Free volume and damping in a miscible high performance polymer blend: Positron annihilation lifetime and dynamic mechanical thermal analysis studies

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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 behavior at different compositions of PEI using positron annihilation lifetime spectroscopy (PALS). The damping property of the blend was studied using tan-δ obtained from dynamic mechanical thermal analysis (DMTA). The dependence of tan-δ on temperature revealed that the blend is miscible in all compositions, in agreement with earlier studies. The tan-δ peak height is found to increase with increase in free volume fraction for the entire blend composition signifying that the free volume plays an imperative role in understanding the damping property. Using DMTA, master curves were obtained at a reference temperature T_0 by applying the time-temperature-superposition (TTS) using Williams-Landel-Ferry (WLF) relationship. From the shift factor a_T, the WLF coefficients c_1^0 and c_2^0 were evaluated, using which the free volume fraction was found. Both PALS and DMTA methods were found to give similar results for the dependence of free volume for various PEI contents studied in this blend. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42961.

INTRODUCTION

Thermoplastic aromatic polyketones are commonly referred to as high performance polymers as a result of their rigid aromatic backbone structure, which confers outstanding physical and mechanical properties and enables them to be used in many engineering applications. Amongst high performance polymers, poly(ether ether ketone) (PEEK) is a semi-crystalline thermoplastic polymer having good chemical resistance and outstanding mechanical properties. This polymer finds use as a matrix material in the preparation of thermoplastic composites owing to its good adhesion to glass and carbon fibers but possess a low glass transition temperature (T_g) of ca. 145°C.[1–3] The polymer poly(ether imide) (PEI) is an amorphous polymer with comparatively high T_g of around 215°C but has a lower chemical resistance than that of PEEK.[2,3] To combine the complimentary properties of both the polymers, PEEK/PEI blend has been under several investigations for more than two and half decades.[1–7] Earlier studies have revealed that PEEK and PEI forms a miscible blend at the molecular level.[2,3]

The PEEK, PEI, and their blend find application in aerospace and automobile industries.[8] When used in such industrial applications, structural crashworthiness will be an essential requirement and so the knowledge on their damping behavior is essential. Damping is an important model parameter for the design of various structures that are required to be dynamically stable. Damping in polymers indicates the ability for energy absorption and subsequent dissipation, which in turn depends on the internal friction between the chains.[9] More often, damping in polymeric materials is considered as a boon. For example, high damping is an essential requisite for products like vibration dampers, bridge bearings etc., which reduce the amplitude of undesirable vibrations in various structures including those used in aerospace applications. If a polymer possesses good damping property, it can significantly enhance its impact energy dissipation. Failure to dampen the excessive vibrations can lead to fatigue failure of the polymeric material.[10]

Free volume is one of the important parameters that influences the impact strength of a polymer.[5,11–13] Free volume exists in polymers due to imperfect packing of the long polymer chains and controls the molecular mobility.[14] The impact strength of a polymer depends on its ability to absorb or dissipate energy, which in turn requires certain chain mobility.[11,15] Thus, impact resistance of the sample improves with the increase in chain flexibility and is also related to free volume and damping. Since amorphous polymers in glassy phase possess less free volume

than in rubbery phase, the glassy phase has low impact strength compared to rubbery phase.[15] Incorporation of flexible diamines into epoxy network has been reported to show improvement in impact strength.[16] Studies on physical ageing in polymers have resulted to reduced free volume as well as low impact strength.[17]

Polymers with good impact strength will have good damping ability.[17,18] It is necessary to highlight here the high impact strength of polycarbonate (PC).[19] The high free volume in polycarbonate is due to methyl substituents that hinders chain packing and flexible carbonate linkages that reduces rigidity. Thus the impact strength of PC is high.[15,18] Imperative contribution that relates free volume and damping property in PC has been reported by Bo Wang and coworkers.[20–22] In their study on multi-walled carbon nanotubes (MWCNTs) incorporated PC, the authors have found a weak interfacial slip between the MWCNT and PC that lead to high mechanical damping due to increased free volume.[20–22] The above examples clearly reveal that free volume, impact strength, and damping in polymers are interrelated and thus needs a clear understanding of their behavior in various polymeric systems.

