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Influence of free volume on the mechanical properties of Epoxy/poly (methylmethacrylate) blends

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Positron lifetime measurements have been performed to investigate the free volume dependence of the mechanical properties of Epoxy/poly methyl methacrylate (PMMA) blends of varying composition of PMMA (2.5, 5, 7.5, 10, 12.5, 15, and 17.5 wt%). The mechanical properties of the blends have been evaluated according to the (ASTM) standard. The positron results indicate that the mechanical properties like tensile strength and surface hardness have a significant dependence on the free volume of the blends. It is also found that the blends of the present study show positive deviation from the familiar linear additivity rule suggesting the immiscible nature of the blends. Further, up to 5-wt% of PMMA in the blend, an increase in relative fractional free volume correlates well with a decrease of tensile strength. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

It has been realized that many physical and mechanical properties of the polymers can be significantly improved by a process called blending [1]. The process of blending may yield phase separation or miscibility in the resulting polymer blends [2]. There has been an increased research with great attention paid to the study of the process of phase separation and miscibility especially from the point of view of the polymer blend applications. In this pursuit, understanding the nature and the underlying process of blending at the molecular level is very essential in order to predict and enhance the material properties of the blends.

In the past, attempts have been made to understand the toughening mechanism by incorporating small amounts of thermoplastic materials into the thermosetting material as toughner [3]. Many investigations in the past had focused attention to correlate the mechanical properties of such material systems to their microstructure [4, 5]. It has been established that microstructural characterization of polymers can be made in terms of the free volume present in the system and in recent years, Positron Annihilation Spectroscopy (PAS) has emerged as a unique and potent probe for directly characterizing the free volume properties of polymers and blends [6]. The ability of a polymer to deform and dissipate energy under impact also depends on the ease with which the chains can slide past each other or change conformations via chain rotations. Hence the chain mobility influences the yield and impact behavior of glassy polymers, which in turn depends on the free volume available in the polymer matrix. The annihilation of positrons can proceed through different channels namely; as free positron annihilation, or the positron can get trapped in defects present in crystalline, crystalline-amorphous interface regions and then annihilates from these sites, or form a bound state with an electron of the medium called the Positronium (Ps) atom. Positronium is called para–Positronium (p-Ps) if the spins are aligned antiparallel to each other and has a lifetime of 123 ps. The spin parallel state is called ortho - Positronium (o-Ps) which annihilates with a lifetime of 140 ns in free space. However in molecular media like polymers, the positron of o-Ps picks up an electron from the surrounding medium and annihilates with a shortened lifetime of few nanoseconds. It has been clearly established that, o-Ps preferentially scans the free volume holes of the polymer system [6–13]. Therefore the o-Ps lifetime parameters namely lifetime (τ_3) and its intensity ($I_3\%$) have been widely used in the study of microstructural behavior of polymeric materials. From this method it is possible

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to understand whether the blending process produces a miscible or immiscible blend with the aid of the free volume linear additivity rule [6]. In the present study, an attempt is made to correlate the free volume properties with the measured mechanical properties namely tensile strength and surface hardness of the blends as a function of PMMA wt%.

2. Experimental

2.1. Blend preparation

The blends of Epoxy/PMMA of different compositions (PMMA wt% of 2.5, 5, 7.5, 10, 12.5, 15, 17.5) were prepared by mixing the solutions of PMMA (supplier *M*/s GSFC with $M_w = 98{,}000$) in toluene and the high performance epoxy resin Araldite LY 5052 (M/s Hindustan Ciba–Geigy) with an epoxy content of 6.75 equivalent/kg. The total weight of the solution was always maintained at 1 g/dl. In order to cure the Araldite LY 5052, hardener HY 5052 was added in the ratio of 100 and 38 parts by weight respectively.

A mould was prepared by coating a thin layer of aqueous solution of PVA, which acts as a good releasing agent. Further, a thin coating of hard wax was applied which was followed by another thin layer of PVA coating. Each coat was allowed to dry for 20 min at room temperature. The Epoxy/PMMA mixture was thoroughly stirred and poured into a cleaned mould. The reaction mixture was dried and allowed to cure at room temperature for 12 hrs. The mixture was post cured by loading these into the vacuum oven, which was maintained at 65 °C for 18 hrs to complete the curing. The toughened Epoxy/PMMA blends were taken out from the mold and stored in vacuum desiccator for several hours before using them in experimental measurements.

