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Negative thermal coefficient behaviour, dielectric and mechanical properties of poly(vinyl chloride)/poly(vinyl alcohol) blends



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ABSTRACT

Polyvinyl alcohol (PVA) in polyvinyl chloride (PVC) blends were prepared by using extrusion molding technique in various weight percentages. The prepared blends were characterized by FTIR and SEM for structural and surface morphology study. Further, the DC conductivity was studied by two probe method and found that the 6% of PVC–PVA blends shows high conductivity of $8.34 \times 10^{-7} \text{ S cm}^{-1}$. This increase in conductivity may be due to the extended chain length of blends, which is confirmed by the negative thermal coefficient graphs. The AC conductivity of blends increases with increase in applied frequency. Among all blends, 6 wt % shows high conductivity of $2.59 \times 10^{-6} \text{ S cm}^{-1}$ and low tangent loss of 0.9Ω . The PVC with PVA blends enhances the mechanical strength and modulus property as the percentage of elongation increases up to ~ 660 , hence these polymer blends can be used in many applications like solar cells and gas sensor encapsulation device, low k-dielectric materials, food packing and other electronic devices.

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1. Introduction

Polymer blends is a physical mixture of structurally different polymers which interact with secondary forces like hydrogen bonding. Polymer blends have been widely used in the industry because of environmental and chemical stability, light weight, corrosion resistance, elasticity, high strength and high modulus with a relatively low cost when compared to the conventional materials. It is well-known that the properties of polymer blends are greatly influenced by the method of preparation and surface morphology that is developed during the polymer processing by physical or wet chemical methods [1–3]. The physical properties of polymer blends are controlled generally by many factors such as the nature of polymer, blend composition and interfacial properties such as interfacial adhesion, dispersed phase size, filler factor, shape which are developed during solution blending [4]. In comparison with binary blends, ternary polymer system can be viewed technologically as the next generation multiphase polymers. The fundamental aspect of ternary polymer blends, have substantial commercial significance as adhesives and coating materials [5–8].

In general, plasticisers are well dispersed among plastic polymer molecules and polar group of plasticizer interact with counterpart of polymer molecules by supramolecular force, which is commonly considered as dipole–dipole interactions [9,10].

Poly (vinyl chloride) (PVC) is one of the most common commodity plastics, which has been widely used in the aerospace, automobile, building construction, packaging fields, coating and lamination industries etc., because of its low cost, easy method of preparation, and the broadening of the properties range [11]. Polyvinyl alcohol (PVA) is derived from condensation polymerization of vinyl alcohol. It has low T_g and hence can be used as a plasticizer. It features excellent adhesion to various substrates. Thus large quantities of PVA are produced for use as a binder in emulsion paints, adhesives, and various textile finishing operations [12]. Owing to its inherent high cold flow, PVA is of little value in mouldings and extrusion. PVA is rather brittle and rigid but compounding it with other polymers frequently improves physical properties [13,14]. In order to enhance the mechanical properties and chemical permeability of the blends, the authors made an attempt to fabricate the PVC modified PVA blends with various weight percentages. The prepared blends were characterized by FTIR, SEM. The mechanical property was studied by using Universal testing machine (UTM) and it is found that modified agents significantly improves the fractures and deformation strength in PVC–PVA blends.

2. Experimental

All the chemicals used for synthesis were of Analytical Reagent (AR) grade. Polyvinyl chloride powder form Sigma Aldrich (Aldrich-81387) India has approximately molecular weight (173000,

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M_w/M_n), Poly(vinyl alcohol) (PVA) (Approx, $M_w=10,000$), resin with a $M_w=108,500$ and a $M_n=56,700$ was supplied by Canus Plastics, acetone (TEDIA, 95%) were used as received without further purification. The modified agent is cocoamphodipropionate ($C_{24}H_{44}N_2O_6Na_2$). For conductivity measurements, the pellets were coated with silver paste on either side of the surfaces to provide electrical contacts.

2.1. Preparation of PVC–PVA blends

Polyvinyl chloride (PVC) and polyvinyl alcohol (PVA) were dried for five hours at 100 °C to ensure low moisture levels. PVC/PVA blends were prepared by the extrusion molding technique in a 500 ml step polymerization reactor in the presence of modified agent cocoamphodipropionate. 5 g of polyvinyl chloride and polyvinyl alcohol was dissolved in N-methyl-2-pyrrolidone (25 ml) solvent at 50 °C with constant stirring and preserved in separate beaker. The different compositions of PVA is added in PVC (2, 4, 6, 8 and 10 wt%) were made by weighing the accurate quantities [15,16]. The resulting mixture was sonicated (probe type sonicator was used at lower amplitude of less than 50% at 20 kHz) for 1 h to get a uniform dispersion of the PVA. The mixed solution was added drop-wise in cold ethanol (anti-solvent) under constant stirring, in order to precipitate out the solid mass. The precipitated solid fibrous mass was then vortexed (turbulent motion) using an Ultra Turax at 15,000 RPM for 10 min, kept for 1 day and then filtered off. The obtained mass was dried in ambient condition and grinded using a mortar and pestle. Similarly neat PVC and PVA were processed, which was also subjected to a pre-treatment process, as the blends. This grinded mass was pressed under teflon coated metal mould in a compression moulding machine INC-385 S.C Dey & Co. Upper and lower half portion of the compression moulds were maintained at 170 °C and a pressure of 2 ton was applied for 5 min to fabricate the composite films. The flexible and transparent films were quenched to room temperature, taken out from teflon mould (average dimension – $10 \times 10 \text{ cm}^{-1} \times w$) and used for further studies.