The free volumes in polymers are characterized mainly using positron annihilation lifetime spectroscopy (PALS) for decades[23] and later, it has also been applied to study the polymer blends.[3,24–26] In the physical aspect, PALS considers two most fundamental parameters time and dimension. This technique is based on the fact that the lifetime of positron and its bound state with an electron called positronium (Ps) are sensitive to the existence of structural inhomogenities in polymers. This localized annihilation in "free volume holes" makes it the microprobe of choice since the obtained lifetime becomes a measure of the electron density and free volume size, both of which helps to understand the polymer microstructure.[14,27]

A common method to measure the damping in polymers is by dynamic mechanical thermal analysis (DMTA). This method provides information both on the storage modulus (stiffness) and damping ability of a polymer upon subjection to dynamical deformation.[28] More precisely, the storage modulus (E') describes the ability to store the energy and is related to the elastic nature of the polymer. The loss modulus (E") is related to the energy dissipation ability of the material and is a measure of viscous component of the polymer. The tan-δ is the damping factor which is the ratio of E" to E' and describes the ratio of the energy dissipated to energy accumulated in one deformation cycle and represents mechanical damping or internal friction in a visco-elastic system.[20,22,28,29] A high value of tan-δ indicates that the material has a high non-elastic strain component, whereas a low value implies that it has more elastic component. Polymers having tan-$\delta > 0.3$ over a wide temperature range show good energy dissipating capabilities and suitable to be used as damping materials.[30,31]

Since free volume plays a significant role in the glass transition phenomenon in polymeric materials,[14] we felt it worth to understand whether there is a correlation between the free volume obtained from PALS and tan-δ obtained from DMTA measurements. This is because tan-δ which is a measure of

damping is also related to the glass transition temperature (T_g).[20,28] Both the methods have yielded similar results in identification of α, β, and γ transitions in polymers,[32] understanding physical ageing in polymers,[33] miscibility of polymer blends,[34] and cross-link density.[35] Furthermore, a number of investigations in various polymers have shown that the visco-elastic properties obtained from DMTA are closely related to free volume obtained from PALS.[16,18,27,36–38]

The time-temperature-superposition (TTS) has long been used to obtain temperature-independent master curves for polymer systems by shifting the values of dynamic storage modulus or tan-δ along the frequency axis.[39,40] By applying WLF relationship which is a corollary of TTS principle and by evaluating WLF constants, it is possible to obtain free volume fraction. Although, the TTS has been successfully applied to compatible polymer blends over the past two decades,[39,40] the correlation between free volume fraction obtained from PALS and that from DMTA has been reported for polymers in the recent years.[16,20,22,29,41] To the best of our knowledge, there are no attempts to check whether such a correlation is possible in miscible polymer blends.

Despite, the PEEK/PEI blend has been the subject of several investigations,[1–7] previous free volume studies have been limited to the constituent polymers PEEK and PEI alone. Recently, we have explored the miscibility of PEEK/PEI blend at the molecular level through free volume studies using PALS.[3] On the other hand, DMTA studies were focused mainly on miscibility and relaxation process in PEEK, PEI, and their blends.[6,42–44] In spite of the prominent utility of PEEK and its blends in aerospace applications,[8] there are no scientific reports to understand the damping behavior of this blend to the available free volume in it. In this work, we have made an attempt to explore the free volume and damping properties in this blend using PALS and DMTA techniques. The study has also been extended to explore whether there is a correlation between the free volume fractions obtained using these two techniques.

EXPERIMENTAL

Sample 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 polydispersity of 2.5 was obtained from General Electric Plastics, Europe (which is now the part of portfolio of Sabic Innovative Plastics). 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. Details of the blend preparation can be found in our earlier reports.[3,7] These blends are designated as PP_0, PP_{10}, PP_{20}, PP_{30}, PP_{50}, PP_{70}, and PP_{100}, respectively (where the subscripts represent the wt % of PEI). The chemical structures of the PEEK and PEI are shown in Scheme 1.

Characterization

Positron Annihilation Lifetime Spectroscopy (PALS). In PALS method, positrons are injected into polymers from a radioactive source. The positrons upon entering a polymer can form a bound state called positronium (Ps) that exist either as *ortho*-positronium (*o*-Ps) or *para*-positronium (*p*-Ps). In *p*-Ps, the
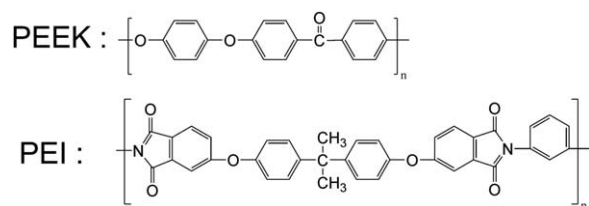
Scheme 1. Chemical structures of PEEK and PEI.

spins of positron and electron are anti-parallel, and has an intrinsic lifetime of around 0.125 ns in vacuum while in o-Ps, the spins of the electron and positron are parallel and has an intrinsic lifetime of 142 ns in vacuum.[14] In condensed matter, the o-Ps annihilate through a fast channel called pick-off annihilation on account of which, the o-Ps lifetime gets reduced to a few nanoseconds. The pick-off annihilation lifetime is inversely proportional to the overlap of the positron and electron wavefunction and this can be related to the size of the "free volume hole", where the annihilation takes place.[14]

