

Free Volume Properties of Thermoplastic Polyurethane/Polymethylmethacrylate Blends: Evidence of Interchain Interaction

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ABSTRACT: A polymer blend based on thermoplastic elastomeric polyurethane and polymethylmethacrylate (TPU/PMMA) has been studied by positron annihilation lifetime spectroscopy (PALS) and thermomechanical analysis. Thermomechanical analysis allowed the determination of two glass transitions for the blends in the overall range of compositions. The first one (T_g^1) showed a constant value of -45°C for all blends, the same value of the pure TPU. The second glass transition (T_g^2), which is associated with a PMMA rich phase, presented variations with composition. T_g^2 showed minimum values for the blends in the 20–40 wt % TPU range, which indicates increase of interaction in this composition region. PALS systematic investigation allowed the determination of relative mean free volume fractions, f_v/C , and binary

interchain interaction parameters, β . These parameters exhibited a noticeable negative deviation from additivity in all range of composition and minima for the 20 wt % TPU blend. PALS results were interpreted as associated to a strong attractive interchain interaction between TPU and PMMA in the PMMA rich phase which contracts the free volume fraction of the blends. Moreover, the miscibility achieved in the PMMA rich phase would allow a good adhesion between this phase and the TPU phase, which was corroborated by scanning electron microscopy images. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 641–646, 2007

Key words: thermoplastic polyurethane; PMMA; blend; PALS; TMA

INTRODUCTION

Polymer blends form, very often, a two-phase mixture that does not hinder any possible technological use.¹ The structure developed during mixing reflects the competition between domain dispersion and coalescence.² The properties of polyurethane (PU) blends have been investigated and a strong dependence of the material morphology was verified.^{3–9}

Solution blending is known as a process that facilitates the attainment of equilibrium as it enhances molecular mobility; however, the solvent removal process influences the nature of the final blend morphology.² Polyurethane blends prepared by solution method were reported to be useful to soft tissue engineering,⁵ ultrafiltration membranes,⁶ reverse osmosis membranes,⁸ and electronic conductor applications.⁷

Solution blends of a thermoplastic polyurethane (TPU) and polymethylmethacrylate (PMMA) have been previously studied by our group using Fourier

transform infrared spectroscopy, temperature modulated differential scanning calorimetry (TMDSC), and scanning electron microscopy (SEM).⁹ The TPU/PMMA blends presented hydrogen bond interaction between the urethane and PMMA, leading to the formation of a PMMA rich phase with some degree of TPU miscibility. A separated TPU phase is observed in all blend compositions, and an interphase with high degree of miscibility between TPU and PMMA was also characterized by TMDSC. These blends were successfully used to prepare membranes for gas separation.⁹

The determination of the structural parameters of polymeric systems can be performed by positron annihilation lifetime spectroscopy (PALS).^{8–26} This technique allows the determination of *ortho*-Positronium lifetime (τ_3) and formation probability (I_3) parameters, which are associated with the free volume average dimension and relative concentration, respectively.^{13,14} Polyurethanes were investigated by several authors, e.g., Wang et al.,¹⁶ who applied PALS technique to study free-volume hole properties of three different PUs. They observed decrease of fractional free volume (f_v) with increasing hard segment content in all three systems.

Polymeric blends have also been systematically investigated by PALS to find information about the

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free volume changes with composition and temperature.^{8,9,11,15,17–24,26} Negative deviations from an additive behavior of a parameter such as mean free volume fraction have been associated with intermolecular interactions and enhanced molecular packing, even in phase separated blends.^{8,17,19,22,26} Strong correlations between PALS parameters and properties have been established for blends,^{8,9,15} copolymers,^{12,23} and nanocomposites.²⁷

Thermomechanical analysis (TMA) is used to determine the coefficient of linear thermal expansion (CLTE)^{28–31} in accord with standard test methods as ASTM E831. The CLTE is measured by applying a small force of 1–100 mN to the specimen only to keep the probe in contact. By using higher forces, in a penetration mode, it is possible to investigate how the thermal transitions influence the dimensional changes of the sample. Thermal expansion of polymer blends^{28,29} and nanocomposites,^{30,31} with different formulations and preparation methods, has been characterized.

