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Characterization of Thermotropic Liquid Crystalline Polymer Blends by Positron Annihilation Lifetime Spectroscopy

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13. ABSTRACT *(Maximum 200 words)*

Positron annihilation lifetime spectroscopy (PALS) has been used to investigate polymer-based molecular composites of two separate thermotropic liquid crystalline polymers (TLCPs) and the thermoplastic matrix polyetherimide. Variations in PALS spectral components were observed as a function of both TLCP content and temperature and are discussed as a function of free volume and molecular structure. It has been shown that these differences, between the matrix and reinforcing phase, has substantial influence on the localization and annihilation of o-Ps. The more miscible HX4000 composites exhibited TLCP dominated lifetime characteristics at room temperature. Differential scanning calorimetry, used as a complementary characterization technique to PALS to investigate the differences in miscibility of the two systems and possible effects on lifetime values, has shown that the greater miscibility exhibited by the HX4000 system over the Vectra system provides the potential to form composites on a size scale closer to the molecular level.

14. SUBJECT TERMS

Positron Annihilation Lifetime Spectroscopy
Liquid Crystalline Polymer Blends, Free Volume

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Statement of the Problem Studied

The importance of free volume in the determination of viscoelastic properties has been the subject of considerable work in the field of polymer science. An understanding of these materials properties and the relationship between macroscopic mechanical properties and atomic scale free volume sites is necessary in any complete materials characterization. It was the intention of this research to explore this relationship and provide fundamental knowledge on the influence of molecular structure on the formation of thermotropic liquid crystalline polymer (TLCP) domains in thermoplastic composites.

Positron annihilation lifetime spectroscopy (PALS) methods were employed to study free volume cavity size and concentration in blends of polyetherimide (Ultem) with TLCPs based on terephthalic acid, hydroquinone, and phenylhydroquinone (HX4000) or hydrobenzoic acid and 2-hydroxy 6-naphthoic acid (Vectra). In addition, differential scanning calorimetry (DSC) was used to investigate thermal transitions as well as polymer compatibility. Finally, tensile testing was used to characterize changes in mechanical properties as a result of TLCP reinforcement.

Summary of Results:

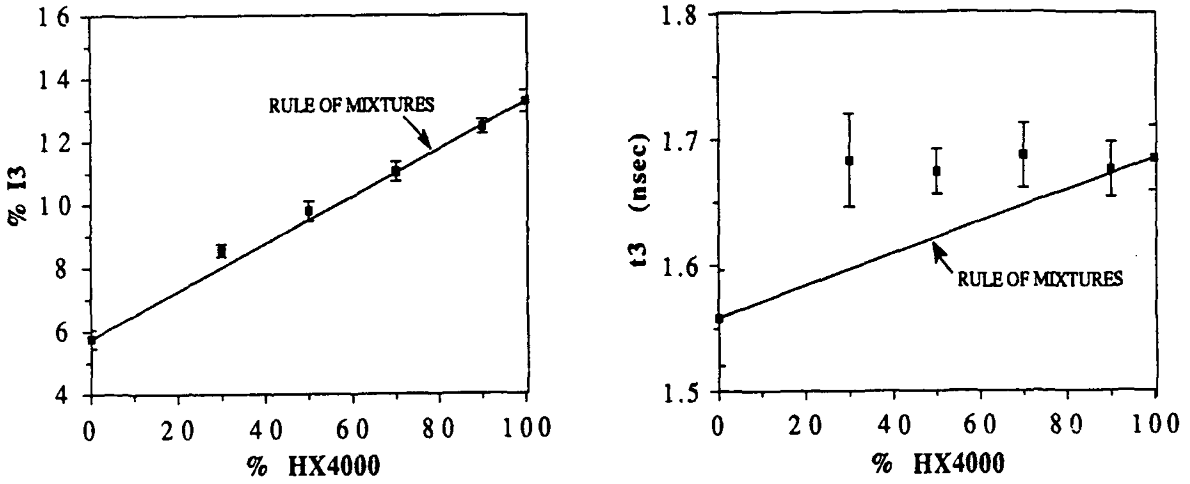

Fig. 1 Ortho-positronium in HX4000 blends at 20°C.

