



Microwave irradiation induced modifications on the interfaces in SAN/EVA/PVC and PVAc/BPA/PVP ternary polymer blends: Positron lifetime study



Meghala Dinesh, Ranganathaiah Chikkakuntappa*

Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore 570006, India

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ABSTRACT

Ternary polymer blends of poly(styrene-co-acrylonitrile)/poly(ethylene-co-vinylacetate)/poly(vinyl chloride) (SAN/EVA/PVC) and poly(vinyl acetate)/bisphenol A/polyvinylpyrrolidone (PVAc/BPA/PVP) with different compositions have been prepared by solvent casting method and characterized by positron lifetime spectroscopy and differential scanning calorimetry DSC. Phase modifications have been induced by irradiating the blends with microwave radiation. These changes have been monitored by measuring the free-volume content in the blends. The results clearly show improved interactions between the constituent polymers of the blends upon microwave irradiation. However, the free-volume data and DSC measurements are found to be inadequate to reveal the changes at the interfaces and the interfaces determine the final properties of the blend. For this we have used hydrodynamic interaction (α_{ij}) approach developed by us to measure strength of hydrodynamic interaction at the interfaces. These results show that microwave irradiation stabilizes the interfaces if the blend contains strong polar groups. SAN/EVA/PVC blend shows an increased effective hydrodynamic interaction from -3.18 to -4.85 at composition 50/35/15 upon microwave irradiation and PVAc/BPA/PVP blend shows an increased effective hydrodynamic interaction from -3.81 to -7.57 at composition 20/50/30 after irradiation.

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1. Introduction

An inexpensive and most versatile method of creating new materials with a set of predetermined customized properties is by blending two or more polymers or copolymers. From the thermodynamic point of view, majority of polymer blends are reported to be immiscible. In such blends, the interfacial adhesion is poor and tension will be high [1–3]. The constituent polymers in immiscible blends are driven to minimize their interfacial strength and hence phase separation always occurs. To predict and to control the interfaces in immiscible blends is of great importance because the final properties of the blend in a way solely depend on the nature of interfaces like a weak interface or a strong interface. In other words, adhesion may be poor or strong at the interface. Recently, a new method to explore, characterize and stabilize the interfaces in binary polymer blends was developed by Ranganathaiah et al. [1,2]. The same group later modified this method for ternary polymer blends and successfully tested for few ternary blends [3]. The uniqueness of this method is that it judges whether an interface is

weak or strong conceptualized on hydrodynamic interaction parameter (α) of Wolf et al. [4,5] for polymer/solvent system based on the KRZ (Kirkwood–Risemann–Zimm) model [6]. If this information is readily available, a weak interface can be easily stabilized by following one of the routes like chemical compatibilization, irradiation with energetic radiation etc. [7,8] to improve its strength.

The primary interest in any of the above mentioned routes of compatibilization is to enhance specific interactions between component polymers of the blend so that dispersed phase attains fine dispersion. Of the successful routes adapted in the past [7,8], irradiation with high energy radiation has been widely accepted for compatibilizing immiscible polymer blends [9,10] because irradiation induces phase modification which is economic and it is a clean method to produce materials with enhanced chemical, physical and mechanical properties [11,12]. The known processes observed in polymers and in blends, upon irradiation, are intermolecular cross-linking and chain scission observed in polymers and in blends [11,13,14]. High energy radiation like electrons and gamma rays had been used. However, recently, owing to some advantages over other radiation, microwave radiation has been used to stabilize weak interfaces in binary polymer blends [11] and found to be very promising.

* Corresponding author.

E-mail addresses: crang1@rediffmail.com, cr@physics.uni-mysore.ac.in (R. Chikkakuntappa).

Microwave irradiation technique was introduced by Gedye and coworkers [15] for organic synthesis and later it has been widely used in chemistry to accelerate chemical reactions [16–18]. Since microwaves are of long wavelength, the energy penetrates deeper than ultraviolet or electron-beam irradiation [19]. Further it has many remarkable advantages over conventional heating such as, enhanced reaction rate, higher chemical yield, uniform processing, short reaction time, economically very cheap and clean. Microwaves are usually absorbed by polar molecules in polymers and initiate or further react. The highly reactive polar molecules bring in improved interaction between the blend constituents if they are provided with energy. Therefore, the effect of microwave radiation depends on the polar group of the molecule; stronger the polar nature (more electronegative) interaction will be more [11,20,21].

The aim of the present study is to investigate the effect of microwave radiation on the interfaces in two ternary polymer blends namely SAN/EVA/PVC and PVAc/BPA/PVP. The pre and post irradiated samples were subjected to positron lifetime measurements followed by the evaluation of hydrodynamic interaction parameters to assess the strength of the interaction. Differential scanning calorimetry (DSC) measurements have been carried out to supplement the positron measurements.

