Free volume study on the miscibility of PEEK/PEI blend using positron annihilation and dynamic mechanical thermal analysis

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Abstract. High performance polymer blend of poly(ether ether ketone) (PEEK) and poly(ether imide) (PEI) was examined for their free volume behaviour using positron annihilation lifetime spectroscopy and dynamic mechanical thermal analysis methods. The fractional free volume obtained from PALS shows a negative deviation from linear additivity rule implying good miscibility between PEEK and PEI. The dynamic modulus and loss tangent were obtained for the blends at three different frequencies 1, 10 and 100 Hz at temperatures close to and above their glass transition temperature. Applying Time-Temperature-Superposition (TTS) principle to the DMTA results, master curves were obtained at a reference temperature T_o and the WLF coefficients c^0_1 and c^0_2 were evaluated.   Both the methods give similar results for the dependence of fractional free volume on PEI content in this blend. The results reveal that free volume plays an important role in determining the visco-elastic properties in miscible polymer blends.

1. Introduction

The polymers poly(ether ether ketone) (PEEK) is a high performance engineering semi-crystalline thermoplastic having excellent chemical resistance and superior mechanical properties. But, the glass transition temperature (T_g) of this polymer is low (ca. 152 ^{o}C) and hence its modulus decreases beyond this temperature. The poly(ether imide) (PEI) is an amorphous polymer with comparatively high T_g of ca. 215 ^{o}C. Blending with PEI improves the T_g of PEEK and thus PEEK/PEI blend turns out to be a suitable matrix resin in the preparation of high performance composites for aerospace applications. Now, it is known that PEEK and PEI are molecularly miscible in the amorphous phase [1].

The experimental determination of free volume in polymers is of great importance both from the theoretical point of view and for practical applications. The free volume of a polymer influences its molecular motion and physical properties. This in turn will have an influence on their mechanical and visco-elastic properties. The positron annihilation lifetime spectroscopy (PALS) is used for characterizing the free volumes in polymers for decades [2] and later, it is also been used to study the polymer blends [3,4]. Recently, we have studied the miscibility of PEEK and PEI in their blend by studying their free volume behaviour using PALS and identified that when the PEI content in the blend is $\geq$ 50%, there is a high degree of miscibility [4].

The linear visco-elastic properties of the polymers are both temperature and time (frequency) dependant. At ambient temperature, the relaxation process in a polymer occurs over considerably longer times than at higher temperatures. The Williams-Landel-Ferry (WLF) relation is one of the

most popular methods based on time-temperature-superposition (TTS) principle to evaluate the fractional free volume in polymers and is applicable in the temperature range $T_g < T < T_g+100$ °C. The WLF relation is given as

$$\text{Log}_{10}\, a_T = -\, c^0_1\, (T-T_o) \,/\, (c^0_2 + T-T_o)$$

where a_T is the shift factor along the frequency (time) axis and T_o is the reference temperature. The dynamic mechanical thermal analysis (DMTA) is a powerful technique to study the visco-elastic behaviour of the sample. Upon performing DMTA measurements in multi-frequency mode as a function of temperature and applying TTS, a master curve can be obtained at T_o. Using the shift factor derived from the master curve, it is possible to evaluate the WLF constants, which in turn is related to the fractional free volume [5].

In this work, the free volume behaviour of the PEEK/PEI blend for different compositions has been investigated by both PALS and DMTA. When the fractional free volume obtained from PALS results is compared with that of the WLF coefficient obtained from DMTA results, a good correlation is found.

2. Experimental

2.1. Blend preparation
Granular PEEK-grade Victrex 450G having molecular weight of 40,000 g/mol, and a polydispersity of 2.8 was purchased from Victrex, U.K. The PEI-grade Ultem 1000 with molecular weight of 30,000 g/mol and a polydispersity of 2.5 was obtained from General Electric Plastics, Europe. Blends with weight ratios of PEEK/PEI 100/0, 90/10, 80/20, 70/30, 50/50, 30/70 and 0/100 were prepared by melt mixing [4]. These blends are designated respectively as PP_0, PP_{10}, PP_{20}, PP_{30}, PP_{50}, PP_{70} and PP_{100} (where the subscripts represent the wt% of PEI).

