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# Morphological, crystallization and plasticization studies on isomorphic blends of poly (vinyl fluoride) (PVF) and poly (vinylidene difluoride) (PVDF): using microhardness, XRD and SEM techniques

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**Abstract** Property modification by blending of polymers has been the area of immense interest. In this paper, the isomorphic blends of two polymers poly (vinyl fluoride) (PVF) and poly (vinylidene difluoride) (PVDF) with different ratios were prepared using solution cast technique. The microhardness studies have been carried out on pure and polyblend specimens at various loads to test the plasticization and hardening effects using Vickers microhardness testing. The X-ray diffraction (XRD) study has been utilized to detect the crystalline and amorphous characteristics of specimens. Thus PVDF acts as plasticizer in the polyblend when the content of PVDF is relatively high as compare to PVF. When the PVF is major component in the polyblend, the microhardness of the blend specimen increases and the isomorphic blend specimens with 50:50 proportion of two polymers exhibit the maximum value of microhardness. Scanning electron microscopy (SEM) micrographs indicate complete chain formation with uniform texture, when the two polymers are blended in equal proportions. The findings of XRD and SEM have been correlated with the microhardness values.

## Introduction

In this era of polymers, when the polymeric materials are replacing most of the conventional materials, there is increasing demand of new materials with improved properties in terms of toughness, strength and dimensional stability. Polymeric materials are widely used in industry; largely due to their valuable mechanical properties. So microhardness studies on polymeric materials are of increasing interest for material scientists [1–3]. In recent years attention has been focussed on mixtures of this distinct class of materials having different properties and chemical structures to form polymer blends. There are blends, which may be either block copolymers (two or more chemically different polymer chains connected together by a chemical bond) or polymer alloys (two or more chemically different polymers that are mechanically mixed [4]). Co-crystallinity or isomorphism [5] is a rare situation in miscible polymer blends. Isomorphism is believed to be possible when the polymer chains (blend) or monomer units (co-polymer) are similar in conformation and size in the crystalline state. Poly (vinyl fluoride) (PVF) and poly (vinylidene difluoride) (PVDF) exhibits isomorphic characteristics. PVF and PVDF, which are vinyl fluoropolymers, have good weather resistance and are used for out door applications [6]. The mechanical properties of these polymers are good as the tensile strength (s) of PVF and PVDF are 68.90–103.35 and 48.35 Mpa, respectively. The manner in which the two polymers are blended affects the resultant mechanical property.

Microhardness testing has been utilized to obtain information on structural features and mechanical property changes for polymer blends [7–13]. Further, the important aspect of the microhardness testing of polymers at low loads is that whether the hardness number is dependent or independent of the load [14, 15]. It is with this view the effect of load on the microhardness of PVF and PVDF polyblends have been studied.

X-ray diffraction (XRD) and Scanning electron microscopy (SEM) techniques have been utilized to detect crystallization and morphological characteristics in isomorphic

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polymer blends. These studies reveal the structure–property relationship in the PVF:PVDF isomorphic blends.

## Experimental

### Materials

For the preparation of the blends, the commercially available polymers poly (vinyl fluoride) (PVF) (BDH, UK), molecular weight 126,000 and poly (vinylidene difluoride) (PVDF) (Aldrich, USA) molecular weight 140,000, in powder forms were used without further purification which were supplied by M/S Redox, Jabalpur.

### Preparation of specimens

The solution cast technique has been utilized to prepare the pure and polyblend specimens of PVF and PVDF. The two polymers were dissolved in dimethylformamide, at a temperature of 60 °C with constant stirring. A known quantity of this homogeneous solution was poured in glass mould. The solvent was allowed to evaporate by keeping glass mould inside the oven for nearly 6 h. The temperature of the oven was controlled automatically. The specimens were obtained in the form of pellets of size 6 cm$^2$ and 0.45 cm thickness.

### Microhardness measurements

Microhardness measurements on various specimens were carried out using mph 160 microhardness tester with a Vickers diamond pyramidal indenter attached to Carl Zeiss NU$_2$ universal research microscope [14]. The Vickers hardness number ($H_V$) was calculated using the relation:

$$H_V = \frac{1.854 \times L}{d^2}\ \mathrm{kg/mm^2}$$

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

### XRD studies

X-ray diffraction (XRD) has been utilized to detect change in crystalline and amorphous characteristics in the PVF:PVDF polyblends. Specimens were kept in aluminium sample holder in such a way that upper surface is smooth and was exposed to X-rays in vertical goniometry assembly. The scan was taken between (10–80°) 2$\theta$ with scanning speed of 0.02 degree 2$\theta$ per min., the operating target voltage was 35 kV, tube current is 20 mA and radiation used is FeK$\alpha$ with wavelength of 1.93735 Å on Rigaku Rotating anode mode RU-H3R (18Kw), X-ray powder diffractometer. The intensity versus 2$\theta$ scans were obtained for pure PVF, PVDF and PVF:PVDF polyblends.