In this work we provide an investigation of the free volume behavior of TPU/PMMA blends as a function of composition. PMMA is a glassy polymer and the TPU used in this work has an elastomeric behavior. Thermomechanical analysis was used mainly to determine the glass transitions. This particular heterogeneous blend has been proposed as membrane for gas permeation.⁹ The phase separated arrangement of this blend is quite complex and, therefore, new insights about the structure of this system can contribute to the general tasks of understanding factors associated with blending and enhance materials properties.

EXPERIMENTAL

The PU was synthesized as described elsewhere,⁹ using MDI (4,4-diphenylmethane diisocyanate, Aldrich, Milwaukee, WI) and poly(tetramethylene glycol) (Aldrich, $M = 1000 \text{ g mol}^{-1}$, supplier data). The average weight molar mass obtained by GPC (gel permeation chromatography) was $100,000 \text{ g mol}^{-1}$, and the dispersion index of 1.3. PMMA (Sigma Aldrich, Steinheim, Germany), with average molar mass of $120,000 \text{ g mol}^{-1}$, manufacturer data, was used as received.

The TPU/PMMA blends were prepared by codissolution of the polymers in tetrahydrofuran and casting. Drying was carried out in oven under vacuum at 30°C for 10 days.

Thermomechanical analysis experiments were performed in duplicate using TMA 2940 TA instruments. Flat samples $\sim 2 \text{ mm}$ thick were heated at 5°C min^{-1} under N_2 flow. The applied force for compression mode experiment was of 0.5 N, which allowed the determination of glass transitions by the

changes in the slopes of the curves of dimension as a function of temperature. Moreover, an alternative parameter similar to a coefficient of linear thermal expansion and named as “CLTE” was determined from the measurements in compression mode. This is not a specific CLTE value, as can be obtained from an expansion mode experiment, and it will be used in this work only with the aim of comparison between the blends.

Scanning electron microscopy of the blends was obtained with a JEOLJSM-8404 scanning microscope. The samples were immersed in liquid nitrogen and were broken. The fractured surfaces were coated with a thin gold layer.

The PALS measurements were performed at 294 K using a conventional fast–fast coincidence system (Ortec), with time resolution of 280 ps given by ^{60}Co prompt curve. The ^{22}Na (Amersham) positron source, with $\sim 0.4 \text{ MBq}$ activity ($11 \mu\text{Ci}$), was sandwiched between two $7.6\text{-}\mu\text{m}$ -thick foils of Kapton, and the source correction was approximately 10%. The lifetime spectra were well resolved into three components by the Positronfit-Extended program,³² after background and source correction were subtracted, leading to the intensities I_i , and lifetimes τ_i . Subscripts $i = 1, 2,$ and 3 refer to p -Ps, free positron, and o -Ps, respectively.

The parameters obtained (τ_1 fixed at 0.12 ns) correspond to the average value of three spectra with 30,000 counts at peak for each sample and the total counts were in the range $0.35\text{--}0.45 \times 10^6$. The analyses were performed in pure and blend polymers samples in the form of disks of 10 mm in diameter and approximately 1.5 mm thickness; the positron

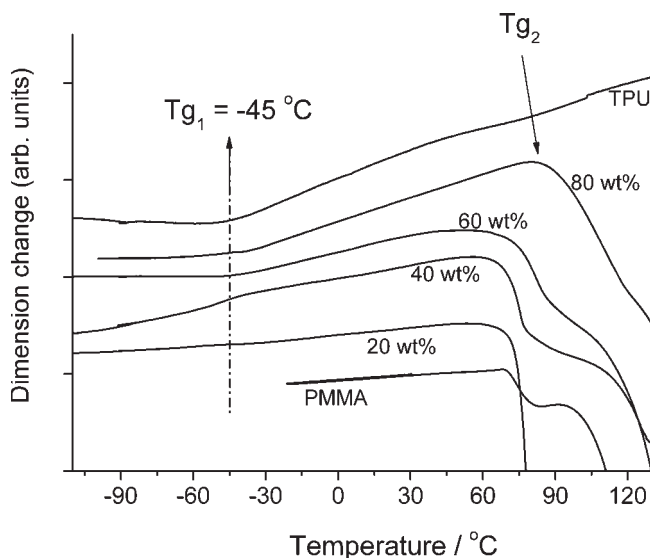


Figure 1 TMA curves for TPU, PMMA, and blends in compression mode. Blend compositions in wt % of TPU are indicated in the figure.