2.2. Positron annihilation lifetime measurements

Positron annihilation lifetime spectra were recorded for the pure samples and their blends of different compositions using Positron Lifetime Spectrometer. The Positron Lifetime Spectrometer consists of a fast-fast coincidence system with BaF_2 scintillators coupled to photo multiplier tubes type XP2020/Q with quartz window as detectors. The detectors were shaped to conical to achieve better time resolution. The two identical pieces of the sample under study were placed on either side of a 17 μCi ^{22}Na positron source, prepared on a pure Kapton foil of 0.0127 mm thickness. This sample-source sandwich was placed between the two detectors of PALS to acquire lifetime spectrum. The positron lifetime spectrometer was operated at 220 ps resolution for faster data acquisition. All the lifetime measurements were performed at room temperature and each spectrum contained sufficient counts. Consistently reproducible spectra were analyzed into three lifetime components with the help of the computer program PATFIT-88 [14] with proper source and background corrections. Three Gaussian time resolution functions were used in the present analysis of positron lifetime spectra for the polymer blend samples to get better convergence.

2.3. Measurement of mechanical property

Mechanical properties namely tensile strength and maximum load at break were determined by using Hounsfield universal testing machine (UTM) H50 KM, 50 kN, following the ASTM D–882 standard. Surface hardness of the samples was measured as per ASTM D–785 standards. The above tests were also performed at room temperature, and at least five runs were made and the averages of these are reported here.

3. Results and discussion

3.1. Positron annihilation lifetime results

The o-Ps lifetime τ_3 is related to the radius of the free volume hole size by a simple relation developed by Nakanishi *et al.* [15], which was developed on the basis of theoretical models originally proposed by Tao [16] for molecular liquids and later by Eldrup *et al.* [17]. In this model, Positronium is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_o with an electron layer in the region $R < r < R_o$. According to this model, the relation between τ_3 and the radius R of the free volume cavity is

$$(\tau_3)^{-1} = 2\left[1 - \frac{R}{R_0} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R_0}\right)\right] ns^{-1} \qquad (1)$$

where, $R_o = R + \delta R$ and δR is an adjustable fitting parameter which is determined to be 0.1657 nm. With this value of δR, the free volume radius R has been calculated from Equation 1 and the average size of the free volume holes V_f is evaluated as $V_f = (4/3)\,\pi R^3$. The relative fractional free volume of the sample can then be estimated as

$$F_{VR} = V_f I_3 \qquad (2)$$

where V_f and I_3 are the parameters described above. The positron lifetime parameters so evaluated are tabulated in Table I.

Fig. 1a shows that τ_3 increases by about 400 ps upon adding 5% PMMA, beyond which the changes are very small at higher concentrations. This is reflected in V_{f3} as well. In contrast, I_3 remains essentially unchanged

TABLE I. Free volume data evaluated from positron results

PMMA (wt.%)	τ_3 (ns) ± 0.01	I_3 (%) ± 0.21	V_f (Å)^3 ± 1	$F_{VR} = V_f I_3$ (%)
0	1.57	21.17	59.6	12.6
2.5	1.75	21.28	74.9	15.9
5.0	1.93	23.12	91.1	21.1
7.5	1.94	23.90	91.9	22.0
10.0	1.93	22.18	91.1	20.2
12.5	1.97	21.97	94.7	20.8
15.0	1.99	22.23	96.7	21.5
17.5	1.96	22.14	93.8	20.8
100	2.06	19.41	103.2	20.1