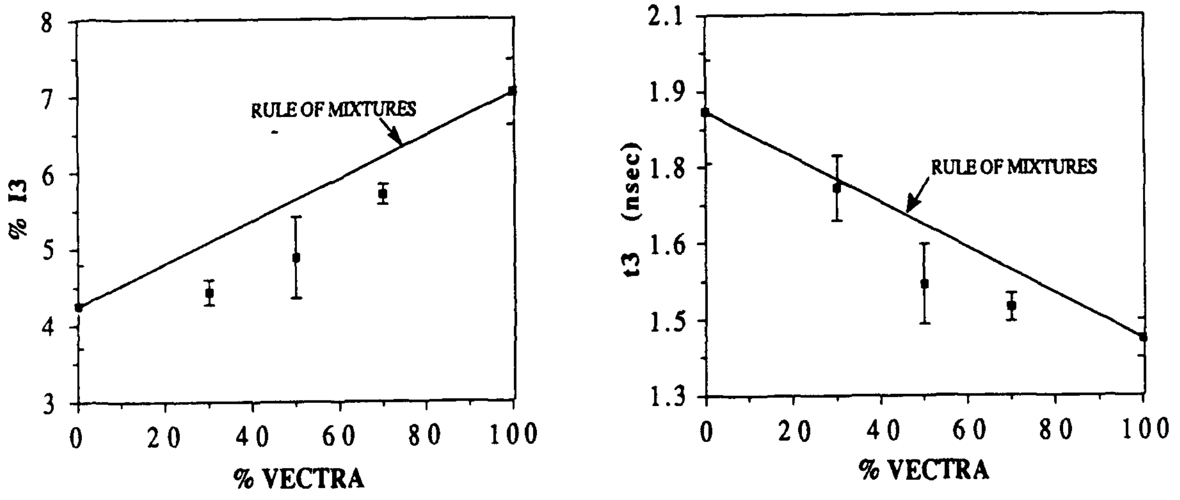

Fig. 2 Ortho-positronium in Vectra blends at 20°C.

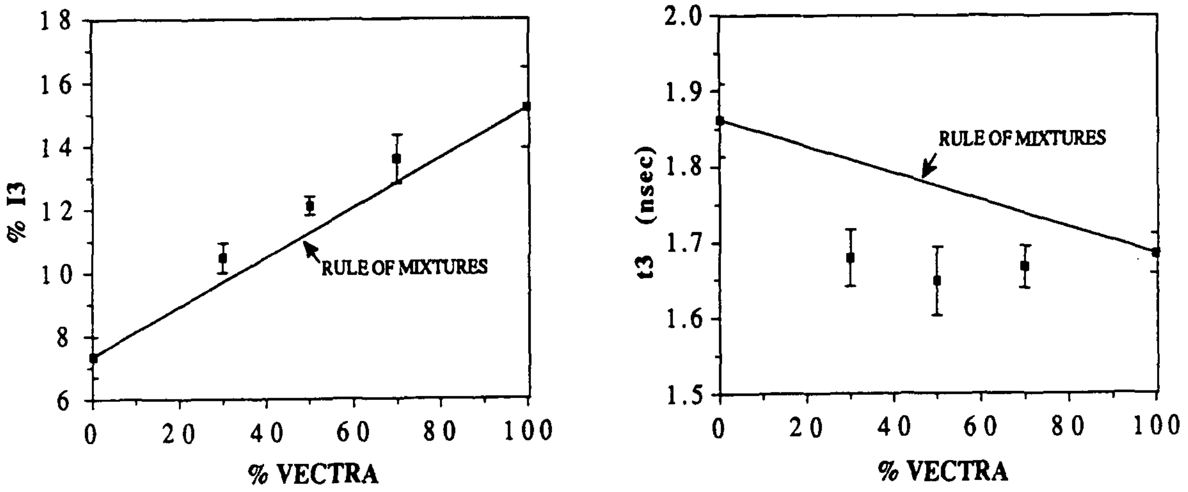

Fig. 3 Ortho-positronium in Vectra blends at 120°C.

