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Study on structure-property relationship of polyimide blends

I. A dynamic mechanical study of the miscibility of polyimide/polyimide blends

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Summary

Three pairs of polyimide/polyimide blends (50/50 wt%) with different molecular structures were prepared by two ways, i.e. mixing of the polyamic acid precursors with subsequent imidization,and direct solution mixing of the polyimides.The blends were studied with DMA technique.The results obtained show that all the blends prepared with these two different ways are miscible, as there existed only one glass transition temperature(Tg) for all the blends. It is suggested that the miscibility of these polyimide/polyimide blends is a result of the strong inter-molecular charge-transfer interaction between the chains of their components.

Introduction

Polyimides(PIs) constitute the biggest and most popular family of high temperature polymers. Because of the availability of certain monomers, more PIs with different structures have been synthesized. However, it is quite difficult to make one kind of PI possess all the functions demanded.On the other hand, fundamental studies of the phase states of blends of different polymers have been remarkedly advanced. Hence, in recent years,a number of novel polymer blends based on PI have been developed and used in various fields.It has been reported that various PIs are miscible with PBI(1-6),PEEK(7),PES(8),and sulfonated PEEK(9). Although the mechanism of miscibility of PBI/PIs was shown to be related to H-bonding between the chains of the two components, the mechanism of other blends is not yet clear.It has been shown that most soluble PI chains are very flexible, and the high thermal stability and outstanding mechanical property of PIs are due to their strong inter- or intra-molecular charge-transfer interaction between imide groups and aromatic groups in the chains(10, 11). Therefore, we consider,the mechanism of miscible blends of PIs with PEEK, PES, and sulfonated PEEK may be due to the interaction between imide groups in PI chains with the aromatic groups in the chains of the other polymers. From the above point of view,it may be expected that two different PIs having electron-donor and electron-aceptor in their chains respectively should have much more opportunity to form intermolecular charge-transfer interaction between the chains of

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**Formerly E. T. L. Voong and Voong Tse-Liu different kinds, which might lead to the formation of miscible or semi-miscible blends. This is the purpose of our investigation.

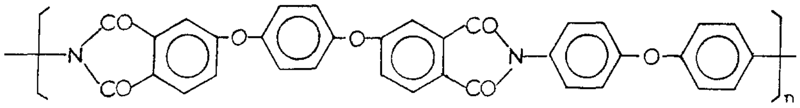
Experimental

Preparation of blend specimens

The polyimide blends were prepared in two ways. In the first way, the PI blends were obtained by solution blending of two PI precusors, i. e. polyamic acids, in DMF with a concentration of 15%(wt/v) at room temperature. Film specimens were produced by casting the solution onto a glass plate, drying at 40°C for 16 hours, then transfered into a vacuum oven, maintained at 100°C for 3 hours, and afterwards heated to 280°C in about 3 hours. In the second way, the blends were prepared directly by solution blending of two polyimides in m-crosel, followed by precipitation in ethanol, filtration and drying.

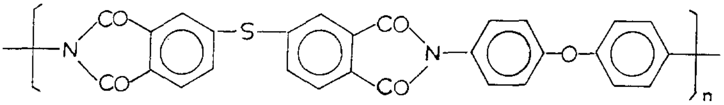
The binary blends of PIs studied included PEI-E/PTI-E, PEI-E/PSI-E and PTI-E/PTI(3,3)-E, the composition of which were 50/50 by weight. The molecular structure and glass transition temperatures(Tg) of these PIs are as follows. Meanwhile, the inherent viscosities(ni) of PIs used in solution blending experiment measured at 30°C in 0.5 wt% m-cresol are also given.

PEI-E



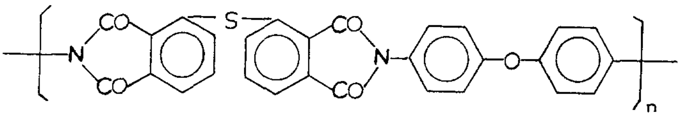
Tg=241°C ni=1.50 (dl/g)

PTI-E



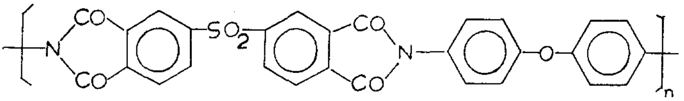
Tg=267°C ni=1.05(dl/g)

PTI(3,3)-E



Tg=288°C ni=0.67(dl/g)

PSI-E



Tg=335°C ni=0.40(dl/g)

Dynamic mechanical analysis (DMA)

DMA was carried out with a DuPont 982 DMA at a heating rate of 5°C/min from room temperature to 400°C. The PI specimens used for DMA were 2mm thick,compression molded at 370°C,cooled to 200°C in press, and then quenched with water.