The PALS measurements were performed at room temperature using the 'fast-fast' coincidence system of the Department of Studies in Physics, University of Mysore, Mysore, India. The spectrometer has a time resolution of 220 ps when measured using a ^{60}Co source with energy windows set to ^{22}Na events. The positron lifetime spectra were analyzed into three components using PATFIT program.[45] Since the o-Ps pick-off annihilation characteristics (τ_3, I_3) were the main parameters of interest for polymeric materials, only they have been considered for discussion.[3,14]

To calculate the average hole size from the o-Ps lifetime (τ_3), we have used the relation between τ_3 and the radius of free volume (R) which is based on Tao-Eldrup model[46,47] and is given by

$$\tau_3 = 0.5 \left[1 - (R/R_o) + (1/2\pi) \sin 2\pi(R/R_o)\right]^{-1} ns \quad (1)$$

where $R_o = R + \Delta R$ with $\Delta R = 0.1656$ nm is the fitted electron layer thickness.[14] Using this value of R, the average free volume size at different compositions of the blend was found as $V_{f3} = (4/3)\pi R^3$. The o-Ps intensity I_3 depends on the probability of o-Ps formation and is often considered by many authors[3,14,18,20,27,28,35,41] that it may be proportional to the number of free volume holes in the matrix in which the o-Ps gets localized. The free volume fraction F_v in a polymer can then be estimated using the relation $F_v = C V_{f3} I_3$, where the parameter C is termed as structural constant that can be obtained from other experiments.[14,20] However, to observe the relative change in free volume fraction, the parameter, $F_{vr} = V_{f3} I_3$,[3,14,20] has been used to discuss the results.

Dynamic Mechanical Thermal Analysis (DMTA). The DMTA measurements were carried out using a GABO EPLEXOR 150N with rectangular samples ($10 \times 45 \times 3$ mm^3) in a three point bending geometry. Samples were heated from ambient temperature up to 250°C at a rate of 2°C/min in air medium, with a measurement frequency of 10 Hz. Displacements and force amplitudes were set and the parameters were kept constant for all the measurements. The variation of storage modulus (E') and tan-δ with temperature were registered. To obtain master curves, fresh set of DMTA measurements were conducted

between 1 and 100 Hz in isothermal conditions in glass transition region of the samples (130°C to 250°C) at every 2°C. Master curves for E" and tan-δ were generated using the data for a particular reference temperature ($T_0 = 220$°C), applying Williams-Landel-Ferry (WLF) relationship which is based on time-temperature-superposition (TTS) principle.[39–41] The WLF relationship is given as

$$\log a_T = -c_1^\circ (T - T_0)/(c_2^\circ + (T - T_0)) \quad (2)$$

where c_1^0 and c_2^0 are the constants evaluated at the reference temperature T_0, T is the temperature in Kelvin and a_T is the dimensionless horizontal shift factor along the frequency (time) axis. This WLF relation is usually valid for polymers over the temperature range $T_g < T < T_g + 100$°C.[48] This equation is based on the assumption that above T_g, the fractional free volume f increases linearly with T. Here, $f = V_f/V$ where V_f is the free volume and V is the total volume. The total volume V is the sum of free volume V_f and an occupied volume V_o which includes not only the volume of the molecules as represented by their van der Waals radii but also the volume associated with vibrational motions.[16] The shift factor a_T was evaluated from the analysis of E' master curve by shifting the values obtained along the frequency (time) scale using the EPLEXOR-8 software. The WLF parameters c_1^0 and c_2^0 can be evaluated using eq. (2) and are related to the free volume fraction f_0 as[16,41]

$$c_1^0 = B/2.303 \ f_0 \quad (3)$$

$$c_2^0 = f_0/\alpha_f \quad (4)$$

$$\alpha_f = B/2.303 \ c_1^0 c_2^0 \quad (5)$$

where f_0 is the free volume fraction at the reference temperature T_0, α_f is the thermal expansion coefficient of free volume relative to the total volume, and B is an empirical constant assumed to be unity.[16,41] Using the value of α_f (obtained from eq. (5)) the free volume fraction f_0 can be found.

RESULTS AND DISCUSSION

First, we will discuss the free volume results from PALS and then compare it with the damping and free volume fraction obtained using DMTA measurements. Since we have recently reported the detailed free volume study on this blend using PALS,[3] we briefly discuss the salient features here for the sake of completion as well as to strengthen further discussions and understanding of DMTA results.