### SEM studies

The Scanning Electron Microscopy (SEM) of the specimens were recorded on a scanning electron microscope (JEOL-JJM-5600LV) instrument.

## Result and discussion

### Microhardness analysis

The variation of Vickers hardness number ($H_V$), as a function of applied load ($L$) is graphically shown in Fig. 1, for pure PVF, PVDF and their isomorphic blends. The trend is almost similar for all the specimens. Initially, the microhardness increases with the load and thereafter; beyond certain load, $H_V$, tends to attain a saturation value. The load values at which $H_V$ tends to saturate are different for different specimens, the increase in the value of $H_V$, as the load increases, can be explained on the basis of strain hardening phenomenon in polymers [4]. There are micromodes of deformation in the polymer chain [8]. When sufficient numbers of micromodes become active, large-scale plastic

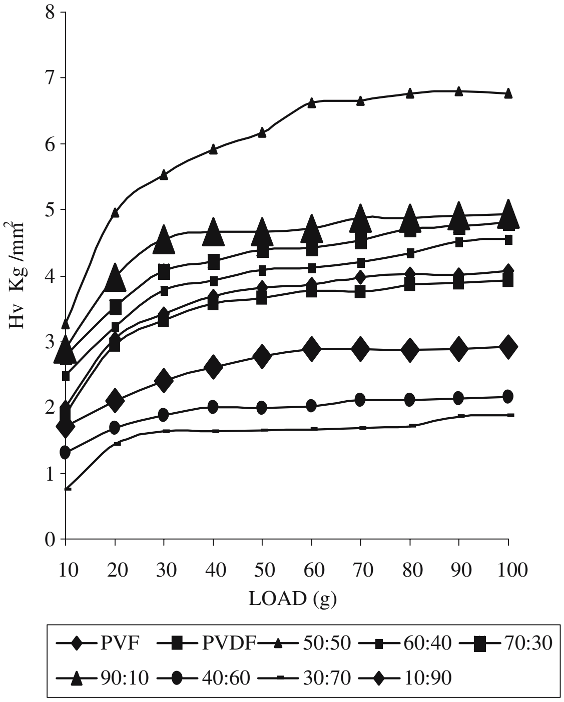

**Fig. 1** Variation of $H_V$ with load for pure PVF and pure PVDF and isomorphic polyblends of PVF:PVDF

deformation begins. As the load is increased, the specimen is subjected to greater strain hardening and $H_V$ is increased [16–18]. Finally, when $H_V$ tends to saturate the polymer specimen is fully strain hardened as no appreciable change in the value of $H_V$ is observed. Pure PVF has higher level of microhardness as compared to Pure PVDF, which is also true from the known strength values of these two polymers. The effect of blending on the microhardness can also be studied from Fig. 1. Initially, when PVDF is blended with PVF in relatively low weight proportion, PVF:PVDF (90:10), the microhardness of the polyblend increases and its value is greater than both pure PVF and PVDF. As the content of PVDF is further increased to 30 wt% and 40 wt% in the polyblend, the level of microhardness is found to progressively decrease, but it is still higher than for pure PVF and PVDF specimens.

Thus, hardened isomorphic polyblends can be obtained when the content of PVDF is relatively low. PVDF, which is a crystallizable polymer when added upto 10 wt% in the polyblend, introduces some crystallinity, which hardens the polyblend. However, the degree of order of this crystallinity decreases with increase in the content of PVDF to 30 wt% and 40 wt% in the polyblend. Moreover, when the content of PVDF is increased to 50 wt% in the polyblend, the microhardness increases to a remarkable extent and attains the maximum value. Also, the shape of $H_V$-load profile for this specimen is found to be curvilinear. This indicates that the blend morphology, when the two polymers are in equal weight proportion is such where the miscibility of the two polymers yields a homogeneous and a compatible isomorphic blend system with greater degree of crystallinity and hardening. However, when the content of PVDF is further increased to 60 wt% and onwards, the microhardness of the polyblend decreases and more plasticized blends are obtained. Thus PVDF acts as plasticizer in the polyblend when the content of PVDF is relatively high as compare to PVF, where PVDF induces softening in the polyblend [18]. When the PVF is major component in comparison to PVDF in the polyblend, the microhardness of the blend specimen increases and the isomorphic blend specimens with 50:50 proportion of two polymers exhibit the maximum value of microhardness.

