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Solid state properties of phenylquinoxaline-arylene ester copolymers

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Summary

The thermomechanical behavior and mechanical properties were studied for a series of poly(phenylquinoxaline-arylene ester) block copolymers. The copolymers investigated were composed of a phenylquinoxaline oligomer of block length 12,900 g/mol, and the weight percent of the polyester coblock varied from 15 to 50 percent. Both homo- and heterogeneous morphologies were observed depending on the weight percent of polyester incorporated. Improved elongations were observed as the polyester compositions increased at a minimal sacrifice to the bulk properties (*i.e.*, modulus).

Introduction

Poly(phenylquinoxalines), PPQ, and related structures were first reported in the late sixties by Hergenrother and co-workers (1). These structures have many desirable properties including excellent thermal stability, low dielectric constant, high T_g and dimensional stability over a wide temperature range. Owing to these excellent properties, we believed it would be useful to prepare segmented or block copolymers from PPQ and a variety of other structures, e.g., polyesters, polysiloxanes, poly(arylene ethers) and others. Incorporation of appropriate coblocks with crystalline, glassy, or rubbery character could afford new PPQ-based materials with improved modulus, ductility, *etc.* Moreover, through judicious choice of block molecular weight and solubility parameter, either random or microphase separated morphologies should be possible, allowing an additional means of influencing the properties of these materials. We are currently developing the synthetic capabilities to prepare novel PPQ-based copolymers derived from well defined phenylquinoxaline oligomers with functional end groups. Through our synthetic efforts we hope to prepare a variety of new phenylquinoxaline copolymer systems, which will be investigated with respect to their solid state properties.

Multiphase polymeric materials in the form of block, graft, segmented and ion containing copolymers with thermoplastic elastomer properties have achieved significant commercial status and a number of reports concerning their preparation and properties have appeared in the literature. In contrast, there has been very little research in the area of block copolymers composed of two or more hard or glassy components. McGrath and co-workers (2) have reported the synthesis and characterization of homo- and heterogeneous glassy-glassy block copolymers based on polysulfone and polycarbonate. It was demonstrated that the structure or solubility parameter of the polysulfone block used together with the relative block lengths governs the microphase separation. The effects of having a two phase structure influenced such properties as ductility, modulus and melt viscosity. In contrast, polystyrene-poly(alpha methy styrene) glassy-glassy di-and triblock copolymer systems have shown single phase morphologies at block lengths as high as 200,000 g/mol (3). These results were in good agreement with the theoretical predictions of Krause (4,5) who pointed out that such diblock structures should be homogeneous up to block lengths of 8 x 10^5 g/mol. Other examples of "glassy-glassy" copolymer systems include polystyrene-polymethylacrylate (6), poly(alpha methylstyrene)-polymethyl methacrylate (7), polystyrene-polyacrylonitrile (8), poly(xylenyl ether)-poly(arylene ether sulfone) (9) and others (10).

We have recently reported the synthesis of phenolic hydroxyl terminated phenylquinoxaline oligomers (11) and their copolymers with polyarylates (12,13). The incorporation of the ductile coblock or segment may impart impact strength to these rigid high temperature polymers. Possibly, such properties as T_g and melt viscosity may be sufficiently depressed to allow these materials to be processed from the melt making them candidates as matrix resins for board materials. In addition, there is very little known on the effects of microphase separation on the mechanical properties, environmental stress cracking and physical aging in such systems. In this communication we shall discuss the solid state mechanical properties and the morphology of the novel poly(phenylquinoxaline-arylene ester) copolymers.

Experimental

The synthetic routes for the preparation of phenolic hydroxyl terminated phenylquinoxaline oligomers and the phenylquinoxaline-arylene ester copolymers are given elsewhere (11-13). Films of the copolymers and the poly(arylene ester) and PPQ homopolymers were cast from a 3:1 mixture of tetrachloroethane and m-cresol at approximately 10% solids and heated to 325°C (5°C/min.) to remove solvent. Glass transition temperatures were performed on a DuPont DSC 1090 instrument at a 10°C/min heating rate. Stress-strain measurements were measured on an Instron at a strain rate of 10 mm/min (23°C). The dynamic mechanical measurements were performed on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) at 10 Hz and a heating rate of 10°C/min in the tension mode.

