Microhardness investigation on thin films of virgin and electrically aged pure PVF and isomorphous polyblends of PVF/PVDF

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Abstract. Replacement of conventional materials by polymeric materials (blends/composites) with improved mechanical performance is of immense importance for modern technology. Blending of fluoro polymers can contribute to such synergistic properties. PVDF, as a semi-crystalline fluoro polymer, has been blended with PVF fluoro polymer to form isomorphous polyblend specimens by altering the wt% of PVDF using a solution casting technique. Microhardness investigations have been undertaken using the Vicker's indentation technique; measurements of Vicker's hardness number (H_v) were carried out on virgin (untreated) and electrically stressed pure PVF and PVF/PVDF isomorphous polyblend specimens by a fixed step voltage at a fixed high temperature. The results of variation of H_v as a function of applied load are explained in terms of strain hardening phenomenon in virgin samples along with their mechanical properties. The increase of hardness produced as a result of variation of PVDF wt% within the PVF matrix has been interpreted in terms of a change in chain crosslinking. The observed higher value of hardness number in the case of electrically stressed specimens is suggested to result from modification in inter- and intramolecular interactions in such samples.

Keywords: polymer blends and alloys, microhardness, mechanical properties, electrical stress, crosslinking

1. Introduction

Synthetic polymeric materials have been used extensively as electrical insulators because of their high electric strength and good dielectric and mechanical properties [1]. They have also made a great contribution to the miniaturization of electrical equipments [2]. In spite of such wide-spread practical uses, surprisingly little is well understood about the fundamental electrical properties of polymeric materials (electrical conduction, dielectric breakdown etc.). All electrical equipments are subjected to various severe aging effects leading to changes in mechanical behaviour of the polymeric materials. These aging factors are known to contribute more to the deterioration in electrical behav-

iour during operation than when the device is not in service. When the gradual aging becomes severe, the leakage current tends to increase and arcing discharge may occur. This can be interpreted as an indication of an incipient fault that will eventually lead to device failure. Thus, investigation of the mechanical performance changes is a key issue to anticipate and detect equipment incipient faults and hence its average useful life span.

Fluoropolymers, i. e. poly (vinyl fluoride) (PVF) and poly (vinylidene fluoride) (PVDF) have been used in important specialized applications. Both PVF and PVDF have good weather resistance and their mechanical properties are excellent. The two polymers are known to exhibit co-crystallinity or isomorphism on mixing. Isomorphism is believed

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to be possible when polymer chains (blend) or monomer units (co-polymers) are similar in conformation and size in the crystalline state [3]. The compatibility and the possibility of improving mechanical performance of these two polymers in blend form are of immense interest.

Microhardness testing is a well-known non-destructive technique to obtain information on structural features and change in mechanical properties of pure polymers and polymer blends [4–9]. Further, the dependence of microhardness on load in (g) was studied using Meyer's law [2] on the prepared polyblend specimens. In the present work the effects of thermal and electrical aging stress on the microhardness behaviour of pure PVF and isomorphous polyblends of PVF and PVDF have been investigated with the view to correlate the changes in mechanical properties with the useful electrical lifetime of the polymeric blend. Vicker's microhardness testing has been employed to measure the microhardness.

2. Experimental

The present investigation was undertaken on laboratory prepared samples.

2.1. Materials

Commercially available polymers of PVF (BDH, UK), with 126 000 M_w and PVDF (Aldrich, USA) with 140 000 M_w , in powder forms were supplied by M/S Redox, Jabalpur and were used without further purification. DMF, methanol and toluene were supplied by E-Merck Chemical Co. and were used as received due to their high purity (over 99%).

2.2. Preparation of samples

The solvent casting technique was utilized to prepare pure and polyblend specimens of PVF and PVDF. The polymers were dissolved in their common solvent dimethylformamide (DMF), at a temperature of 60°C with constant stirring. A known quantity of the homogeneous solution so obtained was poured on a circular glass plate of 4 cm diameter, which was balanced on a mercury pool for uniform thickness of the resulting thin film and the solvent was allowed to evaporate completely in a clean atmosphere inside an oven over nearly 6 hours. Further, for the minimization of DMF,

Soxhlet test was carried out. The temperature of the oven was controlled automatically at 60°C. The specimens obtained were in the form of thin films 4 cm in diameter and 150 microns in thickness.

2.3. Soxhlet test

Soxhlet test was performed, to completely remove the DMF solvent from PVF/PVDF polyblend specimens using Soxhlet apparatus. A 30×32 mm specimen was cut from the 150 micron thick specimens and placed in the Soxhlet cavity (which was filled with toluene) and heated. The condensing toluene leaches out the DMF from the samples. This process was repeated for 2 hours, so that maximum solvent would leach out and then the residual toluene was evaporated.

3. Characterization

3.1. Microhardness measurement

Microhardness measurements on various specimens were carried out using Carl Zeiss NU₂ Universal Research Microscope model No. mph-160 with a Vicker's diamond pyramidal indenter attached to it. The Vicker's Hardness Number (H_v) was calculated using the Equation (1):

$$H_v = 1.854 \cdot \frac{L}{d^2} \text{ [MPa]} \quad (1)$$

where L is load in kg and d is diagonal of indentation in mm. Minimum five indentations were obtained at various loads and the average hardness number was calculated.