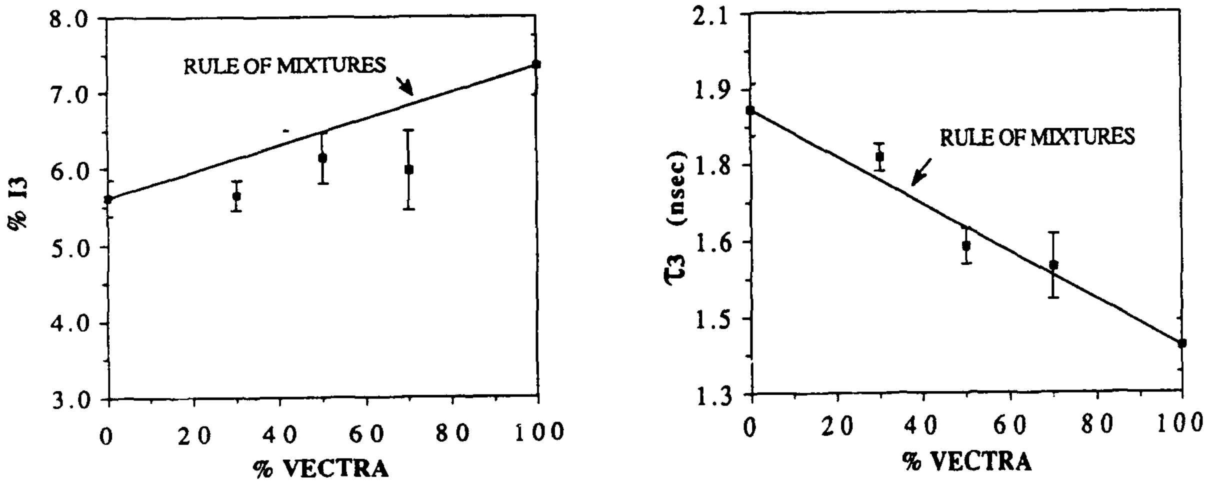

Fig. 4 Ortho-positronium in Vectra blends recooled to 20°C.

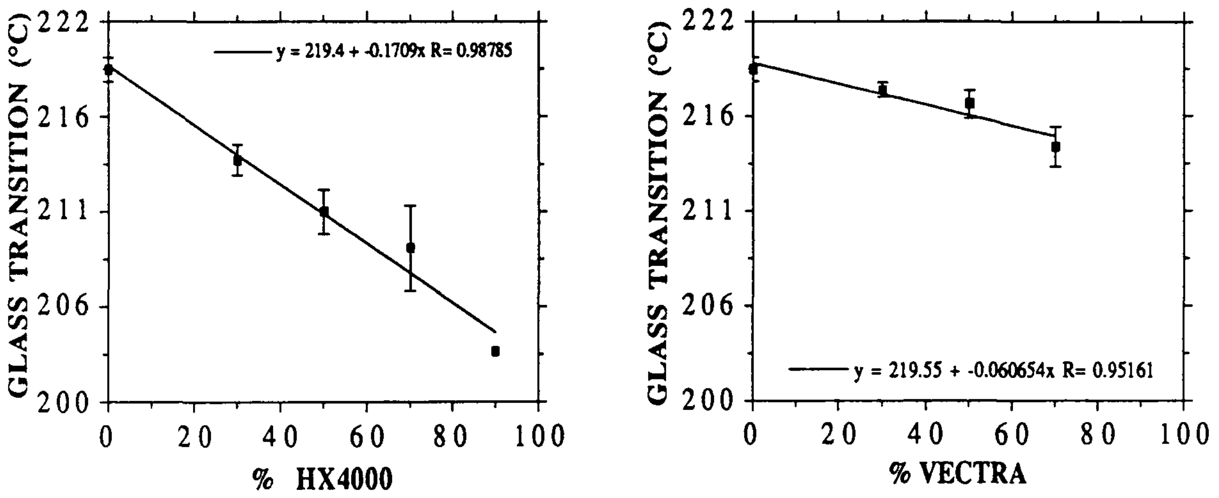

Fig. 5 Glass transition behavior of LCP blends.