Results and Discussion

We have recently reported the preparation of phenylquinoxaline-arylene ester copolymers synthesized from preformed phenolic hydroxyl terminated phenylquinoxaline oligomers, bisphenol-A and isophthaloyl chloride (12,13). This preformed oligomer/monomer(s) synthetic approach produces the ester linkage between the blocks simultaneously with the growth of the polyarylate block. In this series of copolymers, the molecular weight of the phenylquinoxaline oligomer was held constant at 12,900 g/mol and the weight percent of poly(arylene ester) composition was varied from 15 to 50 weight percent. Table I contains the intrinsic viscosities and T_gs of the homo- and copolymers synthesized. A single T_g was observed for the copolymers containing the 15

TABLE I

Characteristics of PPQ Oligomer and Poly(phenylquinoxaline-arylene ester) Copolymers

Sample	$[\eta]_{25^\circ C}$ (dl/gm)	T_g (°C)
PPQ (Mn = 12,900 g/mol)	0.77	345
PPQ/PE(15)	0.93	335
PPQ/PE(30)	0.82	300
PPQ/PE(50)	0.84	195,300
PE (100)	0.85	195

and 30 weight percent of poly(arylene ester) and two T_gs (200 and 300°C) were observed in the copolymer containing the 50 weight percent poly(arylene ester) indicating microphase separation was achieved in this case. In the latter case, the precipitated copolymer powder showed a single T_g (260°C) on the first scan. However, the second scan, as well as the polymer film, clearly shows the development of the two phase morphology. The copolymers containing the lower weight percentages of polyester have T_gs intermediate to those of the polyester (190°C) and PPQ homopolymers (370°C). We believe that the molecular weight of the polyester segments or blocks between the PPQ blocks may not be sufficient to afford a microphase separated system. In such cases, a homogeneous morphology is achieved with a T_g which is between the homopolymers depending on the weight percentages of each component. Fox (14) has published a modification of the Gordon-Taylor equation (15) for the prediction of T_gs of amorphous-random copolymers. This may be written as equation (1), where T_g is the T_g of the copolymer; and T_{gA} and T_{gB} are the T_gs of homopolymers A and B, respectively, and w_A and w_B are the weight fractions of homopolymers A and B, respectively.

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}} \quad . \tag{1}$$

A plot of $1/T_g$ *versus* weight percent of polyester is a straight line as predicted by equation 1 (Figure 1). The experimentally obtained T_g values for the copolymers containing the 15 and 30 weight percent polyester are also shown on this plot, and excellent agreement observed between these values predicted and the values by equation (1). In addition, the T_g obtained from the first scan of the copolymer containing 50 weight percent poly(arylene ester) which exhibits a single phase morphology is also shown on this plot. Clearly, these data indicate that homogeneous morphologies were obtained.

The dynamic mechanical behavior for the copolymers is shown in Figures 2a and b. These data, consistent with the DSC results, reflect the single phase morphology of the copolymers containing the 15 and 30 weight percent poly(arylene ester). In contrast, two T_gs were observed for the copolymer containing 50 weight percent polyester, suggesting a two phase morphology. The storage modulus decreases at both 190 and 280°C, and the tanδ damping peaks increases in these regions clearly illustrating the two phase structure (Figure 2). In this copolymer, the mole percent of PPQ oligomer in the polymer is relatively small allowing high molecular weight polyester to form. Since phase separation in such "glassy-glassy" structures is a function of both block lengths and segment interaction parameters (4) it follows that a two phase morphology may be obtained in this case. The T_g of the poly(arylene ester) block or segment in the copolymer is identical to that of the homopolyester (195°C). This suggest minimal phase mixing or PPQ contamination in the polyester domain. In contrast, the PPQ T_g is depressed nearly 45°C from that of PPQ oligomer (345°C). Apparently, the extent of phase separation or more precisely the phase purity of the PPQ domain is limited. The synthetic route used produces copolymer system having homogeneous morphologies at low poly(arylene ester) compositions presumably resulting from a molecular weight effect, where at these compositions sufficient molecular weight segments or blocks of poly(arylene ester) cannot be achieve affording a single phase system. The copolymers with the higher compositions of poly(arylene ester) allows larger sequences or blocks between the PPQ blocks to develop, however these blocks have a fairly broad molecular weight distribution. It is likely the lower molecular weight polyester sequences are micsible in the PPQ and will decrease the PPQ T_g in the copolymer. In addition, the modulus drop after the T_g of the poly(arylene ester) is not sharp and does not level off prior to the PPQ T_g. This breadth may result from either continous mixing above the T_g of the polyester or a broad interfacial region between the domains.