3.2. Mechanical test

Mechanical characterization of the blend films was carried out according to ASTM test method No. D-638. Crosshead speed was maintained at 5 mm/min at room temperature. The samples were conditioned at 110°C for 24 hours in air before the testing.

The tensile tests were conducted at room temperature on an Universal Testing machine (Model No. 4302). The tests were made on 4 cm² size samples. The crosshead speed (initial strain rate) was 5 mm/min and grip length 40 mm. In each case five samples were tested and the average of five readings was taken. The tensile strength, modulus and

elongation at break were measured using the stress-strain curves.

3.3. Thermally and electrically stressed samples

In order to investigate the effect of thermal and electrical aging on the microhardness behaviour of PVF/PVDF isomorphous blends, prepared sample of pure PVF and PVF:PVDF with varying weight percentage (50:50, 70:30 and 90:10) were electrically stressed by applying a voltage of 400 volts at 80°C. Specimens were placed between the two metal electrodes of the measuring cell, which was mounted inside an oven and heated to 80°C. After 30 min, 400 Volts was applied for a time period of 45 minutes while the temperature was maintained at 80°C. The specimen was then slowly cooled to room temperature within 45 minutes, while the electrical field was still on. The total time of application of electric field was kept at 1.5 hr in each case. The electric field was then removed and the thermally and electrically aged specimens were taken out for microhardness measurements.

4. Result and discussion

The Soxhlet extraction was performed to minimize the common solvent (DMF) from the polyblend specimens before characterization. In the Polyblend 50/50, common solvent was found to be minimum in comparison to other samples i. e. 70/30 and 90/10. The variation of Vicker's hardness number

Figure 1. Variation of H_v with load for pure PVF and isomorphous polyblends of PVF:PVDF

(H_v), as a function of applied load (L), is shown in Figure 1 for pure PVF and the isomorphous blends with varying weight percent of PVDF. The increase in the value of H_v , as the load increases can be explained on the basis of strain hardening phenomenon in polymers [2, 3, 10]. There are micromodes of deformation in the polymer chain. When sufficient number of micromodes becomes active, large-scale plastic deformation begins. As the load is increased, the specimen is subjected to greater strain hardening and H_v is increased. Finally, when H_v tends to saturate the polymer specimen is fully strain hardened so no appreciable change in the value of H_v is observed.

4.1. Strain hardening index

The dependence of microhardness on load can be studied using Meyers equation (2):

$$L = a \cdot d^n \quad (2)$$

Taking logarithm of both sides of the Equation (2), we have Equation (3):

$$\log L = \log a + n \cdot \log d \quad (3)$$

where L is load, d is the length of the diagonal, a is a constant representing load for unit dimension and (n) is the logarithm index number, which is the measure of strain hardening from the plots of $\log L$ versus $\log d$ for pure PVF as shown in Figure 2 and as on for PVF/PVDF isomorphous polyblend specimens. For all specimens, the strain hardening index has two values: one for the low load region ranging

Figure 2. Graph between $\log d$ vs. $\log L$ for pure PVF for calculating values of n

Table 1. Different calculated values of (*n*) for pure PVF and blended specimens (i. e. PVF50:PVDF50, PVF70:PVDF30, PVF90:PVDF10 wt%) in the two load regions are shown

Samples	n (Slope in low regions)	n (Slope in high regions)
Pure PVF	2.93	2.33
PVF50:PVDF50 wt%	3.45	2.74
PVF70:PVDF30 wt%	3.15	2.45
PVF90:PVDF10 wt%	3.33	2.66

10 to 50 g and one for the high load region ranging from 80 to 100 g. The value of *n* is greater for low load than for high load region. In most of the blend specimens, the value of *n* tends to be nearly 2.5 in the high load region. The different values of *n* for pure PVF and PVF/PVDF isomorph polyblend specimens in the two-load region are listed in Table 1.

Meyer’s law indicates that the value of H_v increases continuously with load when *n* is greater than 2 and the value of *n* approaches 2 in the saturation load region when H_v becomes independent of load. Hence, the logarithmic index number, *n*, can be considered as a measure of strain hardening in different specimens. In fact the different values of *n* in the different load regions reflect the elastic and plastic characteristics of deformation.

4.2. Mechanical analysis

Generally mechanical properties of any polymeric system depend on the macromolecular segments and crosslinking between the macromolecular units. Tensile properties are basically characterized by measuring yield stress and corresponding elongation at break as function of polymer compositions. Tensile modulus is one of the most important small strain mechanical properties. It is the key indicator of the stiffness or rigidity of the material and quantifies the resistance of the specimens to mechanical deformation in the limit of infinitesimally small deformation. Modulus of any material is approximately proportional to the strength of the link between the atoms in a material and to the number of links per unit of cross-section area. When stress is applied, the weakest link i. e. the non-bonded interchain interaction deform much easily than the strong individual bounded chains. Thus the non-bonded interchain interactions play a

Table 2. Mechanical properties of pure PVF & varying PVDF with different weight percentage in PVF

Sample designation of polyblend specimens	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation [%]
Pure PVF	68.90	13.50	40.76
PVF90:PVDF10 wt%	70.50	14.00	48.00
PVF70:PVDF30 wt%	73.20	16.90	49.23
PVF50:PVDF50 wt%	78.10	18.50	50.98

crucial role in determining the magnitude of the modulus of the polymeric matrix.