PALS Results
The PALS results of PEEK/PEI blend and the free volume parameters derived from them are tabulated in Table I. At the initial stages of PEI addition, the slight increase in free volume size could be attributed to stearic hindrances experienced by the chains due to the addition of dissimilar moieties. The o-Ps lifetime (τ_3) decreases when the PEI content in the blend is ≥ 50% due to decrease of free volume size on account of close packing of PEEK and PEI chains.[3] 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. The pure PEEK has I_3 value of ca. 4.7% and with increase in PEI content, the I_3 value increases and for pure PEI, it reaches to ca. 20%. Addition of amorphous PEI to semi-crystalline PEEK leads to an increase in the

Table I. PALS Results of PEEK/PEI Blend

Sample	τ_3 (ns)a	I_3 (%)a	V_{f3} (Å)^{3a}	F_{vr} (%)a
PP$_0$	1.690 ± 0.032	4.7 ± 0.2	69.7 ± 2.2	3.28
PP$_{10}$	1.682 ± 0.024	5.2 ± 0.2	69.0 ± 1.7	3.59
PP$_{20}$	1.713 ± 0.023	7.1 ± 0.2	71.6 ± 1.7	5.08
PP$_{30}$	1.782 ± 0.018	7.0 ± 0.2	77.7 ± 1.3	5.44
PP$_{50}$	1.776 ± 0.013	8.3 ± 0.2	77.2 ± 1.0	6.41
PP$_{70}$	1.765 ± 0.012	11.9 ± 0.2	76.2 ± 0.9	9.08
PP$_{100}$	1.703 ± 0.010	20.0 ± 0.2	70.8 ± 0.7	14.16

a Extracted from results published in Ref. 3.

amorphous content of the blend and hence the number of *o*-Ps annihilation sites also increases in accordance with the known concept.[14] If there is a favorable interaction between the two components of a polymer blend, generally a reduction in free volume content is observed than that is predicted by a simple additivity rule (negative deviation) indicating that the blend is miscible. A positive deviation from additivity suggests an immiscible blend and a partially miscible blend will show neither positive nor negative deviation.[24] In this blend, the F_{vr} value exhibits a negative deviation from additivity rule indicating that the blend is miscible in all proportions. However, maximum negative deviation has been observed when the PEI content in the blend is 50%, which infers that PEEK/PEI blend has achieved high degree of miscibility at this composition.[3]

DMTA Results

The ability of DMTA to determine the molecular relaxation behavior of small chain segments helps it to detect the phase inhomogeneity even at low scales.[49] Hence, it has been considered as a classical method for the determination of blend miscibility. In DMTA, the glass transition temperature (T_g) is generally identified from the temperature at which the storage modulus (E') value starts to drop significantly or the temperature at which the damping factor (tan-δ) becomes maximum.[21,28] The Differential Scanning Calorimetry (DSC) is the more commonly used method to determine the T_g of polymers and blends. The DSC measures the differential heat flow between the sample and the reference. Since, mechanical changes are more dramatic than heat flow changes, DMTA can detect short-range motion due to β and γ transitions that occurs before T_g, which is not possible by DSC. Also, the T_g of highly cross-linked polymers cannot be easily detected by DSC since the amount of heat exchange is small during the transition but can easily be identified by DMTA. Thus, DMTA that can able to identify the onset of main chain motion even if the amorphous content is less and has been realized as more sensitive to T_g than DSC.[49]

The variation of E' and tan-δ as a function of temperature for various compositions of the blend are given in Figure 1(A,B), respectively, and the results are also tabulated in Table II. The temperature profiles of E' exhibit some characteristic mechanical features. All of them show three distinct regions; a high modulus glassy region where the segmental mobility is restricted, a transition zone where a substantial decrease in E' is observed and a rubbery region (flow region) where the modulus remains minimum. The high modulus in the glassy phase is because the molecular motions are largely restricted to vibration and short rotational motions in this state, as there is less free volume. The drop in modulus is due to micro-Brownian motion of the main chain associated with glass transition temperature and subsequent segmental relaxation. At high temperatures > 220°C, the rubbery plateau is reached in which the modulus remains minimum. In the rubbery phase, the translatory motions that occur in the liquid state are prevented by chain entanglements that act as temporary cross-links and this contributes to the observed minimum modulus.[44]