## XRD analysis

The morphology of most of the polymers is semicrystalline, which is formed by folding and stacking of the polymer chains, the crystalline material shows the higher degree of ordering while in the amorphous structure no long range ordering is observed. The crystallization depends on the degree of miscibility and mobility of crystallizable and non-crystallizable components in the blend specimens. Crystallinity is a measure of regularity in arrangement of structural element. Crystallinity can be estimated by comparing the intensity and width of lines [19, 20]. In crystallization process, a crystallizable substance crystallizes from its melt. The crystallization process of polyblend with crystallizable and amorphous components is affected by the properties of constituent polymers [16, 17]. In the present paper, the crystallinity has been measured on the premise that increasing amorphousness tends to broaden the line width where as increasing crystallinity increase the intensity. For obtaining crystallinity index from XRD patterns of samples, the approach of Hermans and Weidinger has been utilized [11, 14, 21]. Accordingly, the scan is resolved in crystalline peaks, amorphous peaks and the background. The following assumptions are made: (a) the total scattering from the sample is divided between crystalline peaks from the crystallites and amorphous peaks from the remaining amorphous regions. (b) The total scattering from the sample is that included in the resolved crystalline and amorphous regions. (c) The relative areas of the crystalline peak and the amorphous peak are, respectively, proportional to the mass of polymer in the crystalline and amorphous regions. With these assumptions the crystallinity index ($X_c$) is calculated for each sample from the resolved peak areas:

$$X_c = [A\ (\mathrm{Cr})/A\ (\mathrm{Cr}) + KA\ (Am)] = 1/(1 + KR)$$

where $A$ (Cr) is the area of crystalline peak, $A$ (Am) is the area of amorphous peak, $R$ is the ratio of amorphous to crystalline peak areas and $K$ is constant. For comparison, $K$ is set to unity.

XRD pattern has been observed for pure PVF, PVDF and their isomorphic blends. Pure PVDF is crystallizable, showing sharp and narrow peaks (Fig. 2), the calculated values of $X_c$ also supports this observation as shown in

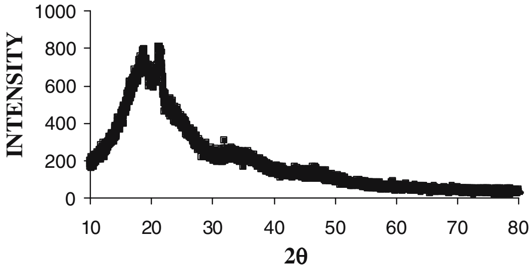

**Fig. 2** X-Ray diffraction for pure PVF

**Table 1** Calculated values of crystallinity for the given crystallizable material pure PVDF and PVDF:PVF polyblend specimen

| S.No. | Specimens | Calculated crystallinity index ($X_c$) |
|---|---|---|
| 1 | Pure PVDF | 2.96 |
| 2 | 50 PVF:50PVDF | 3.46 |

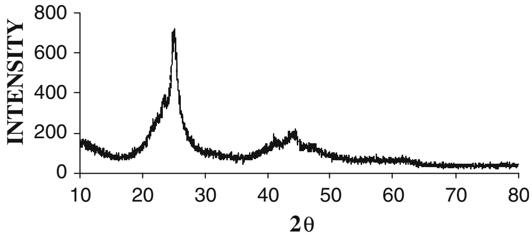

**Fig. 3** X-Ray diffraction for pure PVDF

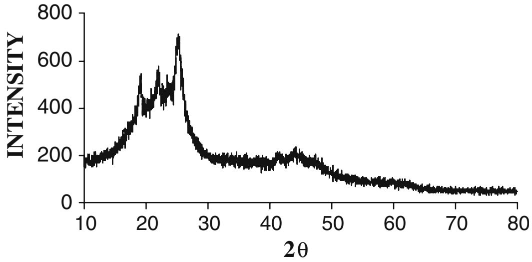

**Fig. 4** X-Ray diffraction for isomorphic polyblends with PVF 50 wt%:PVDF50 wt%

Table 1. Pure PVF is non-crystallizable polymer, and hence the XRD of this specimen shows broad peak (Fig. 3). As the content of PVDF in the polyblend increases, the crystallinity increases. Figure 4 reveals that the maximum crystallization is observed for specimens when the two polymers are blended in equal weight proportion (50:50). The calculated value of crystallinity index shown in Table 1 is also high for this specimen. This feature can be correlated with the microhardness values, where the $H_V$ values are maximum for this specimen amongst the various polyblend specimens. The crystallization of PVDF is affected by the content of PVF present in the polyblend. Thus the crystallization process of the polyblends under investigation having crystallization and amorphous components is affected by the properties of constituent polymers. In the polyblends of PVDF and PVF as PVDF crystallizes, the non-crystallizable component is rejected from the crystal region resulting in broad amorphous population, which has been reported to often affect the properties of polymeric materials like glass transition temperature, crystal growth rate and bulk crystallization rate etc. [22, 23].