TABLE I
TMA Results for TPU, PMMA, and Blends

Wt % TPU	"CLTE" ^a /10 ⁻⁵ K ⁻¹	T _g ² /°C
100	47	-
80	34	90
60	26	75
40	21	72
20	12	74
0	8	115

^a Determined in the linear region between -45 and 50°C in compression mode with force of 0.5 N. The mean deviations for "CLTE" and T_g² parameters are ±2 × 10⁻⁵ K⁻¹ and ±2°C, respectively.

source was sandwiched between two identical samples.

According to the free volume model, the *o*-Ps lifetime τ₃ is related to the free volume hole size through an expression obtained by considering a simple model in which the Ps particle is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R₀ with a homogeneous electron layer with a thickness of ΔR = R₀ (R, where R₀ is the infinite spherical potential radius and R is the hole radius.^{13,14,33} The relation between τ₃ and the radius R of the free volume hole or cavity is

$$(1/\tau_3) = \lambda_3 = 2[1 - R/R_0 + 1/2\pi(\sin(2\pi R/R_0))]ns^{-1} \quad (1)$$

where ΔR is an empirical parameter determined by fitting the measured lifetimes with the known hole and cavity sizes in molecular substances and the best value was found to be 0.1657 nm.³³ With this value of ΔR, the free volume radius has been calculated from eq. (1), and the average size of the free volume holes is obtained as V_f = 4/3 (πR³).

The relative intensity of *o*-Ps formation, I₃, is frequently used as a measure of mean free volumes concentration, and this approach has been applied to PUs and PMMA materials.^{8,9,16,26} The fractional free volume is evaluated from PALS parameters τ₃ and I₃, using the following equation^{14,35,36}

$$f_v = CI_3V_f \quad (2)$$

where C is an empirical scaling constant determined from specific PVT measurements, which varies from 1.0 to 2.0 when V_f is in nm³ and I₃ in %.^{33,37} The relative fractional free volume, f_v/C, as proposed by different authors (see, for example, ref. 38 and 39), was used to compare the materials in this work.

RESULTS AND DISCUSSION

Figure 1 and Table I present the results of the TMA experiments conducted with TPU, PMMA, and blends. Figure 1 shows the TMA curves in compression mode in the range -100 to 120°C, except for PMMA. A change in the slope of the curves was observed at approximately -45°C, which is assigned to the glass transition (T_g¹) of the TPU and TPU phase in the blends. TMA results corroborated the TMDSC data presented in our previous work,⁹ which shows that a TPU phase is always present in the blends. The value of T_g¹ obtained from the TMDSC study was -51°C, which can be considered in good agreement with the TMA result presented here, taken into account the differences between the techniques.

The TMA compression experiment is especially adequate to quote the final glass transition (T_g²) through the penetration of the probe. This event is associated with a more thermal stable phase, which is rich in PMMA. It should be noted that in our pre-