The PEI (sample PP$_{100}$) shows an initial modulus of ca. 2.9 GPa and a drastic modulus drop at ca. 170–210°C as it passes the glass-rubbery transition [Figure 1(A)]. But, PEEK (sample PP$_0$) exhibits comparatively higher storage modulus (ca. 3.9 GPa) and the drop in modulus (ca. 140–190°C) is less severe at the T_g region. This is because PEEK is a semi-crystalline polymer, where the crystalline chains will remain intact until they reach their melting temperature T_m (ca. 340°C),[7] while the amorphous part
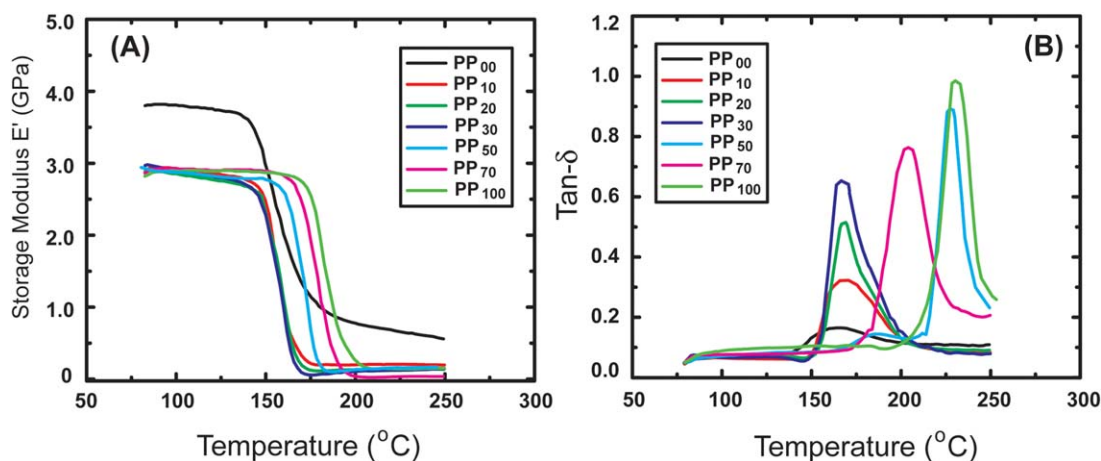

Figure 1. The DMTA results of PEEK/PEI blend for various PEI contents showing (A) storage modulus (E') versus temperature and (B) damping factor (tan-δ) versus temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. DMTA Results of PEEK/PEI Blend

Sample	c_1°	c_2° (°C)	$\alpha_f \times 10^{-4}$ (°C^{-1})	T_g from E' (°C)	Tan-δ			
					T_g from tan-δ peak value (°C)	Temperature range (°C) (having tan-$\delta > 0.3$)	ΔT (°C)	Damping intensity (tan-δ_{max})
PP$_0$	29.23	51.06	2.91	140.2	163.1	–	–	0.165
PP$_{10}$	27.40	38.48	4.12	143.7	163.9	162 to 176	14	0.342
PP$_{20}$	22.73	32.40	5.90	144.2	164.2	162 to 179	17	0.523
PP$_{30}$	21.74	29.28	6.82	146.7	164.9	159 to 188	29	0.689
PP$_{50}$	19.60	25.08	8.83	161.2	201.2	188 to 224	36	0.762
PP$_{70}$	15.38	21.90	12.89	168.8	225.8	220 to 242	22	0.943
PP$_{100}$	11.62	20.67	18.08	174.2	226.3	220 to 248	28	0.992

only undergoes segmental motion on passing T_g. So, PEEK exhibits its modulus drop to a lesser extent as it passes T_g as compared to PEI. The obtained values of E' for PEEK and PEI are comparable to that reported.[6,50] Even with a small addition of PEI (10 wt %) to PEEK, the E' value drops significantly and the mechanical stiffness reaches close to that of PEI. However, in the transition zone, the drop in modulus occurs at slightly higher temperature for the blend with PEI. This reveals that PEI addition has significantly reduced the elastic nature of PEEK and its T_g is increased.[21] With the increase in PEI content in the blend, the modulus drop occurs at increased temperatures, but remains within the temperature limits of modulus drop for PEEK and PEI. The single step drop in modulus for all the blend compositions suggests that PEEK and PEI are completely miscible in all proportions, in agreement with earlier studies.[6,43] Even in the rubbery phase, PEEK retains a high modulus of ca. 0.65 GPa while PEI loses most of its stiffness to retain a modulus of only ca. 0.04 GPa. It is interesting to note that all the blends show modulus close to that of PEI both in the glassy and in rubbery phase.

Figure 1(B) shows the variation of tan-δ with temperature for various compositions of the blend along with their pure polymers. The temperature corresponding to tan-δ peak is regarded as T_g of the polymer.[21,28] The tan-δ of PEI exhibits a sharp peak at ca. 226°C while that for PEEK the pattern remains broad with a maximum at ca. 163°C. The tan-δ maximum for PEEK is almost six times lower than that of PEI. The crystalline domains of the semi-crystalline PEEK impose constraints on the segmental mobility of its amorphous part and hence the tan-δ peak appears broad. The reduced tan-δ peak height signifies that only fewer chains are participating in the relaxation process.[27] The absence of broadness in tan-δ peak of PEI indicates its amorphous nature.[43]

