ORIGINAL RESEARCH PAPER

Engineering

QUANTITATIVE X-RAY DIFFRACTION ANALYSIS OF POLYBLEND THIN FILM OF IODINE DOPED POLYVINYLIDIENE FLUORIDE (PVDF) AND POLY METHYL METHA ACRYLATE (PMMA)

KEY WORDS: 'Solution cast method', percentage of amorphousness/crystallinity, 4:1 (PMMA+PVDF), AC conductivity, dielectric constants etc.

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ABSTRACT

In the present work X-ray diffraction of PMMA and PVDF (4:1) blend sample have been investigated. The measurement of XRD diffraction scans of the polymer blends is also used as a criterion to determine its miscibility. If two polymers have low compatibility then each polymer would have its own crystal region in the blend films and the X-ray scans of the samples would be expressed as simply mixed scans of the two polymers with the same ratio as those for blending. XRD diffraction scans of PMMA blends with different PVDF contents. The blend compositions show a broad and diffuse peak, which indicates the amorphous nature of the blend. The results have been presented in the form of graphs.

INTRODUCTION

When two or more polymers are mixed together, polyblends or polymer alloys are obtained. This physical mixing or blending of two polymers produces alloys with quite different properties, which can be potentially useful. Two polymers are generally incompatible as they have very low combinatorial entropy of mixing for the components. This is insufficient to overcome the positive heat of mixing of polymers to make the Gibb's free energy of mixing negative. Only in the presence of specific interaction between two polymers (e.g. Hydrogen bonding, acid-base type interaction etc.), heat of mixing is negative that makes the free energy of mixing a negative quantity and then the mixing is spontaneous. Unlike the mixing of small molecules, the dictum *like likens like* does not hold good for mixing of macromolecules. However, both compatible and incompatible blends are industrially important materials. Two polymers may form the compatible blend, which exists as single phase. The incompatible blends on the other hand exist as two- phase system. Since most blends combine immiscible components and so the material that results contains tiny particles of one polymer in a matrix of the other. Controlled mixing and cooling of the blend makes it possible to form the .particles in the optimum concentration and range of sizes. Blending makes it possible to combine the good properties of several polymers. The most direct method to obtain a polyblend is to mix two component polymers in the molten state (melt mixing). In this case the extent of mixing depends on the rate of diffusion of the molecules. Since such a mixing requires high temperature, the polymer may decompose and undergo chemical changes.

X-ray powder diffraction is widely applied for the characterization of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections.

In recent years, applications have been extended to new areas, such as the determination of crystal structures and the extraction of three-dimensional microstructural properties. The method is normally applied to data collected under ambient conditions, but in situ diffraction as a function of external constraints (temperature, pressure, stress, electric field, atmosphere, etc.) it is important for the interpretation of solid state transformations and materials behaviour. Various kinds of micro- and nano- crystalline materials can be characterized from X-ray and neutron powder diffraction, including inorganics, organics, drugs, minerals, zeolites, catalysts, metals and ceramics. The physical states of the materials can be loose powders, thin films and polycrystalline and bulk materials. Quantitative phase analysis involves the determination of the amounts of different phases present in a multi-component mixture. The powder method is widely used to determine the abundance of distinct crystalline phases, e.g., in rocks and in mixtures of polymorphs, such as zirconia ceramics.

Microstructural imperfections, such as lattice distortions, stacking and twin faults, dislocations and crystallite size distributions, are usually extracted from the shape of individual diffraction lines. Recently, profile modelling (synthesis) techniques have extended the frontiers of microstructural investigations. They include the effect of crystallite size distributions, the effect of lattice distortion parameters and the effect of strain fields in crystalline materials [1].

Experimental Technique

Method of preparation of PMMA-PVDF (4:1) Undoped and doped blends film:

Preparation of thin films using Pool of Mercury (As shown in fig 1). In the present work, Isothermal Evaporation Technique [2-3] has been used, as it is best suited to the conditions in the laboratory. The two polymers PMMA-PVDF were taken in the ratio 1:1 were dissolved in the common solvent Dimethyl Formamide (DMF) with iodine doped of 0%,0.5%,1%,2%. The solution was kept for 1-2 days to allow polymers to dissolve completely to yield uniform solution. The solution mixture was stirrer with constant slow uniform speed for 1 hour at room temperature to get completely homogeneous solution.

A glass plate (15 cm x 15 cm) thoroughly cleaned with water and later with acetone was used as a substrate. To achieve perfect levelling (and uniformity in thickness of the films), a pool of mercury was used (figure given below) in a plastic tray. The solution was poured on the glass plate and was allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber at room temperature. The solvent in the solution was thus allowed to evaporate completely and get air-dried.

The film on the glass substrate was then removed and cut into small pieces of suitable sizes. In this way the films were prepared by isothermal evaporation technique. Further it was dried for 1 day to remove any traces of solvent.