Results and Discussion

The films of polyamic acid blends drying at 40°C prepared by the first way were clear and transparent. However, after imidization at 280°C, the films were still transparent, but their color changed to pale yellow or reddish-brown. This result implies that these PI blends prepared by the first way are miscible.

In order to confirm the above phenomenon, the DMA study was carried out for PEI-E/PTI-E and PEI-E/PSI-E blends, the results of which are shown in Fig.1 and 2 respectively. It is clearly shown that there exist two relaxation peaks, α and β , in the the blends as well as in their components. The α relaxation is the glass transition, while the β relaxation is related to the motion of aromatic and benzimide rings(10, 12). For both blends, a single, sharp glass transition located in between the two Tgs of its components, confirms that these two blends are completely miscible. The location of the β relaxation of the blends being in between the two β relaxations of their component PIs might be operated by the same mechanism, both interchain and intrachain barriers, as suggested in the literature(7).

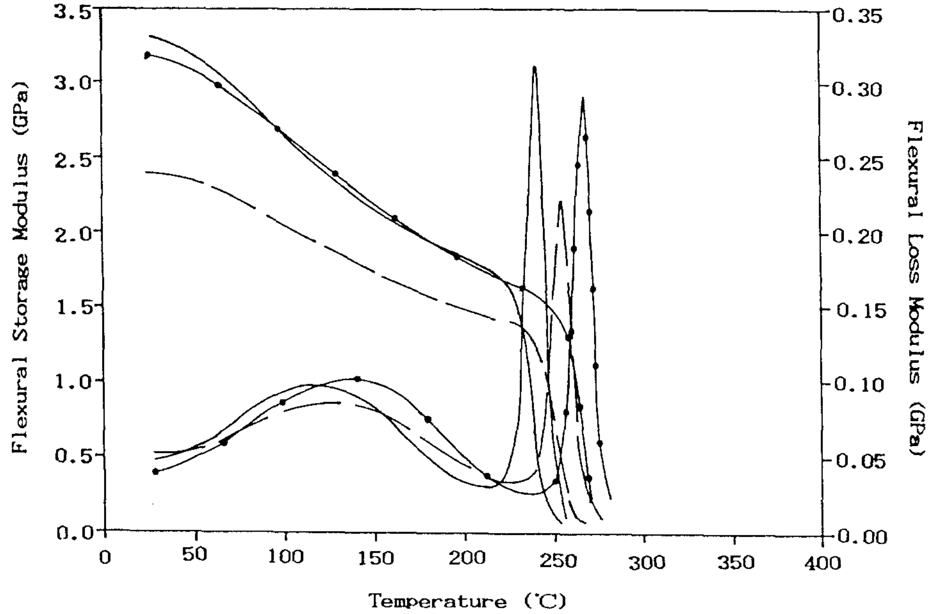


Fig. 1 DMA curves of PEI-E, PTI-E and their 50/50 blend obtained by the first way of blend preparation.
———— PEI-E, —●——●——● PTI-E
— — — PEI-E/PTI-E=50/50