When amorphous PEI is added to semi-crystalline PEEK and upon crystallization of the latter, PEI is rejected into the amorphous domains of PEEK. Hence, there is a progressive enrichment of PEI in the amorphous regions of PEEK and subsequent composition change.[50] On application of a sinusoidal stress, the coiling and uncoiling process of amorphous chains makes more deformation and thus registers high damping, while crystalline parts poses restriction towards cyclic loading and thus exhibits less damping. Hence, the nature of tan-δ peak appears to be broad and less height when PEEK is in the major phase while it becomes narrow and more height when PEI is in the major phase (see Figure 1(B)). Thus, with increase in PEI content in the blend, there is a regular shift of tan-δ peak temperature to higher side as well as its peak height increases. This signifies that with the increase in PEI content, there is an improvement in T_g of PEEK as well as its damping ability in the blend. The decrease of tan-δ peak height with increase in PEEK content is in consistent with the reports on other rigid semi-crystalline polymers that exhibits less damping at T_g.[18]

Damping ability of a material is mainly determined by its energy dissipation rate. The energy utilized to deform an elastic solid is stored with no dissipation of energy. The work done to deform the viscous fluid is not stored but dissipated as heat during the irreversible flow. This reduces the kinetic energy of the system and causes damping. The amount of energy dissipated is a measure of the damping ability of the material.[51] However, polymers being visco-elastic exhibit behavior intermediate to perfect viscous and elastic materials. So, when a polymer is subjected to external vibration, the storage modulus (E') that represents the elastic nature of the polymer signifies the stored part of the energy. The loss modulus (E") that represents the viscous nature of the polymer signifies part of the energy that is dissipated. It is interesting to note that except PEEK, all the blends as well as pure PEI exhibits good damping behavior with tan-$\delta > 0.3$ (see Table II).

It is to be noted here that the damping remains low below T_g because the thermal energy is insufficient to cause rotational and translational motion of the segments as the chain segments are frozen-in. The damping remains also low above T_g because molecular segments are free to move about and there is very little resistance for their flow. Thus, when the segments are frozen-in or when they are free to move, damping is low. Frozen segment stores energy upon deformation and it ultimately releases as viscous energy on approaching T_g.[31] Thus, the ability of the chain motion increases near T_g, which results to increase of internal frictional energy dissipation between polymer chains due to higher visco-elastic nature.

When the PEI content in the blend is 50% (sample PP$_{50}$), the E' value is ca. 3 GPa, the tan-δ value is ca. 0.762 and the
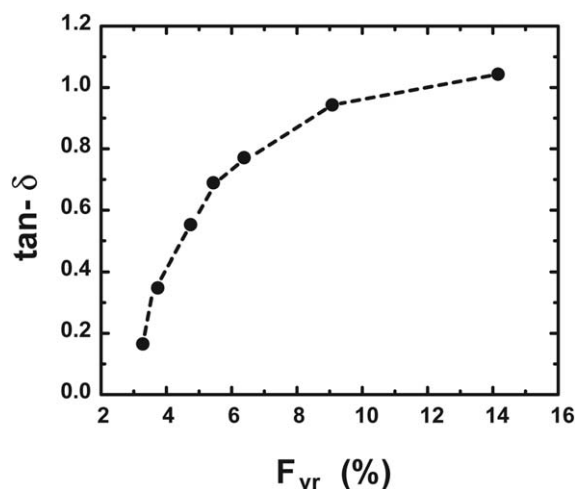
Figure 2. Variation of damping factor (tan-δ) versus fractional free volume F_{vr} (%).

corresponding temperature range with tan-$\delta > 0.3$ is ca. 36°C ($188°C < T < 224°C$; see Figure 1(A,B) and Table II). Please note that it is difficult to obtain a polymer possessing high damping and high modulus values but needs to be compromised.[51] Thus, we propose that 50/50 blend (sample PP$_{50}$) to be the optimum composition exhibiting good damping behavior with moderate stiffness. It is interesting to note that this blend with 50/50 composition exhibited best miscibility at the molecular level as revealed from free volume studies.[3]

Free Volume and Damping
Damping in polymers originates from the energy dissipation associated with microstructural defects such as free volume assisted chain motion.[18,20,51] Hence, we have made an attempt to understand whether there is a correlation between free volume and damping in this blend. Figure 2 depicts the peak value of tan-δ at the glass transition temperature correlating positively with the values of F_{vr}. This plot reveals that the damping factor increases exponentially with the free volume content. It is clear from this plot that increased values of F_{vr} correspond to stronger damping intensities. The validity of this correlation is debatable since PALS is performed at room temperature and the tan-δ peak associated with glass transition occurs at high temperature. This could possibly be interpreted as free volume quantified by PALS at room temperature is responsible for the damping behavior at the glass transition in this blend, as discussed for polymers.[18] Since free volume is roughly frozen below T$_g$, this explanation may found to be reasonable. It is also possible that the highly aromatic nature of PEEK and PEI do not permit considerable change in free volume up to T$_g$. This means that greater the free volume, higher would be the chain mobility at T$_g$ and tan-δ value also remains high. This infers that the free volumes act as energy dissipating centers and thus assists damping in this blend.