2. Experimental

2.1. Sample preparation

Polymers for the preparation of ternary blends were procured from M/s Sigma–Aldrich Chemicals Ltd., Bangalore, India. Ternary blends of SAN/EVA/PVC and PVAc/BPA/PVP of different weight proportions were prepared by conventional solution casting technique. Known weights of SAN, EVA and PVC were dissolved in a common solvent tetrahydrofuran (THF) at 60 °C in four different combinations (a) 50/15/35, (b) 50/35/15, (c) 70/15/15 and (d) 70/21/9, and each solution was cast onto a clean and flat glass plate. The solvent was allowed to evaporate at room temperature for five days and then the samples were dried in an oven at 60 °C to remove any traces of the solvent left in the sample. The neat films so obtained were approximately 1 mm thick. Similarly, blend samples of PVAc/BPA/PVP in four combinations (a) 18/10/72, (b) 42/30/28, (c) 20/50/30 and (d) 7/65/28 were dissolved in THF and prepared in the same way as described above and dried at 60 °C. All the samples were stored in a desiccator before the actual use in experiments.

2.1.1. Microwave irradiation

The ternary polymer blend samples of SAN/EVA/PVC and PVAc/BPA/PVP were first used to measure positron lifetime spectra and DSC scans. Then they were irradiated with microwave radiation using a 30 W (0.03 kGy) Microwave facility available at Department of studies in Physics, University of Mysore, Mysore. All the samples were irradiated for 60 s. By visual inspection, no change in physical condition of the samples after irradiation like color or brittleness etc. was observed. They visually appeared similar to un-irradiated samples.

2.2. Experimental measurements

2.2.1. Differential scanning calorimetry (DSC) scans

The glass-transition temperatures of the homopolymers and their blends of different compositions were measured using a Universal VA.7A TA Instruments DSC Q 200 connected to a liquid nitrogen cooling accessory with a nitrogen purge. For the DSC scan, samples weighing roughly 10 mg were used at a heating rate 10 °C/min, in the temperature range –40 °C to 120 °C for the blend

samples of SAN/EVA/PVC and from 20 °C to 140 °C for PVAc/BPA/PVP blends.

2.2.2. Positron annihilation lifetime measurements

Positron lifetime spectroscopy (PLS) is an established technique to measure directly angstrom-sized free-volume cavities, the fractional free volume and their distribution in polymers [22]. The positron, anti-particle of electron from a radioactive source when injected into a condensed medium like polymer, thermalizes quickly and annihilates with an electron of the medium. Positron in a molecular medium annihilates from different states like free annihilation or trapped annihilation (in defects) or form a bound state called Positronium (Ps). Ps is formed in two spin states: singlet or para (*p*-Ps) and triplet or ortho (*o*-Ps) state. The *p*-Ps annihilates into two photons with ~ 0.125 ns and *o*-Ps annihilates with a lifetime of 140 ns in free space into three photons. However, in polymers, the lifetime of *o*-Ps decreases to a few ns (1–5 ns) due to pickoff annihilation process. The probability of Ps annihilation depends on the overlap of Ps wave function with the electron wave function with which it annihilates. Therefore, the *o*-Ps lifetime depends on the size of the *o*-Ps traps namely free volume cavities [23]. Larger the cavity size (trap size), smaller is the overlap and, hence longer is the lifetime. So, the *o*-Ps pick-off lifetime and its intensity are a measure of the free-volume cavity size and their relative number density respectively [24]. The high sensitivity of PLS arises from the fact that the small size (1.06 Å diameter) of Positronium preferentially localizes in atomic scale free volume cavities [25].

In the present study, the positron lifetime measurements were made using a standard fast–fast coincidence spectrometer equipped with conically shaped BaF₂ scintillators (Scionix, Holland) coupled to photomultiplier tubes of type XP2020/Q having quartz window as detectors. A 17- μ Ci ²²Na positron source, deposited at the center of a pure kapton foil of 12.7 μ m thick, sandwiched between two similar pieces of the sample was placed between the two detectors of the lifetime spectrometer to record the lifetime spectra. A time resolution of 220 ps was measured as monitored by ⁶⁰Co source spectrum. Typical spectrum accumulation time was around 1–2 h with more than a million counts under each spectrum. All the measurements were carried out in an air conditioned room with temperature maintained at 25 \pm 1 °C. The source correction term and instrumental time resolution were estimated from the measured lifetime spectrum of a well-annealed aluminum using the program RESOLUTION [26]. All the acquired lifetime spectra were deconvoluted into three discrete lifetime components using a finite-term lifetime analysis method using PATFIT-88 [26] computer program. The experimental and procedural details of this technique could be found in an earlier work [2].

3. Results and discussion

3.1. Differential scanning calorimetric results

Differential scanning calorimetric experiments were conducted to determine the glass transition temperatures (T_g s) of pure polymers and their respective blends. A phase-separated ternary polymer blend exhibits two or more glass transitions while a miscible blend or a single phase system produces a single T_g . Fig. 1 shows the DSC thermograms for SAN, PVC and EVA polymers in pure form together with untreated and microwave irradiated ternary polymer blends SAN/EVA/PVC for selected compositions only. Fig. 2 shows the DSC scans of pure PVAc, BPA and PVP together with selected compositions of PVAc/BPA/PVP blends. From Fig. 1, we observe that the DSC traces shows two distinct T_g s (scan C around 44 and 80 °C) at composition 70/15/15 and (scan D around

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