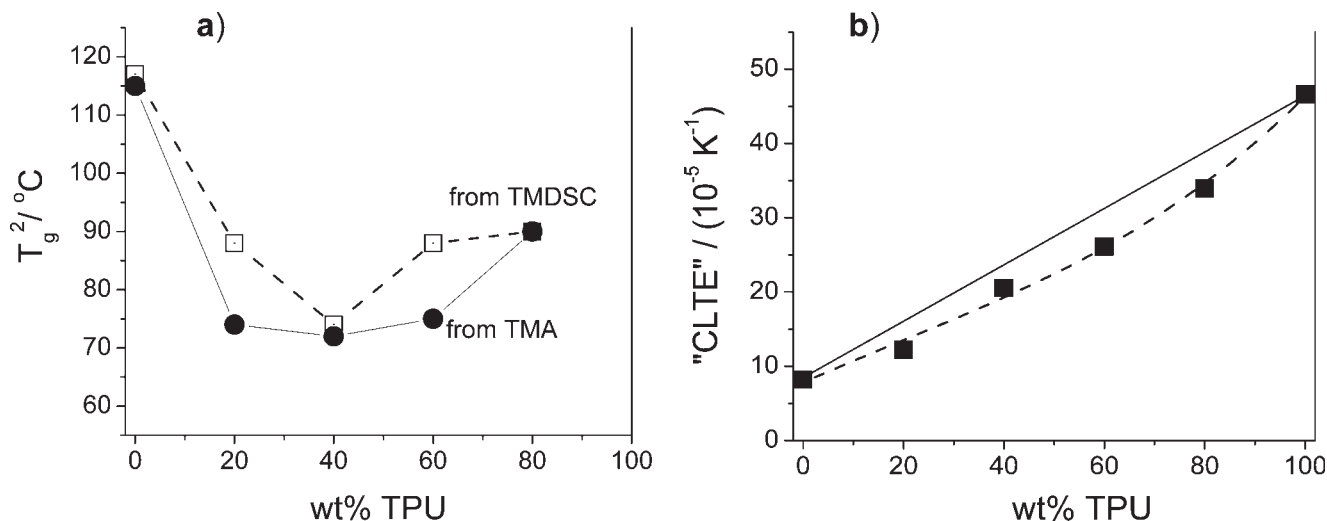


Figure 2 (a) Glass transition of the PMMA rich phase (T_g²) from TMDSC⁹ and TMA (b) "CLTE" from TMA.

TABLE II
PALS Parameters τ_3 , I_3 , Free Volume Radius R , Free Volume Hole Size, V_f , Relative Fractional Free volume, f_v/C , and Interaction Parameter, β , Obtained using eq. (1)–(3)

Wt % TPU	τ_3 (ns)	I_3 (%)	R (nm)	V_f (nm ³)	f_v/C (nm ³ %)	β
100	2.33	33.1	0.313	0.129	4.26	0
80	2.24	32.4	0.306	0.120	3.88	-0.112
60	2.19	32.3	0.302	0.115	3.71	-0.096
40	2.13	31.1	0.297	0.109	3.39	-0.155
20	2.08	30.5	0.292	0.104	3.23	-0.260
15	2.16	30.9	0.299	0.112	3.46	-0.205
0	2.24	31.9	0.306	0.120	3.82	0

The mean deviations of a minimum of three spectra for τ_3 and I_3 parameters are ± 0.03 ns and $\pm 0.5\%$, respectively.

vious work⁹ the TMDSC measurements allowed the determination of three glass transitions associated with a TPU phase, a PMMA rich phase, and a large interface or interphase. This is not the case for the TMA experiments, which were not sensitive to a possible broad thermal transition of an interphase. In summary, two glass transitions were characterized by TMA associated with pure TPU and PMMA rich phase named T_g^1 and T_g^2 , respectively. A minimum of T_g^2 is observed between 20 and 40 wt % TPU from both types of measurements TMDSC and TMA [Fig. 2(a)]. This behavior indicates that the PMMA rich phase incorporates a relative higher content of TPU for the blends 20–40 wt %. This can be interpreted as associated to higher interaction, or partial miscibility, between TPU and PMMA, in this range of composition.

Table I shows the values for the parameter named “CLTE” obtained from TMA curves (Fig. 1) by using the slope between T_g^1 [-45 ± 2]°C and 50°C, as it was limited by the proximity of T_g^2 of some samples. An approximately linear increase was observed for “CLTE” with the TPU content as shown in Figure 2(b). Other authors have discussed the morphology influence on the CLTE, specially in the case of blends.²⁹ The parameter “CLTE” obtained in this work behaves close to additivity in the overall range of blend compositions. A slightly negative deviation is observed in Figure 2(b), even considering the accuracy of the determination (see Table I). However, the high force applied in compression mode might be responsible for this deviation.

Table II summarizes the PALS parameters τ_3 , I_3 , as well free volume radius R , free volume hole size, V_f , and fractional free volume, f_v , obtained using eqs. (1) and (2). All PALS measurements were performed at (21 ± 1) °C. This is a temperature located in an intermediary position in the range used for the determination of “CLTE,” i.e., between T_g^1 (-45 °C) and T_g^2 for all blends. Therefore, the behavior of PALS parameters changes with composition obtained at 21°C, and the structure insights derivate from them are associated with a blend material based on an

elastomeric (TPU) phase and a glassy (PMMA rich) phase.

It should be noted that Ps is a subnanometric probe (size 0.106 nm). Jean and coworkers^{14,37,40} suggested that Ps atom is preferentially trapped and localized in small free-volumes in a size range of 0.1–2.0 nm. This proposition was based on the diffusion coefficient values measured on oxide powders, porous organic resins, and polymers.⁴⁰ In this context, micrometric defects, such as holes left by the drying procedure, are not in the sensitive region of detection of the technique. Therefore, the PALS results, as obtained in this work, are associated to the free volume available between the macromolecular chains in the bulk material.

