Polymer Bulletin 30, 33–38 (1993)

Polymer Bulletin

Adhesion characteristics of imide-aryl ether ether ketone block copolymers with poly(ether-imide)

J. L. Hedrick[1], W. Volksen[1], and D. K. Mohanty[2]

[1]IBM Research Division, Almaden Research Center 650 Harry Road, San Jose,
CA 95120-6099, USA
[2]Department of Chemistry, Central Michigan University, Mount Pleasant, MI 98859, USA

Abstract

Imide-aryl ether ether ketone block copolymers were prepared and the adhesion characteristics with poly(ether-imide) were investigated. The copolymers were prepared via the poly(amic alkyl ester) precursor to the polyimides which is hydrolytically stable and may be isolated and characterized prior to imidization. Solutions of the copolymers were cast and cured to effect the imidization, producing clear tough films which showed two transitions, indicative of a multiphase morphology. Mixtures of the copolymers with poly(ether-imide) also produced clear films, and the shift in the T_g of the aryl ether ether ketone component of the block copolymer indicated miscibility with the poly(ether-imide) within this phase. This miscibility of the poly(ether-imide) with the aryl ether ether ketone component of the block copolymer produced significant improvements in the adhesion of the thermoplastic poly(ether-imide) with the rigid polyimide copolymer.

Introduction

High temperature polymers are important materials for the microelectronics industry. The polymer properties required for applications as interlayer dielectrics and passivation layers generally include high thermal and dimensional stability, low thermal expansion coefficient and residual stress upon thermal cycling, planarization, low dielectric constant and good mechanical properties. The aromatic polyimide derived from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA), poly(4,4'-oxydiphenylene pyromellitimide), is one of the most widely used due to its availability, ease of processing, excellent thermal and dimensional stability, and high modulus and elongation. These good mechanical properties and low thermal expansion coefficient can be attributed, in part, to the liquid crystalline or crystalline order exhibited by these materials (1). Although the rigid and semi-rigid polyimides fulfill many of the material requirements, drawbacks to their ordered morphology and the absence of a T_g results in poor planarization and self-or auto-adhesion.

The auto- or self-adhesion of polyimide, i.e., the adhesion of polyimide to itself, is important in the fabrication of multilayer components. It has been demonstrated that the interfacial strength of polyimide depends on the interdiffusion between layers which, in turn, depends on the initial cure temperature (T_1) and the temperature (T_2) where interdiffusion takes place (2). If $T_1 \geq 400°C$ the strength between the bonds was weak, however, good auto-adhesion was found when $T_1 < T_2$ and adhesion was improved with lower T_1 values (2). Improved auto-adhesion has also been demonstrated by the use of imide random and block copolymers. For instance, imide-aryl ether phenylquinoxaline statistical copolymers were prepared with various phenylquinoxaline compositions (3). At the high phenylquinoxaline compositions, the interchain packing was sufficiently hampered to disrupt the ordering, and this variation in ordering ultimately defined the properties of the copolymers including lowering the T_g. Significant improvements in the auto-adhesion characteristics were observed on films sequentially cast and cured to temperatures above the T_g. Likewise, imide-aryl ether phenylquinoxaline and benzoxazole block polymers, prepared from the reaction of pyromellitic dianhydride diethyl ester diacyl chloride, 4,4'-oxydianiline and either bis(amino) terminated phenylquinoxaline or benzoxazole oligomers, also showed improved self-adhesion in sequentially cast and cured layers (4,5).

These microphase separated materials showed improved auto-adhesion, while retaining the ordered morphology and desirable mechanical properties of the polyimide.

It is also of interest to adhere or laminate rigid polyimide films to themselves with thermoplastic adhesives, eliminating the use of solvents. Although many of the poly(aryl ether) based thermoplastics are known to be hot melt adhesives once heated approximately 50-70°C above their T_g's, adhesion to rigid polyimides is particularly difficult due to both the polymer-polymer immiscibility and absence of mobility in the rigid polyimide. Consequently, it is of interest to design new materials to circumvent these drawbacks. Harris and coworkers (6) have recently reported that two such thermoplastics, the amorphous poly(ether imide) and semi-crystalline poly(ether ether ketone), are miscible over their entire compositional range. Therefore, we have prepared imide-aryl ether ether ketone block polymers and investigated the adhesion to thermoplastic poly(ether-imide) with the intention that the miscibility would facilitate the auto-adhesion.

Experimental

Materials

Diethyl pyromellitate diacyl chloride was prepared according to literature procedure (7). N-[bis(4-fluorophenyl) methylene]benzenamine was prepared by the reaction of 4,4′-difluorobenzophenone with aniline according to literature procedures (8,9). The bis(amino) aryl ether ketimine oligomer was prepared from the polymerization of N-[bis(4-fluorophenyl)methylene]benzenamine, hydroquinone and 1,3-aminophenol in NMP containing K_2CO_3 according to previously published procedures (8-10).