3. Characterization

The above synthesized PVC modified PVA blends were characterized by using Fourier transform infrared spectroscopy (FTIR), the surface morphology of the composites were studied using scanning electron microscopy (SEM).

The FTIR spectra of PVC and its blends were recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature. For recording FTIR spectra, sample powders were mixed with KBr in the ratio of 1:25 by weight and grounded to ensure the uniform dispersion of samples in KBr pellets. The mixed powders were pressed in a cylindrical dye to obtain clean discs of approximately 1 mm thickness [17].

The surface morphology of PVC and PVC / PVA blends were studied by using Phillips XL30 ESEM scanning electron microscope (SEM). The thin film samples are coated on the surface of carbon tape which is mounted on aluminium tab, conducting gold is sputtered on the sample to avoid charging at the sample surfaces and selected areas were photographed.

DC conductivity was measured by using two probe method with Keithely 2100 electrometer to measure the resistance of the copolymer. The samples were prepared in circular disc of 10 mm diameter and 1 mm thickness by pressing with hydraulic press (De-Luxe Trading Company, India. Ltd). The pellets were coated with silver paste on either surface for better contact between electrodes and sample surface [18]. Frequency-dependent electrical conductivity was measured by two probe technique using laboratory made setup. The dielectric tangent loss and dielectric constant are studied by sandwiching the

pellets of these composites between the silver electrodes in the frequency range of 10^2 – 10^6 Hz using the Hioki LCR Q meter.

The tensile properties of PVC and PVC–PVA composites films for different weight percentages (2, 4, 6, 8 and 10 wt%) were measured with a universal testing machine (Instron-5543) under a 1 kN load cell at a constant cross-head speed of 3 mm/min. At least five specimens were tested for each sample, and the tensile properties are measured on an average.

3.1. Microhardness test

The hardness (Shore A) of the studied samples was determined with a Zwick/Roell 3130/3131 DGM 93 18 389.5 hardness tester (Ulm, Germany) in accordance with ASTM D 2240-05. The tests were performed on samples 30 mm in diameter and 6 mm thick. The readings were taken after 10 s of indentation after firm contact had been established with the specimen.

4. Results and discussion

4.1. FTIR spectroscopy and surface SEM

Fig. 1 shows FTIR spectra of pure PVC, which is the most common form used in industry. To the low wave number side of the strong CH_2 deformation mode band near 1375 cm^{-1} , the mid-infrared spectrum of crystalline isotactic PVC has many weak characteristic bands, many sharp bands, which includes bands with maxima near 1330, 1310, 1255, 1220, 1166, 1103, 999, 975, 841 and 809 cm^{-1} . The relative intensity of bands within the infrared spectrum of crystalline, isotactic PVC will be affected to small extents by both the degree of crystallinity and molecular orientation by adding small amount of PVA [19,20]. In blends of PVA doped PVC is commonly polymerized with vinyl group, which gives rise to additional absorption features in the 740 – 710 cm^{-1} region. A weak $-\text{C}=\text{O}$ band observed near 1074 cm^{-1} is usually indicative of the presence of a vinyl group. Fig. 2 shows the SEM images of (a and b) where pure PVC free standing film indicates the smooth surface with some folded lines on it and PVA shows smooth surface without any crack. The blends of 6 wt % shows the PVA is intercalated into the PVC matrix causes internal folding result in the formation of small ribs on its surfaces as shown in Fig. 2(c).

4.2. DC conductivity and negative thermal coefficient (α)

The Dc conductivity of the poly (vinyl chloride)/poly (vinyl alcohol) blends was studied at various temperatures from 35 to

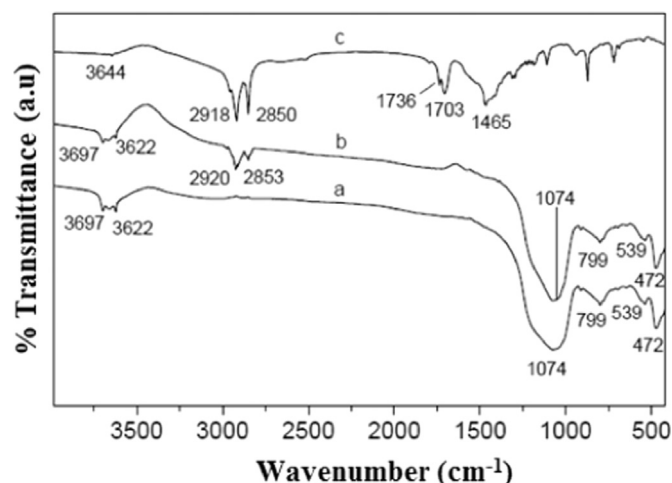


Fig. 1. (a–c) FTIR spectra of PVC, PVA and PVC–PVA blends of 6 wt%.

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