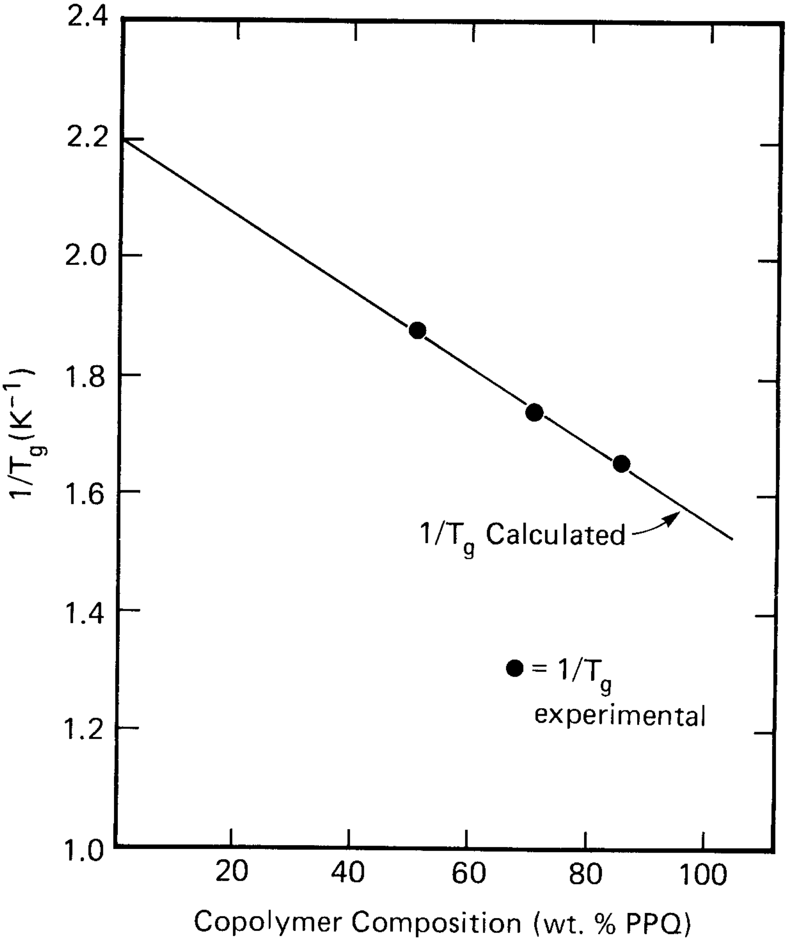

Figure 1. 1/T, *versus* copolymer composition (Fox-Flory relationship) for the phenylquinoxaline-arylene ester copolymers.

TABLE II

Mechanical Properties of Poly(phenylquinoxaline-arylene ester) Copolymers

Sample	Modulus (MPa)	Stress at Break(MPa)	Elongation (%)
PPQ	2,700	128	10
PPQ/PE(15)	2,700	118	10
PPQ/PE(30)	2,480	126	45
PPQ/PE(50)	2,450	120	60

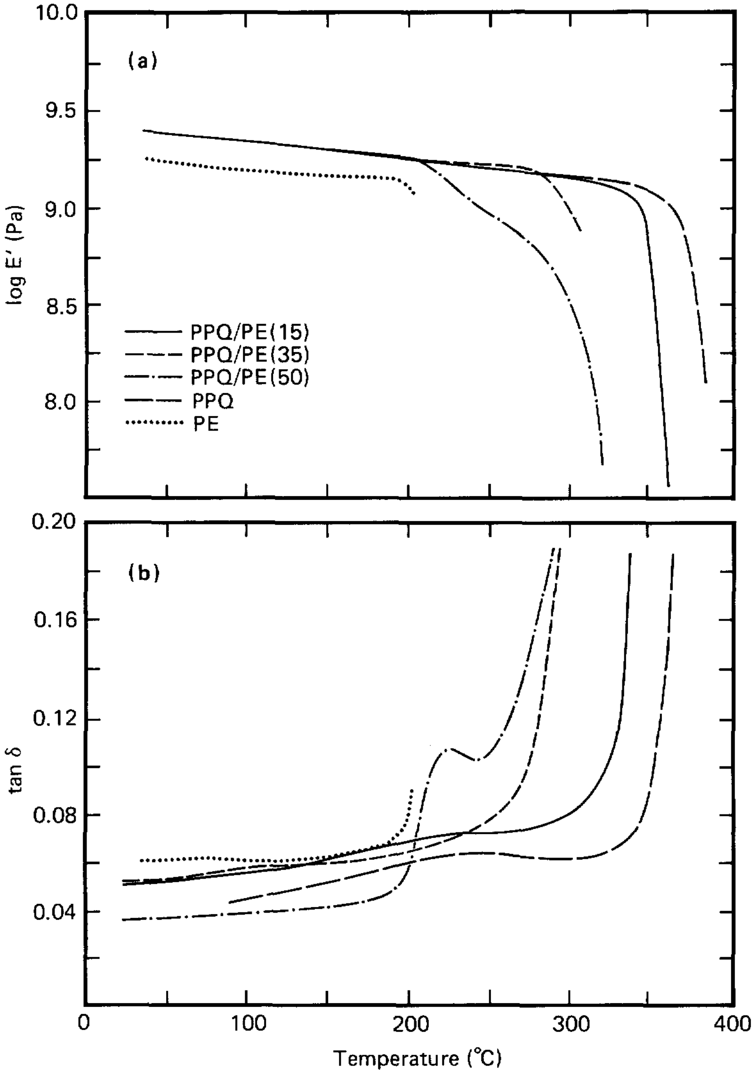

Figure 2. Dynamic mechanical behavior for the phenylquinoxaline-arylene ester copolymers (a) storage modulus *versus* temperature plot and (b) tanδ *versus* temperature plot.