Small-angle X-ray was used to determine a mean free volume for PMMA and a value of 0.105 nm³ was obtained by Curro et al.⁴¹ More recently a good agreement between SAXS and PALS data for PMMA has been obtained by David et al.,⁴² which reported free volumes of 0.113 nm³ at room temperature. The differences in relation to the value in Table II (0.120 nm³ for PMMA) may be related to the sample

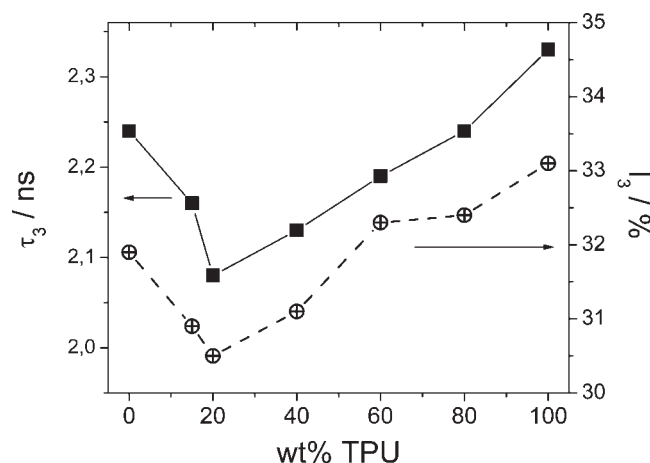


Figure 3 Ortho-Ps lifetimes and intensities, τ_3 and I_3 , for TPU/PMMA pure polymers and blends as a function of composition.

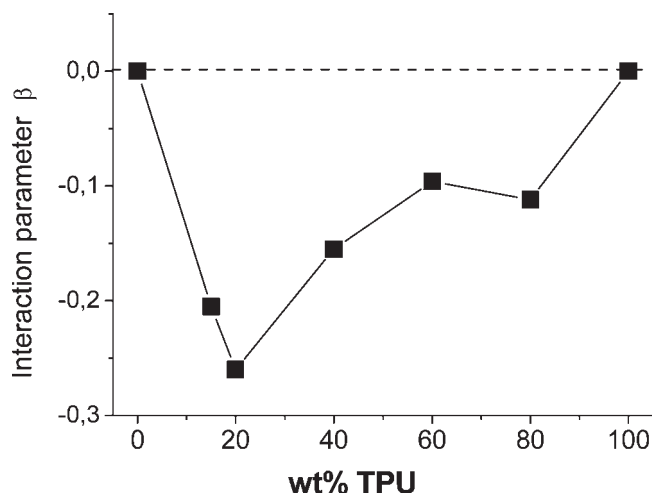


Figure 4 Interaction parameter, β , as a function of TPU/PMMA blends composition.

preparation. Casting from solution can introduce free volumes with higher dimension in our case.

Pure polymers present τ_3 values larger than all blends in Figure 3. Starting from pure PMMA and adding TPU, τ_3 decreases, reaching a minimum value for the blend with 20 wt % TPU. A similar behavior is observed for I_3 . Therefore, as shown in Table II, the relative fractional free volume values, f_v/C , calculated with eq. (2), as a function of blend composition exhibits a noticeable negative deviation from additivity in all range of blend compositions with minimum at 20 wt % TPU. Similar negative deviations have been observed for other polymeric blends in the literature.^{8,17–20} This behavior has been interpreted as an evidence of better molecular packing even in presence of a certain degree of phase separation.

It has been proposed that the mean fractional free volume, f_v , for blends can be correlated to the interaction between dissimilar chains and molecular packing.^{22,24,26} In this approach, f_v for a blend is

expressed as a function of a parameter β related to the interaction between polymer chains:

$$f_v = f_v^1 w^1 + f_v^2 w^2 + \beta f_v^1 w^1 f_v^2 w^2 \quad (3)$$

where f_v^1 , f_v^2 , w_1 , and w_2 are free volume fractions and weight fractions of components 1 and 2, respectively. Figure 4 and Table II show the values of β for TPU/PMMA blends.