The results of various mechanical properties of untreated pure PVF and its blended specimens with PVDF in varying weight percentage are given in Table 2. It can be inferred from the table that incorporation of PVDF in different wt% in PVF has significantly affected the tensile properties. PVF with different wt% of PVDF shows the increase in tensile strength (Table 2). Tensile strength was found to be greater than the neat (pure PVF), which shows the influence semi-crystalline behaviour of PVDF and crosslinking within the PVF matrix. The maximum tensile strength was obtained at 50:50 wt%.

4.3. Electrical stress analysis

Figure 3 depicts the variation of H_v as a function of applied load for specimen electrically stressed with a field of 400 kV/cm. It is evident that the micro-hardness exhibits similar trend as in case of virgin samples. However, the value of H_v is more for these

Figure 3. Variation of H_v with load for pure PVF and PVF:PVDF polyblend specimen of virgin and electrically stressed

electrically stressed samples than the virgin samples in each case.

We know that polymers have flexible chains and internal rotation of parts of chain is possible thermally [11, 12]. Owing to thermal motion the spatial arrangement of atoms keep continuously changing leading to different conformations. Each conformation corresponds to a definite value of potential energy of the molecule, which is determined by all the interactions between atoms, electrons, nuclei etc. The energy required by the molecule to move from the position with minimum potential energy to maximum potential energy is called hindrance potential or rotational barrier. If the supply of kinetic energy is small the groups of molecules do not rotate but only vibrate about the position of minimum potential energy executing restricted or retarded internal rotation. Internal rotation is retarded by interaction between atoms not bonded chemically to each other [13]. There may be interaction between atoms of the same chains (intermolecular) or between atoms belonging to units of neighbouring ionic interactions, orientational interactions, deformational interactions and dispersional interactions. Besides intramolecular hydrogen interactions are also possible. Under the influence of an external force field, chain exhibits kinetic flexibility which refers to rate of transition from one position of energy to another, chain can uncoil to a certain extent depending on the relation between the field energy and potential energy barrier. The rate of conformational transformation depends on the ratio of potential energy barrier and the 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 intermolecular interactions a real polymer chain assumes a smaller number of conformations than a freely joined chain. With insufficient supply of energy its units do not rotate but exhibit only torsional vibrations. Polymers with intense torsional vibrations are flexible chain polymers while polymers with hindered rotation of chain parts are called rigid chain polymers. Prior to the application of the electrical stress field the sample were kept maintained at a high temperature for half an hour facilitating thermal movements of chains. Subsequent application of the electrical stress at this ele-

Table 3. Different calculated values of (n) for electrically stressed pure PVF and blended specimens (i. e. PVF50:PVDF50, PVF70:PVDF30, PVF90:PVDF10 wt%) in the two load regions are shown

Samples	n (Slope in low regions)	n (Slope in high regions)
Pure PVF	2.98	2.39
PVF50:PVDF50 wt%	3.55	2.83
PVF70:PVDF30 wt%	3.24	2.54
PVF90:PVDF10 wt%	3.41	2.76

Table 4. Mechanical properties of electrically stressed pure PVF & varying PVDF with different weight percentage in PVF

Sample designation of polyblend specimens	Tensile strength [MPa]	Tensile modulus [GPa]	Elongation [%]
Pure PVF	70.00	14.00	42.00
PVF90:PVDF10 wt%	71.95	15.70	52.20
PVF70:PVDF30 wt%	74.20	16.90	53.00
PVF50:PVDF50 wt%	79.45	19.20	53.90

vated temperature and hence the directing action of the applied field acting on the polarizing (moieties) results in polarization of the polymer and this state is frozen in on cooling. It appears that in electrically stressed polarized samples inter- and intramolecular interactions are modified in such a way that steric hindrance of rotation of chain or potential rotational barrier is increased restricting kinetic flexibility of polymer chain. This result in a material, which is hard compared to the virgin untreated sample, which is also assured from the calculated value of (n) for electrically stressed specimens as shown in Table 3 and increase in mechanical strength (Table 4). This explains the increase in the value of H_v observed for electrically stressed samples in the present case.

5. Conclusions

When both the polymers are blended in equal weight proportion (50:50) microhardness was found to be maximum with improved mechanical properties. The microhardness study on virgin and electrically aged thin film of pure PVF and isomorphous polyblend specimens of PVF and PVDF helps to understand the modification in properties due to inter and intra molecular interactions. The electrically stressed specimens exhibit higher level of microhardness as compare to virgin specimens.

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