2.2. Characterization
The PALS measurements were performed at room temperature using a conventional fast-fast coincidence system having a time resolution of about 200 ps. The lifetime spectra were resolved in to three lifetime components using PATFIT program. The DMTA measurements were carried out using a GABO EPLEXOR 150N using rectangular samples ($10 \times 45 \times 3$ mm^3) in a three point bending geometry. The storage modulus (E′) and the mechanical loss (tan δ) evolution with temperature were registered. To obtain master curves, fresh set of DMTA measurements were conducted between 1 and 100 Hz in isothermal conditions in the glass transition region of the samples. From the master curves, the horizontal shift factor (a_T) was found by shifting the values obtained along the frequency (time) scale using the EPLEXOR-8 software.

3. Results and Discussion

3.1. PALS results
The positron annihilation lifetime results for PEEK/PEI blend series reveal three lifetime components and the variation of the long-lived lifetime component that corresponds to o-Ps pick-off lifetime (τ_3) was used to obtain the free volume hole size using the Tao-Eldrup relation. The average free volume size was calculated using the formula $V_{f3} = (4/3)\pi R^3$. The relative fractional free volume (F_{vr}) is then found as $F_{vr} = V_{f3} * I_3$, where I_3 being the o-Ps intensity.

The average free volume size remains almost constant (ca. 70 Å^3) when the PEI content is ≤ 10% (Fig. 1A). It increases to a value of ca. 78 Å^3 when the PEI content is 30%, and with further addition of PEI, it gradually reverts back close to its original value (ca. 71 Å^3). Generally, it is expected that in a miscible blend, the free volume to decrease with the increase in composition of the other component. At the initial stages of PEI addition may be due to stearic hindrance, the free volume shows a little increase. However, an increase in free volume in a miscible blend with the change in composition of

its other partner is not something new. The free volume of miscible blends may be additive or decrease and is influenced more by segmental conformation and packing than by specific interactions [6]. The decrease in free volume when the PEI content is $\geq$ 50% could be due to close packing of PEEK and PEI chains contributing to greater extent of miscibility [4].
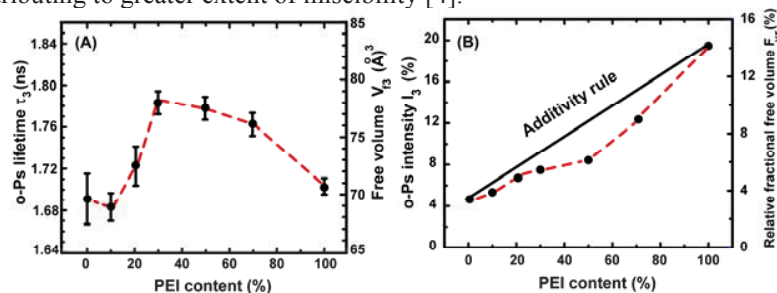

Fig.1. Variation of (A) o-Ps lifetime (τ_3) and average free volume size (V_{f3}) and (B) o-Ps intensity (I_3) and the relative fractional free volume (F_{vr}) as a function of PEI content. The dotted lines are guide to eyes.

Although the change in o-Ps lifetime (τ_3) is not that significant, the o-Ps intensity (I_3) shows a prominent change with PEI content (Fig. 1B). For pure PEEK, I_3 is just ca. 4.7% but with the increase in PEI content, the I_3 value also increases gradually and reaches a value of ca. 20% for pure PEI. The I_3 together with F_{vr} shows a negative deviation from linearity indicating that the blend is miscible at the molecular level and the deviation is more when the PEI content in the blend is $\geq$ 50%. The large negative deviation of F_{vr} when the PEI content is $\geq$ 50% also reveals that the PEEK/PEI blend achieves a high degree of miscibility at higher PEI content.