Since the tan-δ peak height is a measure of damping efficiency,[28] pure PEEK (sample P$_0$) having low tan-δ value has less free volume content and exhibits less damping. With the addition of amorphous PEI, the molecular mobility of the blend increases due to increase in free volume. Accordingly, the damping factor

increases with the free volume content in the blend. We know from the previous discussion that the visco-elastic damping is maximum at the T$_g$ region due to high internal frictional energy exhibited by the polymer chains.[31] Since the rubbery phase possesses more free volume and high flexibility, it can change to new conformations when subjected to external vibration and can relieve the associated vibration energy. Hence, a polymer is generally selected for damping purpose if its T$_g$ is in the region of required temperature.[29] Thus, T$_g$ and associated free volume gains extreme importance in deciding the damping ability of the polymer.

In a work on thermotropic liquid crystalline polymers, Simon and coworkers found a linear correlation between tan-δ and free volume.[18] In another work on nanocellulose incorporated polyurethane, decrease in free volume content with decrease in tan-δ peak height has been obtained.[27] In a recent report on rubber nanocomposites using combined DMTA and PALS, the authors have obtained the nanocomposite with least damping nature (minimum tan-δ value) also has low free volume content.[28]

In a series of work on MWCNTs incorporated polycarbonate, Bo Wang and coworkers have shown that CNT could be used as a promising structural damping material and obtained increase in free volume with increase in damping behavior.[20–22] According to the authors, the weak interfacial interaction between MWCNTs and PC leads to considerable free volume that makes MWCNTs to slip more easily at the interface, which in turn leads to enhancement in the damping properties. Thus, the authors have shown that interfacial slip and associated free volume, although detrimental to stiffness and strength, may result in very high mechanical damping. This has been attributed to nanoscale dimensions and high aspect ratio of the nanotubes, which result in a large interfacial contact area.[9,20–22] All these works discussed above support the obtained positive correlation between tan-δ and F_{vr}.

Time-Temperature-Superposition
To further investigate the effect of PEI on the glass-rubbery transition of PEEK and to quantify the molecular parameters related to the blend, DMTA measurements were performed in the vicinity of glass transition region at three different frequencies. Master curves for E' and tan-δ were constructed by shifting the isothermal data along the log of the frequency axis, according to the TTS principle. The generated master curves at a reference temperature, T$_0 = 220°C$ (here the reference temperature T$_0$ is chosen slightly above or close to the T$_g$ of the entire blend series) are shown in Figures 3(A,B). The master curves allow to predict E' and tan-δ values over a frequency range of nearly 20 decades that are not experimentally accessible.

The data superpose very well and the uniformity of the curves indicates that TTS principle is valid for the entire blend composition.[52,53] In conformity with the temperature profiles, the master curve for E' predicts high modulus for PEEK, low modulus for PEI and the blends exhibit modulus below PEEK throughout the predicted frequency range [see Figure 3(A)]. The master curve for tan-δ shows that there is a shift of the α-relaxation (due to glass transition) to lower frequencies [longer times; see Figure 3(B)]. Such a shift of the tan-δ master curve
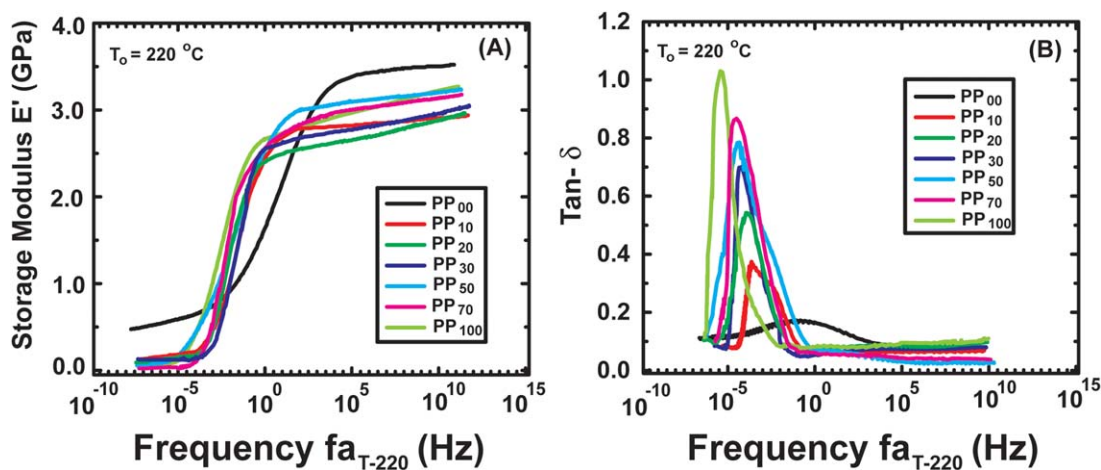
Figure 3. The master curves of PEEK/PEI blend for various PEI contents (A) storage modulus (E') and (B) tan-δ. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to low frequencies reveals the presence of longer relaxation times and is due to increased T_g.[53,54]