Fig. 1 Pool of mercury

The solution was poured on the glass plate and was allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber at room temperature. The solvent in the solution was thus allowed to evaporate completely and get air-dried. The film on the glass substrate was then removed and cut into small pieces of suitable sizes. In this way the films were prepared by isothermal evaporation technique. Further it was dried for 3 days to remove any traces of solvent.

Thickness Measurement

The thickness of each sample film was measured at the four different places by using the Digital Micro meter (Mitutoyo Corporation, Japan) as shown in fig 2. The average of four readings was taken as the sample thickness.

Fig 2. Digital Micrometer

X-ray Diffraction (xrd) Studies

Max von Laue and Co., in 1912, discovered that crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice (Friedrich et al., 1912).

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X-Ray Diffraction (XRD) studies X-ray diffraction is the most useful technique for the determination of the phase identification, nature of sample, particle size analysis, and quantitative identification of the mixture of phases, etc.

The most important and widely used method is Debye Scherrer method for determining the structure of polycrystalline materials including crystalline polymers. This method, known as X-ray Powder Diffraction, was developed by Debye and Scherrer (1916) [5] in Germany.

The uses of this technique are instance qualitative phase identification, characterization of amorphous or crystalline structures, impurity analysis and the study of phase transformation.

The average grain/crystallite size of nono-crystalline products can be determined with XRD [6].

In case of polymer material, the average inter-chain separation can be estimated from maximum intensity in the amorphous halos using the relation [7-8]

$$R = \frac{5}{8}\left[\frac{\lambda}{\sin\theta}\right]$$

Where, R is the polymer chain separation and θ is the diffraction angle at maximum intensity.

The intensity versus 2θ curves is useful for finding out the percentage crystallinity of the sample under investigation. X-ray diffraction is used to identify the second phase and decide the condition of its occurrence. The relation suggested by Kaelble (1967) can be used for the approximate estimation of percentage crystallinity [9-10].

The relation is,

$$\frac{\text{The crystallinity}}{\text{of the sample}} = \frac{\text{Area of crystalline fraction}}{\text{Area of Crystalline fraction} + \text{Area of Amorphous}}$$

Percentage Crystallinity = $[\,I_c \times 100\,] / [\,I_c + k I_A\,]$

Where, I_c - Area of crystalline fraction

I_A - Area of amorphous fractio

k - Constant equal to unity

From optimization study four samples from a series were selected for further study. List of optimized samples along with their wt %, sample codes and thicknesses are given in tables.

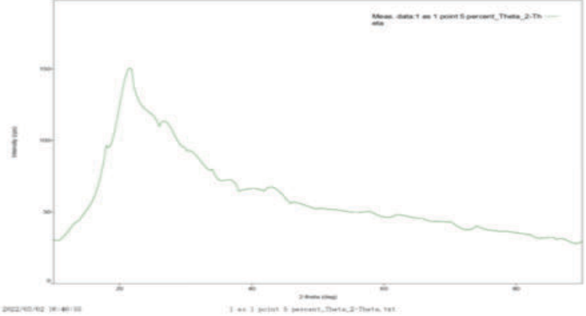
Table: Thickness of Sample of Series

Sr. No.	Sample description	Sample code	Thickness
1	1:1 PMMA-PVDF I2 (0%)	S1	0.041 mm
2	1:1 PMMA-PVDF I2(0.5%)	S2	0.037 mm
3	1:1 PMMA-PVDF I2(1%)	S3	0.040 mm
4	1:1 PMMA-PVDF I2(2%)	S4	0.023 mm

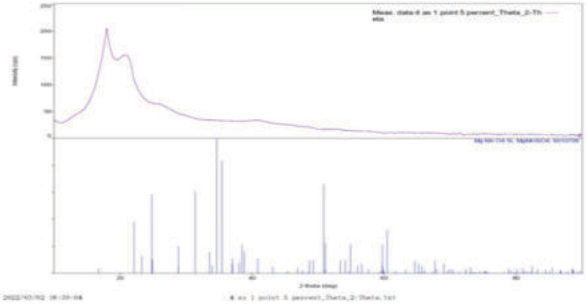
RESULT AND DISSCUSION

In the present work dielectric constant and ac conductivity of 4:1 PMMA-PVDF with iodine doped of 0%,0.5%,1%,2% blend sample have been investigated at various constant temperatures ranging from (313K to 343K), In the frequency range of (1KHz to 500KHz) for X Ray Diffraction. The results have been presented in the form of graphs.

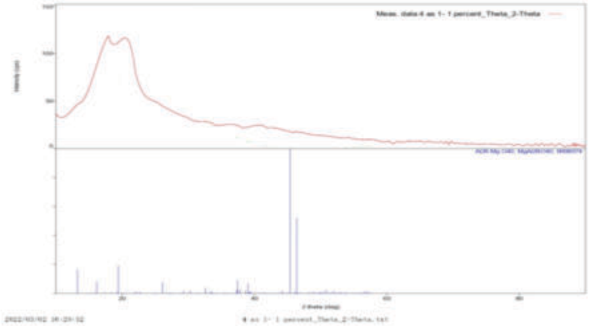
In order to get information about structure and crystallite of sample of prepared polyblends, X-ray diffraction was carried out. XRD pattern of all samples were obtained at room temperature. The scanning angle 2ѳwas varied from 0-80 degree in step of 0.06^{0}and the step time is fixed at 0.2 sec using Cu-Kα radiation.