Copolymer Synthesis

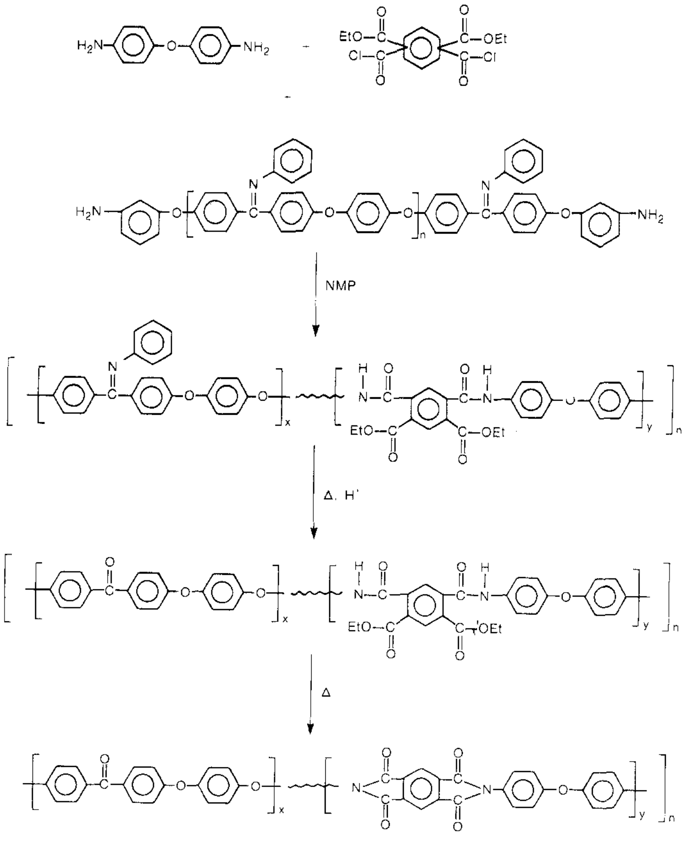
The amic ester-aryl ether ketone copolymers were prepared by the co-reaction of the aryl ether ketimine oligomers with 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) diethyl ester diacyl chloride in N-methyl-pyrrolidone (NMP) in the presence of N-methylmorpholine according to known procedures (7). A detailed procedure designed to prepare an amic-ester aryl ether ketimine copolymer with a aryl ether ketimine oligomer of 6,500 g/mol molecular weight and 20 wt.% aryl ether ketone composition is provided. A three necked flask equipped with an overhead stirrer and addition funnel was charged with the aryl ether ketimine oligomer (1.2500 g, 0.00019 mol), ODA (1.3458 g, 0.0067 mol) and carefully rinsed in with 20 mL of NMP. The solution was then cooled to -5 °C, and N-methylmorpholine (1.433 g, 0.0143 mol) was added and rinsed in with 20 mL NMP. PMDA diethyl ester diacyl chloride (2.4000 g, 0.0069 mol) was added to the addition funnel and dissolved in approximately 25 mL of methylene chloride. This solution was added in small increments over a 2 h period so as to slowly approach the stoichiometric end point. The polymerizations were allowed to proceed overnight, and then the polymerization dope was isolated in an excess of a methanol/water mixture, rinsed with water (to remove excess salts).

Results and Discussion

The bis(amino) terminated aryl ether ether ketone oligomers are not readily accessible since these materials are only soluble in strong acids or diphenylsulfone at elevated temperatures. This insolubility makes the synthesis and characterization of functionalized oligomers and subsequent transformations (i.e., copolymerization) difficult. We have used an alternate synthetic route to poly(aryl ether ether ketone) as described by McGrath et al., which involves derivitization of one of the monomers to afford oligomer solubility and after subsequent transformations (i.e., copolymerization), a deprotection step yields the parent polymer (8,9). It has been demonstrated that the ketone moiety in 4,4′-difluorobenzephenone can be derivatized with aniline to produce a ketimine (8,9,10). The ketimine functionalized 4,4′-bisfluoride was reacted with hydroquinone and 3-aminophenol in a NMP/toluene solvent mixture in the presence of K_2CO_3 via a ketimine-activated nucleophilic aromatic substitution reaction (10). 3-Aminophenol was used as a monosubsituted monomer to control both the molecular weight and end group functionality. The number average molecular weight, as determined by ^{1}H-NMR, was 6,500 g/mol which is in good agreement with that predicted by the charge as calculated for the monomer stoichiometry.