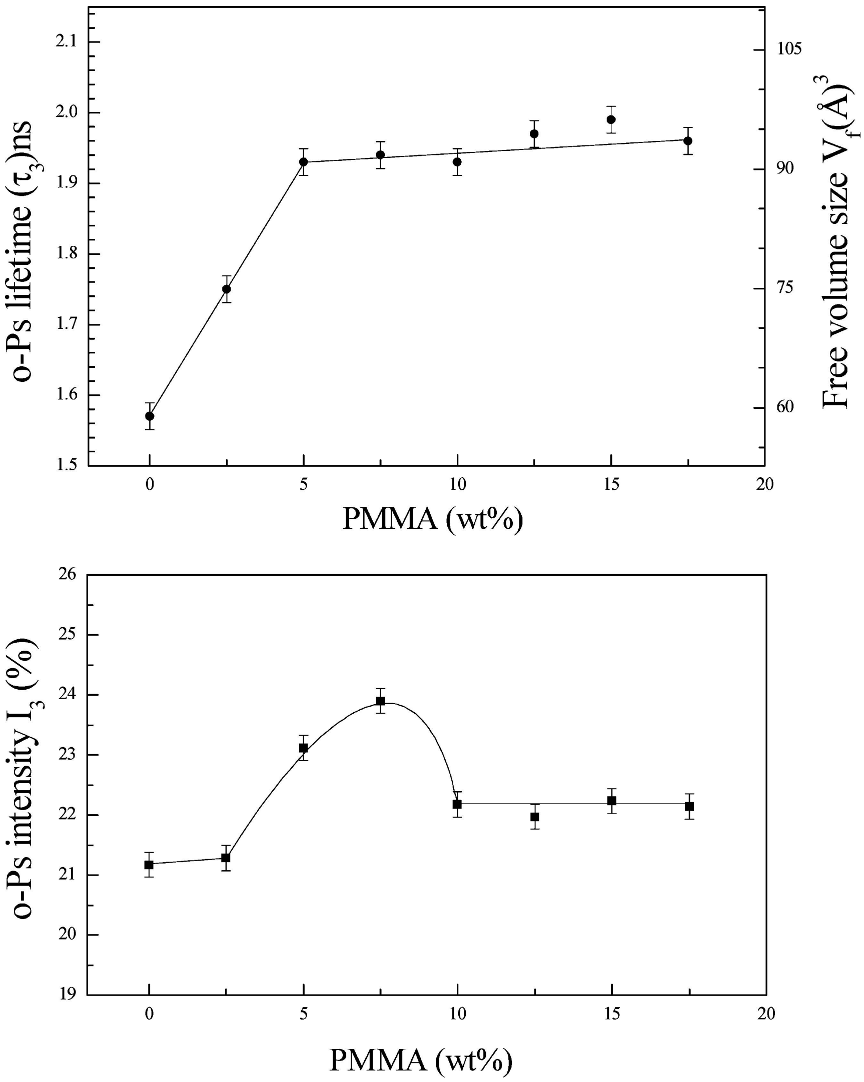

Figure 1 (a) Variation of o-Ps lifetime and free volume hole size (V_f) as a function of PMMA wt%. (b) Variation of o-Ps intensity I_3 as a function of PMMA wt%. A solid line is drawn to guide the eye.

(Fig. 1b). The observed increase in τ_3 from 1.57 to 1.93 ns is due to additional void formation at the interphase between PMMA and epoxy due to poor interaction of the blend components.

The behavior of positron parameters as a function of the polymer blend composition has been explored as a possible criterion in detecting the miscibility [6, 18–20]. A negative deviation from Kelley and Bueche linear additivity relation due to the increased specific interaction has been observed for a blend to be miscible [21]. According to this model the relative fractional free volume of a polymer blend will be the sum of the free volumes of the constituent polymers and is given by

$$F_{VR} = w_1 F_{V1} + w_2 F_{V2} \tag{3}$$

where F_{V1}, F_{V2} and w_1 & w_2 are the relative fractional free volumes and the weight fractions of the constituents 1 & 2 respectively. As we can see from the Fig. 2, the experimental data points show positive deviation from the linear additivity rule, which is a clear indication of immiscibility. In conformity with the earlier observations of Epoxy/PMMA by a different technique namely viscosity measurements, Varada Rajulu *et al.* [22] concludes that the Epoxy /PMMA blends were immiscible which agrees with the present free volume results.

3.2. Tensile strength, maximum load at break and surface hardness results

The measured mechanical properties namely tensile strength, load at break and surface hardness values as a function of PMMA wt% are tabulated in Table II. Fig. 3 shows the variation of F_{VR} and tensile strength as a function of PMMA content. The epoxy system has an average tensile strength of 72.69 MPa, after the incorporation of PMMA, a drastic reduction in tensile strength up to 5.13 MPa is seen. Contrary to this as the PMMA wt% increases, an increase in F_{VR} up to 7.5 wt% of PMMA is observed and there after it remains almost constant. Beyond 7.5 wt% of PMMA, both F_{VR} and tensile strength exhibit constancy within the experimental errors. The variation of F_{VR} and surface hardness as a function of PMMA (wt%) is shown in Fig. 4, and this shows exactly the identical behavior as the tensile strength does.

The above-observed changes in the tensile strength and surface hardness in relation to the relative fractional free volume can be interpreted as follow. The

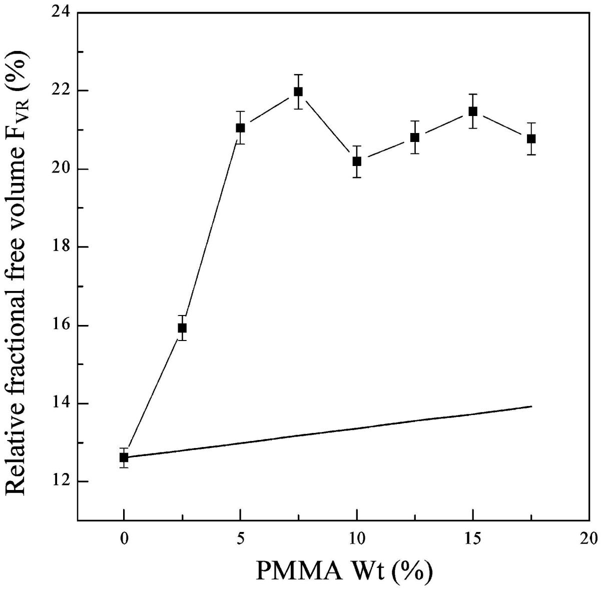

Figure 2 (a) Variation of relative fractional free volume (F_{VR}) as a function of PMMA wt%. Solid line represents the linear additivity rule (Equation 3). Symbols represent experimental points.