Using the values of a_T deduced from master curve, a plot of $(T–T_0)/\log a_T$ against $(T–T_0)$ is made for each of the blends and they found to exhibit a unique straight line (Figure 4). This linear behavior further confirms that the visco-elastic behavior of the blend follows TTS principle.[52–54] From these linear plots, the WLF constant c_1^0 has been obtained from the reciprocal of the slope and the constant c_2^0 from the intercept. The values of c_1^0, c_2^0 as well as α_f for the blend series are presented in Table II. The obtained values of WLF constants for PEEK and PEI are close to that reported.[55,56] Both the constants c_1^0 and c_2^0 decreases while α_f increases with PEI content and are in consistent with PALS results.

Correlation between Free Volume from PALS and DMTA Results

The constant c_1^0 is related to the free volume fraction as $f_o = 1/(2.303\ c_1^0)$. The value of f_o obtained by using WLF relationship

in the DMTA method when plotted against F_{vr} value evaluated from PALS studies, showed a linear behavior (Fig. 5). This plot reveals that PALS data can readily be combined with DMTA data to give

$$f_o = A(F_{vr}) + B$$

with A = 0.00476 as slope and B = 0.01983 as the intercept. Such a linear correlation has been reported for epoxy resins[16] and in styrene butadiene rubber.[41]

The results suggest that PALS in a miscible polymer blend reflect the same basic mechanism as relaxation process in DMTA or else visco-elastic property is closely related to free volume. As positronium parameters are governed by free volume, the relaxation process is also governed by free volume. Thus both the techniques provide similar information and support the free volume theory and the dynamics associated with the free volume.[41] The present results also reveal that PALS measurements can be used to obtain information on dynamic processes in miscible polymer blends similar to other polymers.[16,41]
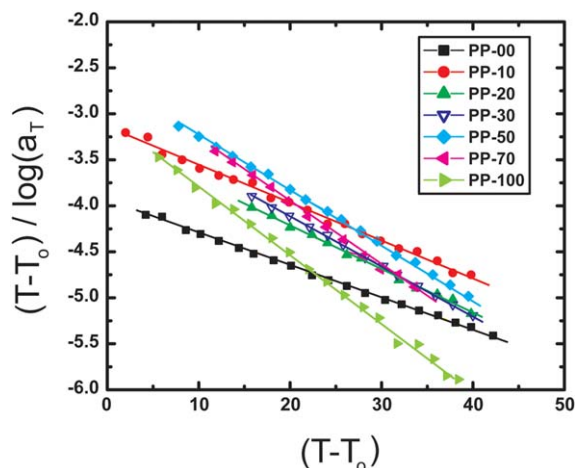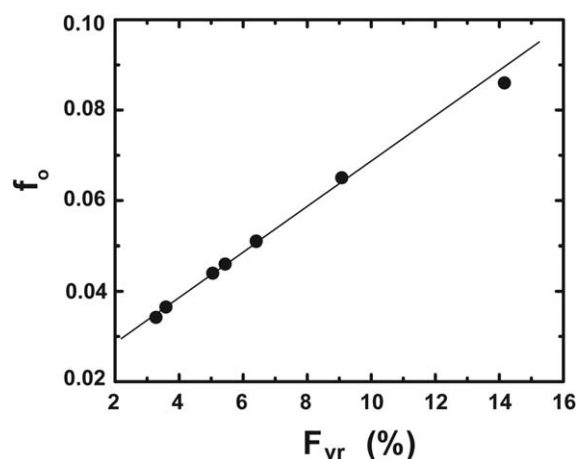

Figure 4. The plot of $(T–T_0)/\log(a_T)$ versus $(T–T_0)$ for evaluating the WLF constants. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. Variation of free volume fraction (f_o) obtained from DMTA results versus fractional free volume F_{vr} (%) obtained from PALS measurements.

Although, the free volume theory has been used to describe the visco-elastic behavior of polymer chains for a long time, up to now, we have not found a report relating the visco-elastic property and fractional free volume for a high performance miscible polymer blend like PEEK/PEI. Herein, we propose that the free volume results obtained by PALS agree well with those obtained by means of analysis of DMTA using WLF relationship and the free volume assists the energy dissipation upon damping in this blend.

CONCLUSIONS

For the first time, we have evaluated free volume in a high performance miscible polymer blend using PALS and DMTA methods and obtained comparable results. The PALS results reveal an increase in free volume with increase in PEI content for which increase in tan-δ peak value has been obtained in DMTA results. This increase of free volume content with tan-δ has been explained as the ease of free volume assisted energy dissipation upon damping. Thus, the chain flexibility and the associated free volumes play a significant role in the energy dissipation leading to damping in this blend.

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