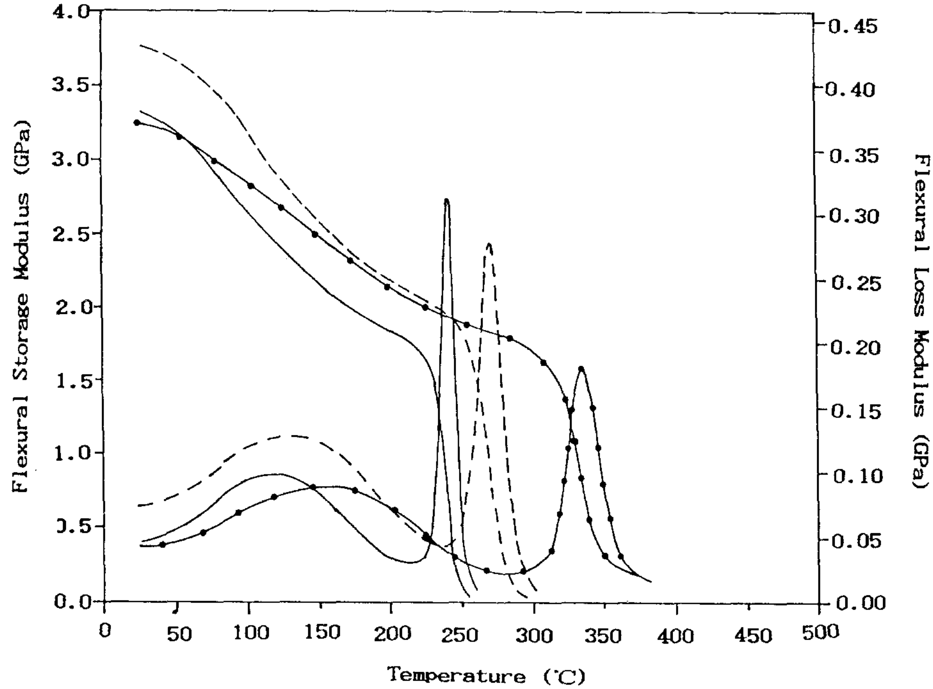


Fig. 2 DMA curves of PEI-E, PSI-E and their 50/50 blend obtained by the first way of blend preparation.
———————— PEI-E, —•—•—•—•— PSI-E
- - - - - - - - - PEI-E/PSI-E=50/50

The prepration of polyimide blends obtained by solution mixing of polyamic acid precursors and subsequent solid state imidization was reported by Yokota et al (13), but the structure of the blends are rather complicated due to the exchange reactions between polyamic acids in solution and during the imidization process. Feger considered that storge at room temperature and slow curing of polyamic acid blends lead to copolymerization (14).

In our preparation of the blends by the first way, copolymerization may also take place, hence if any copolymer produced will have certain influence on the miscibility.

In order to reveal the influence of copolymerization on the miscibility, the blends of PEI-E/PSI-E and PTI-E/PTI(3,3)-E with a composition of 50/50 were prepared directly by solution blending in m-cresol (the second way), during which copolymerization should not occur.

The DMA curves of PTI-E/PTI(3,3)-E, and PEI-E/PSI-E are shown in Fig.3 and 4 respectively. The existance of only a single Tg for all the blends confirms the miscibility of these two pairs of PIs, which also shows that the two different ways of blending used in this work do not affect their miscibility. However, it should be noted that the position, height and broadness of the three Tg peaks are different by different ways of blending and after treatments(Fig.4).The one by direct solution blending has a much broader but less high glass transition than those of the blends prepared by the first way, which implies that the copolymerization occured in the process of mixing polyamic acids in solution could improve the miscibility of the blends on molecular level. Meanwhile, it is also noted that the blends stored with different lengths of time after blending by the first way show different relaxation properties in their modulus and transition temperature, which could be partly explained by the result of copolymerization, but other factors are still to be sought for(14).