A general criterion for a miscible blend could be associated to a contraction of free volume or a negative value for β . Liu et al.²² have reported negative values for the interchain interaction parameter β for a PS/TMPC system, and associated this to polymer miscibility. Fluctuating positive/negative values of β for PS/PMMA, PS/PC,²² and PTT/EPDM²⁴ were assigned to immiscibility or incompatibility of the blends. Moreover, Kumaraswamy et al.^{38,39} recently reported evaluations of β for both miscible and immiscible blends such as SAN/PMMA and PVC/PS. These last works presented as well new parameters based on PALS data, such as a hydrodynamic interaction parameter, α , which may be helpful to assess information about blend miscibility.

Felix et al.²⁶ observed negative values for β in a phase separated PMMA/MMA/TEGDMA blend. They interpret this result as associated to an effect of interphase. Actually, as discussed in our previous work,⁹ the system TPU/PMMA, besides being phase separated, is characterized by an interphase with both components strongly associated. Moreover, the FTIR investigation of TPU/PMMA blends indicates the presence of dissimilar interchain hydrogen bond.⁹ All these considerations support the conclusion that the noticeable negative values of β for TPU/PMMA blends in Figure 4 are related to strong dissimilar interchain interaction in the PMMA rich phase and interphase.

SEM micrographs of cryoscopic fractured blends and TPU are shown in Figure 5. TPU has a ductile

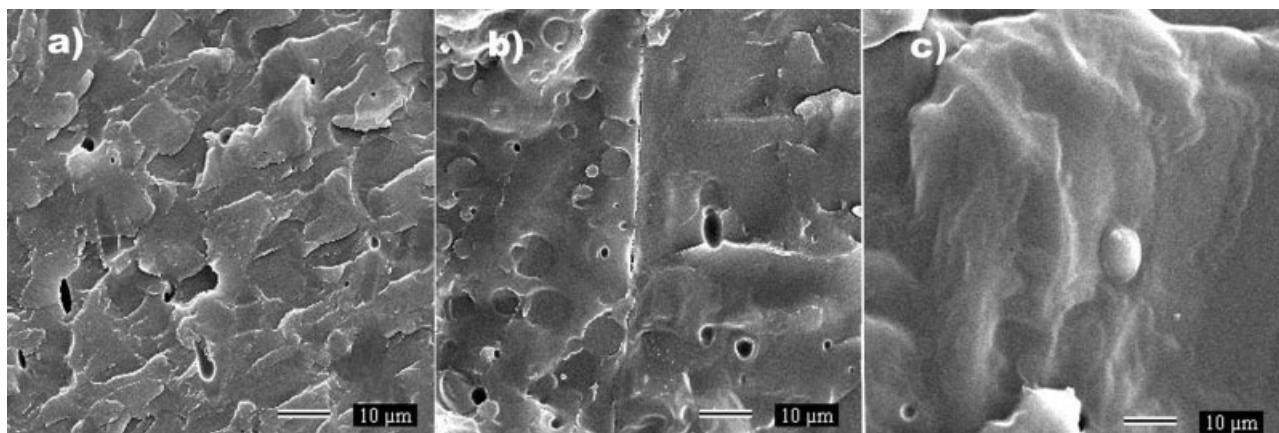


Figure 5 SEM images of blends TPU/PMMA. (a) 20 wt %, (b) 40 wt % TPU and (c) pure TPU.

fracture and PMMA a brittle one. The 20 wt % TPU blend also exhibits a brittle fracture [Fig. 5(a)] as expected considering the high content of PMMA in this material. It is important to note that there are no poor adherent domains with micrometric phase separation on the 20 or 40 wt % TPU blend. Therefore, the SEM images corroborate the picture of a phase separated system with strongly associated phases.

CONCLUSIONS

Two glass transitions, one of a TPU phase (T_g^1) and one of a PMMA rich phase (T_g^2), were characterized by TMA for all blends TPU/PMMA. The glass transitions obtained by TMA and by TMDSC were in good agreement. The relative fractional free volumes, f_v/C , measured by PALS for TPU/PMMA systems as a function of blend composition exhibited negative deviation from additivity in all range of blend compositions, with minimum at 20 wt % TPU. As Ps is a nano probe, this result indicates that a better molecular packing is present in the blends, which is due to efficient interactions between the components in a phase separated morphology. Free volume fractions of the blends and pure polymers were used to calculate a binary interchain interaction parameter, β , which showed noticeable negative values for all blends.

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