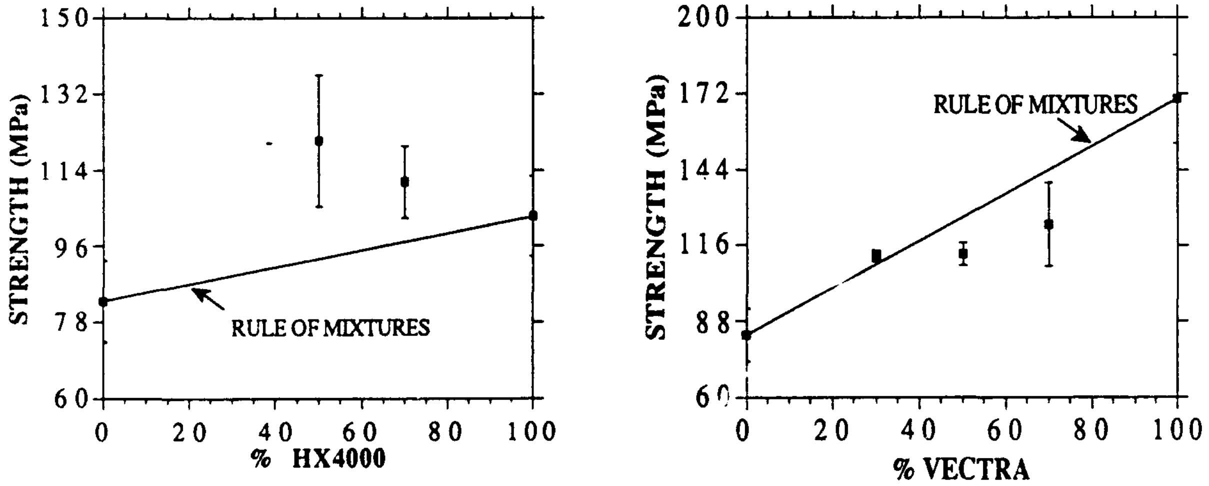

Fig. 6 Strength values for HX4000 and Vectra blend systems.

Summary of Findings:

The results of this investigation have led to the following conclusions:

1. The results of positron annihilation lifetime spectroscopy show that for the Ultem/HX4000 blends investigated isothermally at 20°C, the ortho-positronium (o-Ps) intensity (I_3) component exhibited excellent agreement with a rule of mixtures approximation. In addition, the ortho-positronium lifetime (τ_3) component was found to be constant for all blends and equivalent to that of the pure HX4000 liquid crystalline polymer (see figure 1).

2. In contrast, the ortho-positronium intensity component for the Vectra system at 20°C exhibited a negative deviation from a rule of mixtures approximation (see figure 2). Consequently, the ortho-positronium lifetime component for the Vectra system at 20°C was not LCP dominated, as in the HX4000 system. It was instead crudely approximated by a rule of mixtures behavior, with a negative deviation becoming apparent at higher LCP concentrations.

3. The linear increase in ortho-positronium intensity for the HX4000 blends may be explained by assuming that the free volume cavity site is constant for all blends, as indicated by the lifetime behavior, and assuming that a certain number of free volume sites are associated with each weight percent increase in LCP content. It is important to note that the difference in lifetimes between the pure HX4000 and the pure Ultem was only 127 psec while the corresponding intensity difference was 7.499%. The large difference in intensity was an indication that probabilistically the LCP had substantially more sites available for the formation and annihilation of o-Ps, relative to the matrix. In contrast, the Vectra systems possessed a difference in intensity of only 2.798% while the lifetime differed by a substantial 479 psec. The relatively small difference in intensity values indicated that there were a significantly smaller number of sites available in the Vectra liquid crystalline polymer for the formation and annihilation of o-Ps.

4. PALS results indicate that the ortho-positronium intensity component for the Vectra blends at 120°C also followed an approximate rule of mixtures

behavior (see figure 3). Moreover, the ortho-positronium lifetime component, in contrast to the Vectra blends at 20°C, was now dominated by the liquid crystalline polymer, with all blend lifetimes approximately equal to that of the pure Vectra. A comparison of the data between the Vectra systems at 20°C and 120°C revealed that the intensity of Ultem increased by 3.081%, while the corresponding lifetime value remained essentially constant. In contrast to the matrix values, the Vectra intensity exhibited an increase of 8.123% while the lifetime value showed a substantial increase of 265 psec.