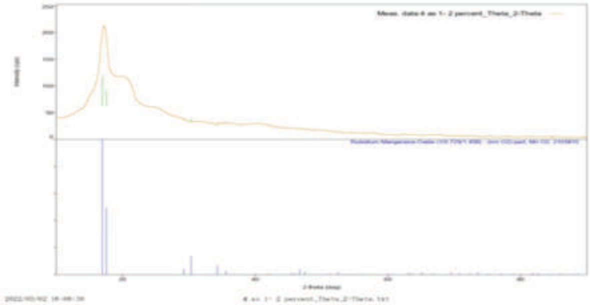
A) XRD Spectra of 4:1 (PMMA: PVDF) with 0% Iodine doped



B) XRD Spectra of 4:1 (PMMA: PVDF) with 0.5% Iodine doped



C) XRD Spectra of 4:1 (PMMA: PVDF) with 1% Iodine doped



D) XRD Spectra of 4:1 (PMMA: PVDF) with 2% Iodine doped

Explanation from Graph

The measurement of XRD diffraction scans of the polymer blends is also used as a criterion to determine its miscibility. If two polymers have low compatibility then each polymer would have its own crystal region in the blend films and the X-ray scans of the samples would be expressed as simply mixed scans of the two polymers with the same ratio as those for blending. XRD diffraction scans of PMMA blends with different PVDF contents are depicted in graphs. All the blend compositions show a broad and diffuse peak, which indicates the amorphous nature of the blend [11].

All samples show the noisy spectra and the peaks were observed between 10° to 25°. This reveals the fact that amorphous nature increases with increase in dopant percentage [11].

Generally, polymer consists of both crystalline and amorphous region. Their conductivity properties are influenced by the presence of amorphous nature.

The peak was observed at the position near about 25°, which is attributed to the amorphous nature. Thus, the x-ray diffractograms of all the samples ensures the amorphous nature with large diffraction maxima that decreases at large diffraction angles. The shape of the first main maximum indicates the ordered packing of the polymer chains. The intensity and shape of second maxima are related to the effect of ordering inside the main chains. The observed broad hymps in the XRD spectrum indicate the presence of crystallities of very low dimensions. The absence of any prominent peaks in the films indicates the predominantly amorphous nature of the films. This is in agreement with the result reported by Na and Rhee [12].

Many polymers are semi-crystalline. The increase in crystallinity reduces conductivity. If the conduction is ionic, ion mobility through the crystalline region will be low; if it is electronic, it will perhaps be faster, but the crystalline-amorphous interface acts as a trapping region. A completely amorphous polymer exists in two states depending upon their temperature (Tg). They undergo transition from glassy to a rubber-like state around Tg. The change in conductivity occurs due to the onset of molecular motion above Tg. The transition between glassy and amorphous states is accompanied by the "freeing up" of charge carriers with the gross molecular motions of the polymer chain. Other types of transitions have also been identified with the onset of other molecular motions in amorphous material. They occur in the order of increasing temperature as under:

a) side chain motions.
b) motion of two four carbon moieties in the main chain (the Schatzki Crank Shaft effect).
c) motion of moieties containing heteroatom in polymer chains.,
d) motion of the entire chain as a unit.
e) motion of segments containing 50-100 backbone atoms (corr. to Tg)

The XRD spectra from graphs shows mostly the amorphous nature of the blends samples.

Therefore we can expect the transition of the samples from glass in to rubbery state thereby increasing the availability of charge carriers at higher temperatures. This explains increase in the conductivity of the blend samples with the increase of temperatures [13-17].

X-ray diffraction analysis revealed the semicrystalline nature of the entire polymer blend which helps for conduction.

CONCLUSIONS

The complexation of the dopant iodine with the host polymer in all polymer electrolyte systems, before and after irradiation is confirmed by XRD studies. XRD study showed the percentage of crystallinity decreases with the increasing concentration of iodine in all complexed systems. Hence the addition of iodine causes a decrease in the degree of crystallinity and a simultaneous increase in the amorphousity. For pure PMMA and PVDF, a slight increase in crystallinity is observed at low percentage of dopant, whereas crystallinity decreases at higher percentage of dopant. This may be due to the cross linking of the polymer chain or by the formation of the single or multiple helices, which induces more crystalline region in the polymer samples. In all polymer electrolyte systems, the presence of dopant iodine prevents polymer chain reorganization resulting in decreased crystallinity compared to pure PMMA and PVDF before and after UV irradiation. Hence it may be mentioned that during irradiation, the energy deposited in the polymer causes chain scission or produce radicals which subsequently decay or cross-link with neighbouring radicals, i.e., both chain scission and cross-linking occur during UV irradiation.

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