus owing to intramolecular interaction, a real polymer chain assumes a smaller number of conformations than a freely jointed chain. With insufficient supply of energy, its unit does not rotate but exhibit only torsional vibrations. A polymer with intense torsional vibrations is a flexible chain polymer. While a polymer with hindered rotation of chain parts is called rigid chain polymer.

It appears that in electrically stressed samples owing to polarization, inter and intramolecular interactions are modified in such a way that hindrance to the rotational movement and torsional vibrations of macromolecular units increases leading to greater value of microhardness up to the field value of 100 kV/cm in case of 90 : 10 blends. The value of hindrance potential increases and attains a maximum value; thereafter, depending upon the nature of polarization and its magnitude, the electrostatic inter- and intramolecular interactions are modified (become moderate) in such a way that the kinetic flexibility of the chain increases and the hardness–field curve exhibits a dip (or decrease). The interaction becomes more intense for sample, which is electrically stressed with the step field of 190 kV/cm. The hindrance-potential becomes maximum and the kinetic flexibility of the chains decreases, which is manifested in the form of peak in the H_v–field curves.

The decrease in value of H_v at the field of 210 kV/cm suggests the breakdown phenomenon, where the excessive charging destroys the hardening characteristic and leads to the softening of samples. Thus, the effect of the strength of electric field can be optimized to 190 kV/cm for the PPO : PS polyblends. It is remarkable to point out that the H_v values of all the electrically stressed samples are less as compared to the untreated sample annealed at 60°C. Thus, the hardening of the samples observed as a consequence of electrical field strength is a relative effect and the degree of hardening is less as compared to untreated samples.

CONCLUSION

In summary, the application of microhardness technique to electrically stressed polymer blend is a relatively new approach to study structure–property relationship of the material. From the results it is observed that the microhardness (H_v) gradually increases with increase in load and attains a saturated value beyond certain load, because of strain hardening.

The effect of blending PS with PPO is found to increase the microhardness with increase in PS up to 10 wt %. The increase in the content of PS beyond this proportion decreases the H_v value because of different phase morphology in various blend samples. Moreover, it is interesting to note that the microhardness behavior of blend sample is modified considerably due to electrical stress. It is observed that the antiplasticization effect is restricted to a certain field value (190 kV/cm) at 110°C, beyond which the plasticization effect sets in due to the presence of charge in the material. Thus, the nondestructive microhardness measurement study on virgin and electrically stressed samples give a good correlation between the electrical and mechanical behavior of PPO : PS polyblends.

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