5. The changes in annihilation characteristics with temperature for the Ultem matrix were explained in terms of its glass transition and the lifetime-temperature schematic. It was hypothesized that the Ultem matrix, with a glass transition of approximately 220°C, exhibited lifetime behavior located below the sub-glass transition temperature, T_S, for all temperatures between 20°C and 120°C. Therefore, the ortho-positronium lifetime component did not change. In contrast to the Ultem matrix at 120°C, the liquid crystalline polymer, Vectra, exhibited a dramatic increase in both its lifetime and intensity values. The glass transition of Vectra, determined experimentally in this thesis, was approximately 150°C. Consequently, 120°C PALS data was generated at a temperature only 30°C below the glass transition of Vectra. Therefore, it was reasonable to believe that the molecular motion of the LCP had increased measurable. In fact, it was hypothesized that at 120°C, the lifetime value could be found somewhere on the weaker variation of τ_3 with temperature between T_S and T_g.

6. The Vectra lifetime data at 120°C possessed a difference in intensity between the LCP and matrix of 7.84%, while the lifetime data exhibited only a 178 psec difference. The increased intensity of the Vectra component, as a result of the 100°C change in temperature, was responsible for the dramatic shift in lifetime data. As in the HX4000 system at 20°C, the LCP free volume cavity sites dominated lifetime behavior. Although the matrix had a larger cavity size by 178 psec, the difference in intensity pointed to the annihilation of o-Ps preferentially in Vectra free volume sites. The probability of a diffusing positronium atom finding a Vectra free volume site was much greater than that of finding an Ultem site. For both blend systems

investigated, it was found that it was the difference in ortho-positronium intensities which was controlling the lifetime characteristics of the blends.

7. The examination of the ortho-positronium characteristics of the recooled Vectra revealed that the free volume cavity size, as reflected by τ_3, was recovered almost instantaneously. Conversely, the intensity seemed to recover more quickly for the pure Vectra and the 70% composite than for the pure Ultem. On the other hand, the lower weight percent blends had a measurable degree of retained intensity; and hence free volume.

8. The question of where the free volume sites exist in the polymers investigated was addressed. The ortho-positronium lifetime behavior of the three polymers was determined as:

$$\tau_3(\text{HX4000}) > \tau_3(\text{Ultem}) > \tau_3(\text{Vectra}).$$

The HX4000 was rationalized to possess the greatest free volume due to the presence of pendant benzene rings. Recent quantum modeling of positronium behavior by Y.C. Jean was used to rationalize the intermolecular free volume associated with the hindrance in packing of the HX4000 molecules caused by the pendant benzene rings. The isopropyl linkage in the Ultem matrix is believed to contribute to the increase free volume of Ultem over the highly linear Vectra LCP, which possessed no pendant side groups.

9. Differential scanning calorimetry demonstrated that the HX4000 system was more miscible than the Vectra system as documented by the suppression of glass transition temperatures. Complimentary mechanical testing collaborated that the HX4000 system was more miscible as indicated by a positive deviation from the rule of mixtures (i.e. synergism) for tensile strength data. The less miscible Vectra system exhibited a negative deviation from the rule of mixtures at high liquid crystalline polymer concentrations.

10. Both differential scanning calorimetry and positron annihilation lifetime spectroscopy results indicate the stop transition temperature, associated with the glass transition of the polyetherimide component, was essentially constant for all Ultem/Vectra blends. The classical approach to glass transition and free volume, which assumes a minimum amount of free volume necessary for the glass transition to occur, was extended to include a

corresponding minimum amount of free volume necessary for the transition to liquid-level molecular motion. The decreasing free volume cavity size associated with increasing Vectra concentration was postulated as constraining the free volume increase necessary for the polymer to undergo the transition to liquid-level motion.

11. Positron annihilation lifetime spectroscopy allows the examination of free volume cavity sizes and distributions in thermoplastic/TLCP composites on the submicron level.

Refereed Publications:

1. R.A. Naslund, P.L. Jones, and A. Crowson, "Characterization of Thermotropic Liquid Crystalline Polymer Blends by Positron Annihilation Lifetime Spectroscopy", Materials Research Society Symposium Proceedings, to be published.

Presentations:

1. "Characterization of Thermotropic Liquid Crystalline Polymer Blends by Positron Annihilation Lifetime Spectroscopy", Materials Research Society, 1992 Spring Meeting, San Francisco, CA.

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