The imide-aryl ether ketimine copolymers were prepared via the poly(amic alkyl ester) route (7). This intermediate route to the polyimide is more versatile than the poly(amic-acid) since copolymers prepared this way can be isolated, characterized, undergo subsequent transformations and given selective solvent rinses to remove homopolymer contamination. In our work we have primarily used the poly(amic-ethyl ester), since it is soluble in a variety of solvents and imidization occurs at a substantially higher temperature. Furthermore, since both the isomers may be isolated prior to polymerization, enhanced solubility may be realized by using the meta-isomer (7).

The copolymer synthesis involved the incremental addition of PMDA diethyl ester diacyl chloride to a NMP solution of 4,4'-oxydianoline (ODA) and the aryl ether ketimine oligomer in the presence of N-methylmorpholine (acid acceptor) (Scheme 1). High molecular weight was readily achieved as judged by the dramatic increase in viscosity, and the resulting amic-ethyl ester based copolymers (**1** and **2**) were isolated in an excess methanol/water mixture (50/50) and finally dried under vacuum (30 °C). The amic ester-aryl ether ketimine copolymers were prepared with compositions below 20 wt% so as



Scheme 1

to maintain the solubility of the subsequent amic ester-aryl ether ketone copolymer. The composition of aryl ether ketimine in the block copolymers was comparable to that charged, and the molecular weights, as judged by the viscosity measurements, were high (Table 1).

Table 1

Characteristics of Amic Ester–Aryl Ether Ketimine Copolymers

Copolymer	Block Length, g/mol	Block Composition, wt.%		$[\eta]^{25°C}_{NMP}$ dL/g
		Theory	Actual	
1	6,500	10	9	0.52
2	6,500	20	16	0.65

Prior to imide formation, the ketimine moiety was hydrolized with para-toluene sulfonic acid hydrate according to literature procedures (8-10), yielding the amic ester-aryl ether ether ketone copolymer. Copolymers **1** and **2** were dissolved in NMP and heated to 50 °C, and subjected to excess acid for 8 h (Scheme 1). The reaction mixtures were isolated to afford the amic ester aryl ether ether ketone copolymers **3** and **4**, respectively. It is important to note that the acid hydrolysis of the ketimine appeared to have no adverse effect on the stability of the amic ester coblock.

Solutions of the copolymers **3** and **4** were cast and cured (350 °C) to effect imidization, yielding copolymers **5** and **6**, respectively. The solutions at ambient temperature were somewhat cloudy, however, upon heating, usually in cast film form, the copolymer solutions became clear at ~80 °C. In each case, clear tough films were obtained, indicative of minimal homopolymer contamination. The thermal analysis for copolymers are shown in Table 2 together with polyimide homopolymers to facilitate comparison. No detectable T_g was observed for the polyimide homopolymer or for any of the copolymers providing no insight as to the morphology of the block copolymers. Table 2 also contains the thermal stability, as determined by the polymer decomposition

Table 2

Characteristics of Imide–Aryl Ether Ether Ketone and Ketimine Block Copolymers

Copolymer	Block Length, g/mol	Block Composition, wt.%	Decomposition Temp., °C	TEC, ppm
3	6,500	13	450	--
4	6,500	19	500	40
PMDA/ODA Polyimide	--	--	480	40

temperature, PDT, for the block copolymers and the polyimide control. The PDT's are high and comparable to the parent polyimide.

The imide aryl ether ether ketone copolymers showed multiphase morphologies irrespective of the aryl ether ether ketone co-block composition. The dynamic mechanical spectra for copolymer **6** is shown in Figure 1. The T_g of the aryl ether ether ketone component in the block copolymer was higher than that observed for the initial oligomer. Likewise, the transition associated with the polyimide component of the copolymers was somewhat lower than that observed for the polyimide homopolymer. This behavior is consistent with poor phase purity or phase mixing, which may have resulted from the restriction of the chain ends due to the shortness of the aryl ether ether ketone block. Crystallization of the aryl ether ether ketone component in the block copolymer was not observed, presumably due to the size scale of the phase separated domains (<500 Å). However, in each case, a reflection at approximately 15.5 Å was observed by WAXS measurements, corresponding to the liquid crystalline type order in the polyimide block (1). However, the reflection was weak and diffuse, consistent with poor phase purity.