## SEM analysis

The SEM micrographs of specimens exhibit interesting trends related to physical properties such as phase structure, chain interpenetrating network and mechanical strength [24–26]. The micrographs of the pure PVF and PVDF and PVF:PVDF blend are shown in Figs. 5–7. SEM of pure PVF (Fig. 5) describes the morphological feature

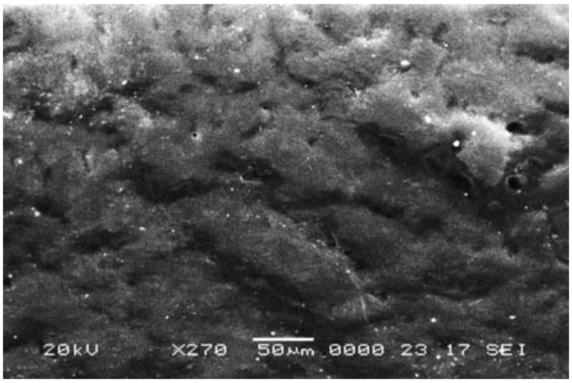

**Fig. 5** Scanning electron microscopy (SEM) photograph of pure PVF

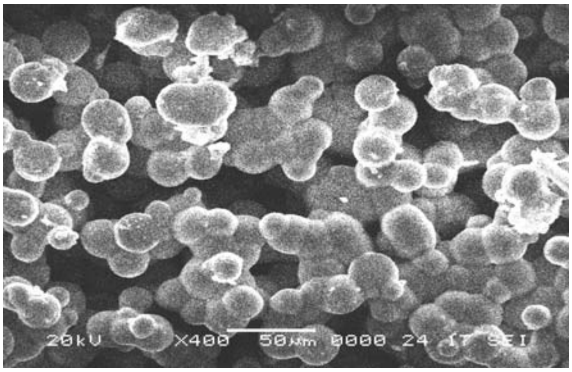

**Fig. 6** Scanning electron microscopy (SEM) photograph of pure PVDF

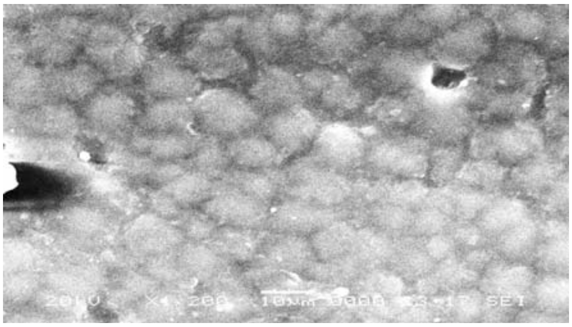

**Fig. 7** Scanning electron microscopy (SEM) photograph of PVF50 wt%:PVDF50 wt%

where a complete chain interaction and formation of pure PVF in a single phase with a smooth surface is observable. The SEM micrograph of pure PVDF (Fig. 6) shows the globular structural morphology with some empty space between the globules.

The SEM photograph of isomorphic blend specimen formed by mixing the two polymers in equal weight proportions (Fig. 7) reveals that voids which were seen in pure PVDF gets completely filled by intertwining allowed by spacing and this blend exhibits a uniform texture with single phase morphology indicating the miscibility of two polymers. A better interfacial bonding between the chains of two polymers can also be inferred from this micrograph. Thus the findings of microhardness, XRD and SEM studies have good correlation for the development of miscible and hardened isomorphic blend with equal weight proportion of two polymers having crystalline characteristic.

## Conclusion

The microhardness, XRD and SEM studies enable us to understand the issues related to the processing, structure and property relationship for pure PVF, PVDF and PVF:PVDF isomorphic blends. These issues include the relationship between morphology, crystallization and plasticization.

The miscibility of PVF and PVDF is clearly shown; when PVF and PVDF are in equal ratio (50:50) in the blend and these specimens have maximum hardening with greater degree of crystallization with uniform texture and single-phase morphology. In the polyblend specimens as the content of PVDF increases the degree of crystallization is increased and as the content of PVF is increased the degree of amorphousness increases. The blends having different weight proportions of two polymers exhibit good correlation with their morphological feature, as obtained from SEM studies. Thus PVF:PVDF isomorphic blends can be developed with optimum weight proportion as a material having a good mechanical properties.

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