High molecular weight poly(phenylquinoxalines) have a high modulus (Table II) and form fingernail creasable films. However, elongations in these structures are limited to about 10 percent. As expected, significant improvements in elongations were achieved by the incorporation of the ductile poly(arylene ester) (Table II). These results are consistent with other reports on glassy-glassy copolymers containing polyesters based on isothphaloyl chloride and bisphenol-A (16). Tough, ductile mechanical properties of engineering polymers have been associated with the major secondary relaxation (β transition) in the dynamic mechanical spectra (17). Figure 3 contains the tanδ versus temperature plot for the homo- and copolymers. The magnitude of the transition (90° at 10 Hz) for PPQ high molecular weight homopolymer is small but increases with the incorporation of the poly(arylene ester) (15 and 30 weight percents). Clearly, the incorporation of the polyester serves to increase the thermoplastic character of the PPQ in the samples where homogeneous morphologies were observed. Thus improved elongations are observed.

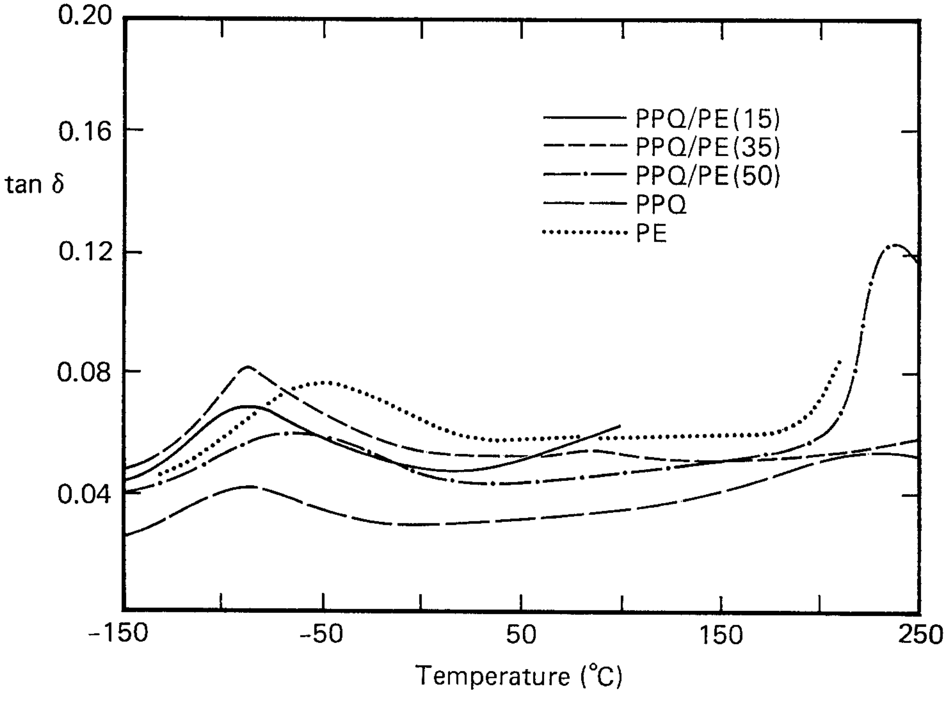

Figure 3. Tanδ *versus* temperature plot for the phenylquinoxaline-arylene ester copolymers.

In contrast, the copolymer containing fifty weight percent poly(arylene ester) has β relaxation shifted toward that of homopolyester. The improved ductility is attributed to the discrete poly(arylene ester) domains which are capable of large scale plastic deformation.

In addition, only a minimal sacrifice in the modulus was observed in these copolymers from that of PPQ homopolymer. We believe that preparing copolymers with a morphology where the PPQ is the continuous or predominate phase will provide a high modulus material.

Conclusions

Significant improvements in elongations were achieved by the incorporation of the ductile poly(arylene ester) into the PPQ structure. This may be very important at dissipating stresses acquired from thermal cycling, or from a mismatch in the coefficient of thermal expansion between a rigid silicon or copper substrate and the copolymer. Moreover, the improvement in elongations was attained with minimal sacrifice to the modulus. Both homo- and heterogeneous morphologies were observed, and the effect of having a two phase morphology on the mechanical properties was investigated. Future publications will discuss the effects of producing a glassy-glassy copolymer with a two phase morphology on the mechanical properties and physical aging in more detail.

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