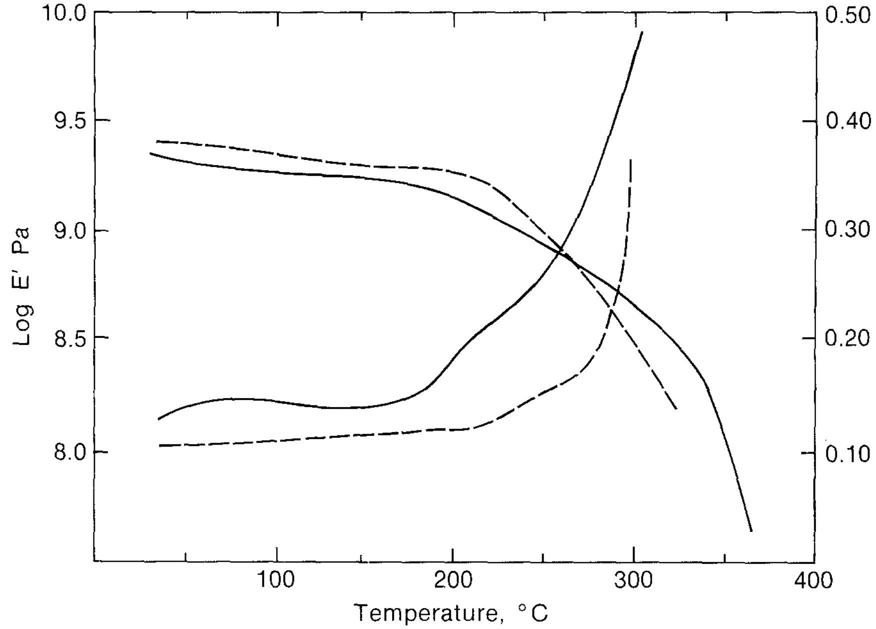


Figure 1. Dynamic mechanical behavior of (imide-aryl ether ether ketone block copolymer, 6, (-----), and coploymer 6 containing poly(ether-imide).

Mixtures of the amic ester-aryl ether ether ketone copolymers with various compositions of poly(ether-imide) were prepared in NMP, cast and cured (350 °C) to effect imidization of the copolymer. Provided the composition of poly(ether-imide) in the copolymer/homopolymer blend was less than ~60% by weight of the aryl ether ether ketone component in the copolymer, clear tough films were obtained. Higher poly(ether imide) compositions produced a morphology where the poly(ether imide) formed domains ranging from ~5 to 15 μm in size. Also shown in Figure 1 is the dynamic mechanical spectra of the imide-aryl ether ether ketone copolymer/poly(ether imide) homopolymer blend containing 40 wt.% poly(ether imide) relative to the weight of the aryl ether ether ketone component in the block copolymer. Clearly, what is seen is a shift in the aryl ether

ether ketone T_g towards higher temperatures, consistent with the miscibility of the poly(ether imide) ($T_g \sim 217°C$) in the aryl ether ether ketone phase (6).

The adhesion, as measured by L-peel test, of sequentially cast and cured layers of poly(ether imide) to PMDA/ODA polyimide is minimal (Table 3). Conversely, the adhesion of poly(ether-imide) to the imide aryl ether ether ketone block polymers showed markedly different behavior. The adhesion, once cured to 350 °C, was exceptional. In fact, L-peel adhesion test could not be performed as the two films were indistinguishable and thus denoted in Table 3 as laminate. The substantial improvements in adhesion presumably resulted from the local miscibility of the poly(ether imide) with the aryl ether ether ketone component of the copolymer at the interface. Thus, this approach allows a means to laminate rigid high T_g polyimides which have T_g's in excess of the lamination temperature with moderate T_g thermoplastic polyimides.

Table 3

Adhesion Studies of Poly(ether imide) on Polyimide

Sample	Peel Strength
PMDA/ODA Polyimide	<3 g/mm
Copolymer 3	Laminate

References

1. Russell TP (1986) J Polym Sci Polym Phys Ed 22:1105
2. Brown HR, Yang ACM, Russell TP, Volksen W, Kramer EJ (1988) Polymer 29:1807
3. Hedrick JL, Labadie JW, Russell TP, Palmer T (1991) Polymer 32:950
4. Hedrick JL, Russell TP, Labadie JW (1991) Macromolecules 24:4559
5. Hedrick JL, Hilborn J, Labadie J, Volksen W (1990) J Polym Sci Polym Chem Ed 28:2255
6. Harris J, Robeson L (1988) J Appl Polym Sci 35:1877
7. Volksen W, Yoon DY, Hedrick JL (1992) IEEE Transactions 1503:107
8. Mohanty DK, Lowry RC, Lyle GD, McGrath JE (1987) Int SAMPE Symp 32:408
9. Mohanty DK, Senger JS, Smith CD, McGrath JE (1988) Int SAMPE Symp 33:970
10. Hedrick JL, Volksen W, Mohanty DK (1992) J Polym Sci Polym Chem Ed 30:2085

Accepted October 28, 1992 K