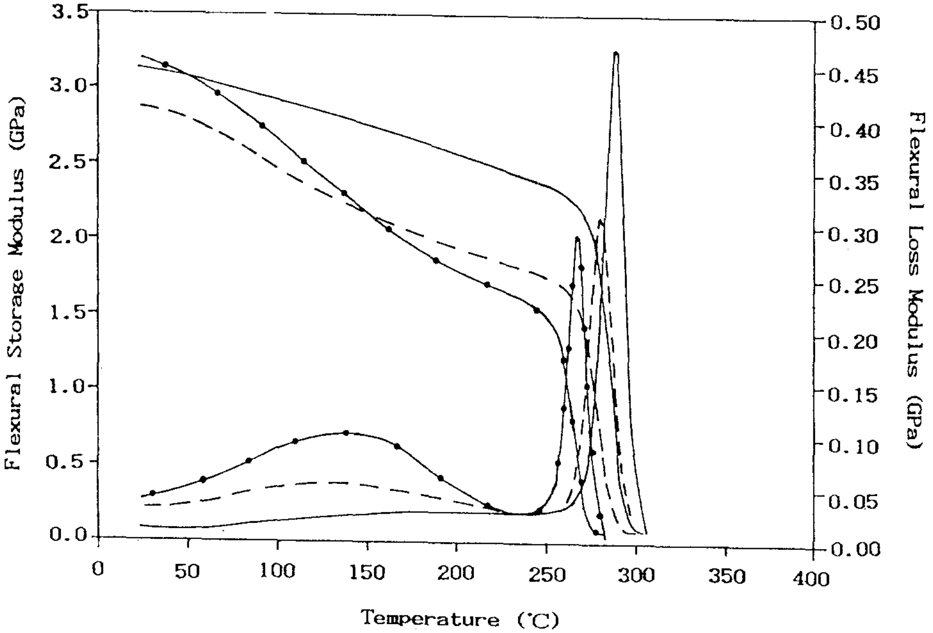


Fig. 3 DMA curves of PTI-E, PTI(3,3)-E and their 50/50 blend prepared directly by solution blending.
—•——•——•—• PTI-E, ———————— PTI(3,3)-E
— — — — — — PTI-E/PTI(3,3)-E

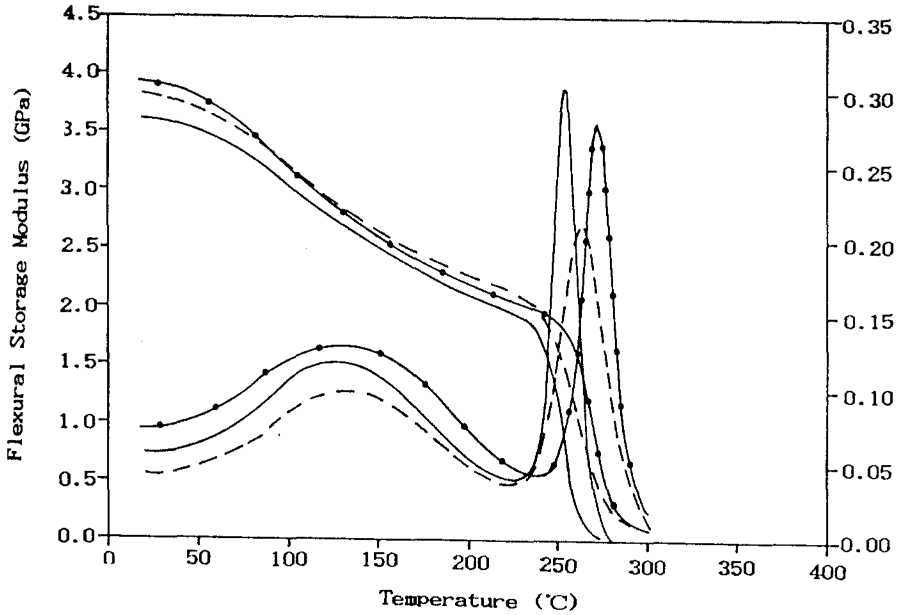


Fig. 4 DMA curves of three PEI-E/PSI-E (50/50) blends obtained by different mixing processes.

———— prepared by the first way of blend preparation, the mixture solution was stored at room temperature for 1 hour.

– – – – – prepared directly by solution blending of the PI components.

—●——●——● prepared by the first way of blend preparation, but the mixture solution was stored at room temperature for 24 houres.

Conclusion

From the above results, it may be concluded that binary blends of polyimides with different molecular structures are miscible due to the strong intermolecular charge-transfer interaction between imide groups and aromatic groups in the chains of their components, since there is no other factor which could play the role of increasing the interaction between two polyimides' chains.

The two methods, used in this work for blending have not much different effects on the miscibility of polyimide pairs as a whole, although direct blending might give some what higher microheterogeneity in the blends. The first way of blending is in favor of obtaining a more even mixture, as indicated by a sharp, narrow and high Tg peak, which might due to its more complicated structure resulted from exchange reaction or copolymerization during curing and storage. The study of its mechanism is in progress.

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