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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Positron annihilation lifetime spectroscopy was used to study thermal response and isothermal relaxation in two different molecular weight polystyrene samples over the temperature range of 50°C to 120°C. The lifetime and intensity of the ortho-positronium pickoff component were observed to vary systematically as a function of time, temperature, and molecular weight. A glass transition and secondary transition were detected in the thermal response data for both samples. PALS was also used to study the effects of physical crosslink density on free volume relaxation in polystyrene and polystyrene based interpenetrating polymer networks. The intensity of the o-Ps pickoff component was observed to vary in a consistent and predictable manner as a function of time, temperature, and crosslink density. Key words:					
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POSITRON ANNIHILATION STUDIES OF INTERPENETRATING
POLYMER NETWORKS

FINAL REPORT

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Introduction

The recent increase in the use of polymer blends as engineering materials has created a need for a detailed understanding of the structure and properties of these complex materials. A unique group of polyblends known as interpenetrating polymer networks (IPNs) is of particular importance because of their enhanced mechanical properties. These properties are theorized to be primarily due to a high density of physical crosslinks. The properties of this class of polymers tend to behave synergistically, thus providing the materials engineer with the ability to synthesize high strength impact resistant polyblends. As discussed in the initial research proposal, the development of this class of high strength light weight materials could have a significant impact on improvements in military mobility and logistics. Potential uses of IPNs may include helicopter structures and rotor blades, portable bridging, armaments, and rocket and missile structures, as well as a variety of other applications which require light weight high strength materials.

Description of Research and Objectives

Positron annihilation lifetime spectroscopy (PALS) in conjunction with more conventional characterization techniques has been used to analyze and relate the structure of polystyrene based IPNs to their physical and mechanical properties. Because of the complex nature of IPNs and the desire to develop a general model, this research has focused solely on polystyrene/polystyrene homo-IPNs. These blends are well suited for the study of the effects of physical crosslinking on structural conformation.

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The initial objective of this research was to verify PALS as an ultra-sensitive probe for monitoring free volume behavior as a function of time and temperature in the polystyrene homo-polymer. A second goal was to use PALS to observe the effect of molecular weight and physical crosslinking on free volume behavior in polystyrene based systems. Although the PALS research of IPNs is still ongoing, both of the above objectives have been successfully accomplished and the results are summarized in the following section.

Results

During the first stage of this research project polystyrene samples were compression molded from high and low number-average molecular weight resins. Gel permeation chromatography and viscometry were used to verify individual sample molecular weights. To verify transition temperatures samples were also characterized using differential scanning calorimetry, differential thermal analysis, dynamic mechanical analysis and dielectric loss spectroscopy.

PALS studies of the high and low molecular weight homo-polymers have shown a predictable change in the lifetime and intensity of the ortho-positronium (o-Ps) pickoff component upon thermal cycling between -20 and 120 °C. Isothermal aging studies using PALS also indicate consistent and predictable behavior of the o-Ps pickoff component as a function of time rather than temperature. The response of the o-Ps pickoff intensity, which is a measure of the density of free volume sites, reveals two transition temperatures at approximately 20 °C and 85 °C. These temperatures were observed to vary slightly depending on the molecular weight of the sample. Transition temperatures depicted using PALS are

consistently lower than those determined using conventional characterization techniques. This difference confirms the superior sensitivity of PALS for detecting the onset of segmental mobility in molecular solids. PALS results have also shown free volume relaxation to be dependent on molecular weight, with the higher molecular weight samples exhibiting slower relaxation kinetics.

While the transition measured at 85°C is known to be associated with the glass transition in polystyrene, the lower transition is believed to be a result of the beta-relaxation in this polymer. The subtle secondary transition is almost impossible to discern using conventional techniques and is therefore not well understood. This investigation suggests that the beta-relaxation is most likely associated with motion of the phenyl side groups. A dielectric loss system was developed to reinforce the PALS results regarding this secondary transition. Preliminary results from this system confirm the PALS findings. A complete discussion of the experimental details, and proposed structural relaxation models for the beta-transition in polystyrene is available in references listed below which have been published under this contract.

The second stage of this research project commenced with the synthesis of four polystyrene boards crosslinked to varying degrees using divinylbenzene as the crosslinking agent. PALS studies of thermal response and isothermal relaxation in these samples have proven this technique capable of resolving the effects of crosslink density on free volume behavior in polystyrene. Optically homogeneous 0.25 " thick sheets of polystyrene homo-IPNs, semi-I and semi-II IPNs have been synthesized and are being studied using PALS. The isothermal relaxation and thermal response data obtained from these studies will be evaluated in conjunction with the corresponding data collected on the four

crosslinked resins. Based on these results structural relaxation will be modelled as a function of physical crosslinking and interpenetration. In addition these findings will be correlated with the specific physical and mechanical properties of each sample.

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Contact with ARO Personnel

Dr. Andrew Crowson (ARO) has contributed to all aspects of this research project. Weekly meetings and telephone conferences were held between Dr. Crowson, Dr. Phillip Jones (Duke), and Anand Kasbekar (Duke). Dr. Crowson was also actively involved in the synthesis of the polystyrene IPNs.