3.2. DMTA results

The DMTA measurements are used to evaluate the stiffness of the polymer and molecular segmental mobility under dynamic conditions. The storage modulus (E') of PEEK is higher than that of PEI. This could be due to the semi-crystalline nature of PEEK while PEI is completely amorphous. The study on mechanical deformation as a function of temperature also helps to find the glass transition temperature (T_g). The T_g is generally identified from the temperature at which the E' value drops significantly or at which the tan-δ is maximum. In the present case, all the blends showed a single transition in terms of drop in E' value as well as a single tan-δ peak that shifts to high temperatures with increase in PEI content. This infers that the blend possess a single T_g and is completely miscible in all the proportions studied, in agreement with earlier findings [1].
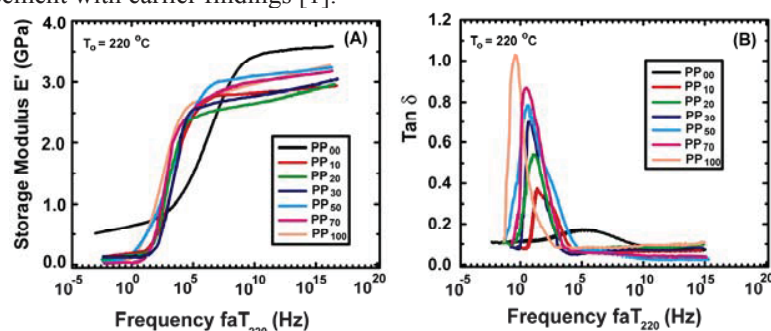

Fig.2. The master curves for (A) storage modulus (E') and (B) Tan-δ for various PEI content in the blend.

The glass transition events in these blends were further explored by the construction of master curves applying TTS using separate isothermal measurements performed at 1, 10 and 100 Hz in the glass transition region. The generated master curves of E' and tan-δ at T_o = 220 °C (T_o is selected close to or slightly above T_g for the entire blend compositions studied) are shown in Fig. 2(A) and (B). The

resulting master curve makes the estimate of E' and tan-δ possible for a wide frequency range. The data superpose very well and the uniformity of the curves indicates that the TTS principle is valid for all the blend samples studied. Both the master curves of E' and tan-δ show a regular shift of T_g to lower frequencies with increase in PEI content. Such a shift of the master curve to low frequencies reveals the presence of long relaxation times due to increased T_g [7].

Using the values of the shift factor (a_T) deduced from E' and tan-δ master curves, a plot of (T-T_o)/log a_T against (T-T_o) is made for each of the blends that showed a linear behavior which confirms that the viscoelastic properties in this blend follow the TTS principle. Using these linear plots, the WLF coefficient c^0_1 has been obtained from the reciprocal of the slope and the coefficient c^0_2 from the intercept.

$$c^0_1 = B/2.303\ f\ ; \qquad\qquad c^0_2 = f/\alpha_f\ ; \text{ and} \qquad\qquad \alpha_f = B/2.303\ c^0_1\ c^0_2$$

where α_f is the thermal expansion of the free volume (V_f) that is related to the total volume (V) as $f = V_f\ /\ V$, where 'f' is the fractional free volume.

3.3. Correlation between PALS and DMTA results

The plot of F_{vr} of PALS results against the fractional free volume of DMTA results, a good correlation is obtained (see Fig. 3). So, PALS measurements can be used to obtain information on dynamic processes in miscible polymer blends.
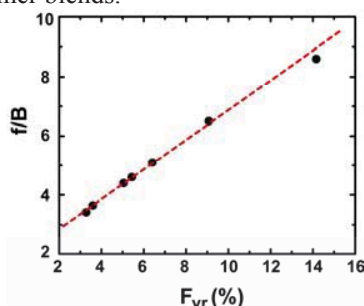

Fig.3. Correlation between relative fractional free volume (F_{vr}) from PALS and *f/B* from DMTA results.

4. Conclusions

The results reveal that PEEK/PEI blend is miscible in all the proportions studied. A good correlation is obtained between the F_{vr} found from PALS and the fractional free volume derived from DMTA results. This reveals that the two techniques provide essentially the same information on free volume in this high performance polymer blend.

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