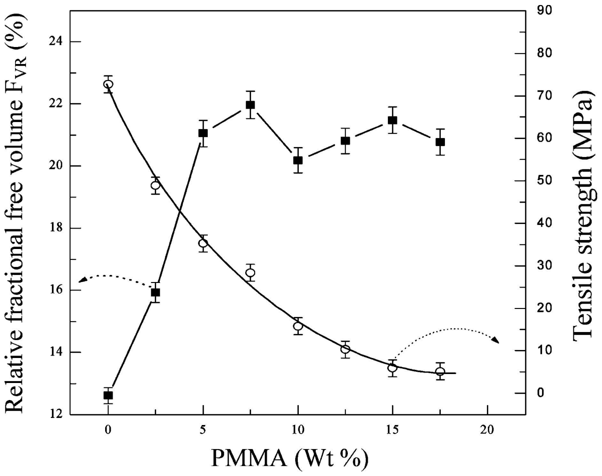

Figure 3 (a) Variation of relative fractional free volume (F_{VR}) and tensile strength as a function of PMMA weight%. A solid line is drawn to guide the eye.

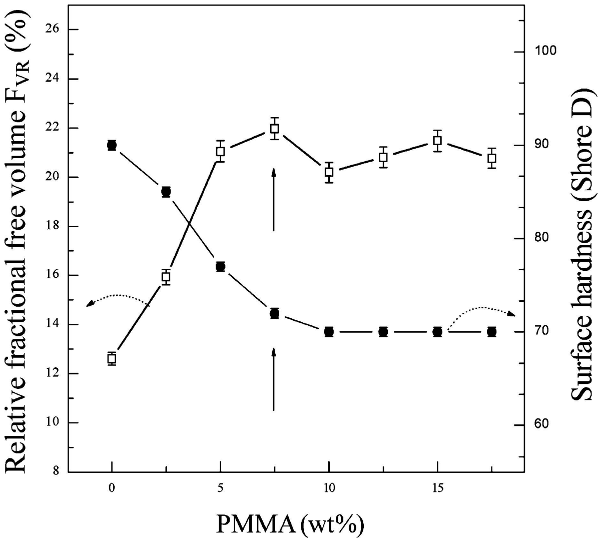

Figure 4 (a) Variation of relative fractional free volume (F_{VR}) and surface hardness as a function of PMMA weight%. A solid line is drawn to guide the eye.

chain mobility influences the yield and impact behavior of glassy polymers [4]. The chain mobility also influences the free volume available in the polymer matrix. Therefore chain mobility; tensile strength, surface hardness and the free volume are interconnected. Reduced chain mobility increases the yield strength but reduces the impact strength [4]. Immiscible blends in general, posses a phase-separated morphology with weak interfaces and inferior mechanical properties. The mechanical properties of partially miscible blends are usually additive in the sense that the blend mechanical properties are resultant of the component polymers or in certain cases, less than additive. The positive deviation from linear additivity with respect to mechanical properties has been discussed in terms of the interactions between the blend components, which lead to greater than additive molecular packing or in other words less than additive free volume [4].

The present study shows that the mechanical properties like, tensile strength and surface hardness are well correlated with relative fractional free volume (F_{VR}) on the lines described above. The possible interpretation that we can offer for the observed variation of F_{VR} with tensile strength and hardness is that, more number of voids i.e., free volume holes have been formed due to debonding of the dispersed phase (PMMA) from the continuous phase (epoxy) [23], which results to poor interfacial adhesion between the components of the blend. In general, a reduction in tensile strength and surface hardness decreases the brittleness of the blends and increases the impact strength of the material. Therefore, it can be concluded that by blending the epoxy with a thermoplastic like PMMA, one can produce a blend with improved impact strength with only about 7.5% of PMMA in it.

4. Conclusions

The positron lifetime results show that the relative fractional free volume (F_{VR}) shows positive deviation from the linear additivity rule. This indicates poor interaction between the blend components resulting in a phase separated morphology and the blends are immiscible. Tensile strength and surface hardness decreases, as the PMMA concentration is increased to 7.5%. This could suggest increased ductility on the blend. No improvement is observed beyond 7.5% concentration. This further confirms the concept that the thermoplastics can be used as the toughner to enhance the toughness of highly cross-linked thermosets like epoxy. The observed variation of relative fractional free volume is opposite to the tensile strength and surface hardness implying the correlation that lesser the free volume more is the tensile strength and surface hardness.

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