

Dynamic mechanical behaviour of polyether ester–nitrile rubber blends

D. J. Hourston and I. D. Hughes

Department of Chemistry, University of Lancaster, Bailrigg, Lancaster, Lancashire LA1 4YA, UK

(Received 22 October 1979; revised 8 April 1980)

INTRODUCTION

In this study a commercial segmented polyether ester (Hytrel) and a nitrile rubber have been blended and the dynamic mechanical properties investigated. Several papers concerned with both the synthesis and properties^{1–4} of polyether esters and with the properties of blends of this type of polymer with poly(vinyl chloride)^{5–8} have been published. For blends with poly(vinyl chloride)⁷ it was concluded that, at least over a limited composition range, there was evidence to suggest that the polyether sequences in the polyether ester were compatible with poly(vinyl chloride).

The extent of the compatibility of nitrile rubber and poly(vinyl chloride) has been the subject of many investigations^{9–13}. In some respects nitrile rubber was found to exert an effect on poly(vinyl chloride) similar to that of the low molecular weight plasticizers in that the softening point of the poly(vinyl chloride) was reduced and its flexibility increased. Such blends are highly compatible¹⁴ when the acrylonitrile content of the rubber is about 40 wt%. The major factor controlling the extent of mixing of these blends appears to be the polarity of the nitrile rubber, which is determined by the acrylonitrile content.

Thus, as there is evidence of compatibility in blends of polyether esters and poly(vinyl chloride) and in blends of nitrile rubber and poly(vinyl chloride), it seems reasonable to investigate whether blends of the polyether ester and nitrile rubber are also compatible.

EXPERIMENTAL

Materials

The segmented polyether ester (Hytrel, grade 4055) was kindly supplied by the du Pont de Nemours Company. This polymer is a random block copolymer⁷ of crystallizable tetramethylene terephthalate sequences and poly-(tetramethylene ether) glycol terephthalate blocks. The nitrile rubber (Breon 1041) was kindly donated by B.P. Chemicals Ltd. See Table 1 for characterization data for both polymers.

Blending

The polymers were solution blended by mixing approximately 2% (w/v) solutions of the polyether ester in methylene chloride and the nitrile rubber in tetrahydrofuran and precipitating the blends by the addition of

methanol. The resulting blends were dried at 20°C under vacuum for at least 10 days prior to sheeting on a hot press. The resulting sheets were translucent.

Dynamic mechanical measurements

The dynamic mechanical results were obtained using a Rheovibron dynamic viscoelastometer (model DDV-II-B) at a frequency of 110 Hz. The temperature range covered was scanned at a rate of 1–2°C min^{–1}.

RESULTS AND DISCUSSION

Figure 1 shows the $\tan \delta$ versus temperature dispersions for the blends and the homopolymers. The blends all exhibit only one clearly resolved glass transition which increases in temperature as the nitrile rubber level is raised. The 75% by wt polyether ester blend exhibits a pronounced shoulder on the low temperature side of this transition, undoubtedly indicating phase separation. Close examination of the $\tan \delta$ –temperature curves for the other two blends also indicates similar, but smaller shoulders. These shoulders occur at approximately the glass transition temperature^{7,8} of the polyether ester. The fact that the values of $\tan \delta$ at the glass transition ($\tan \delta_{\max}$, see Table 2) differ so widely for the polyether ester and the nitrile rubber means that even if the two polymers were

Table 1 Characterization data for the polyether ester and the nitrile rubber samples

Property	Polyether ester	Nitrile rubber
$\bar{M}_n \times 10^{-3}$ ^a	30	
\bar{M}_w/\bar{M}_n ^b	1.56	
$\bar{M}_v \times 10^{-3}$ ^c		193
Density (kg m ^{–3})	1152	1050
Nitrile content (wt %)		40

^a By membrane osmometry with chloroform as solvent

^b By gel permeation chromatography

^c See ref 15

Table 2 Some dynamic mechanical properties

Polyether ester content (wt %)	T_{\max} (°C)	$\tan \delta_{\max}$
100	–32	0.24
75	–13	0.34
50	–6	0.66
25	–3	1.02
0	3	1.84

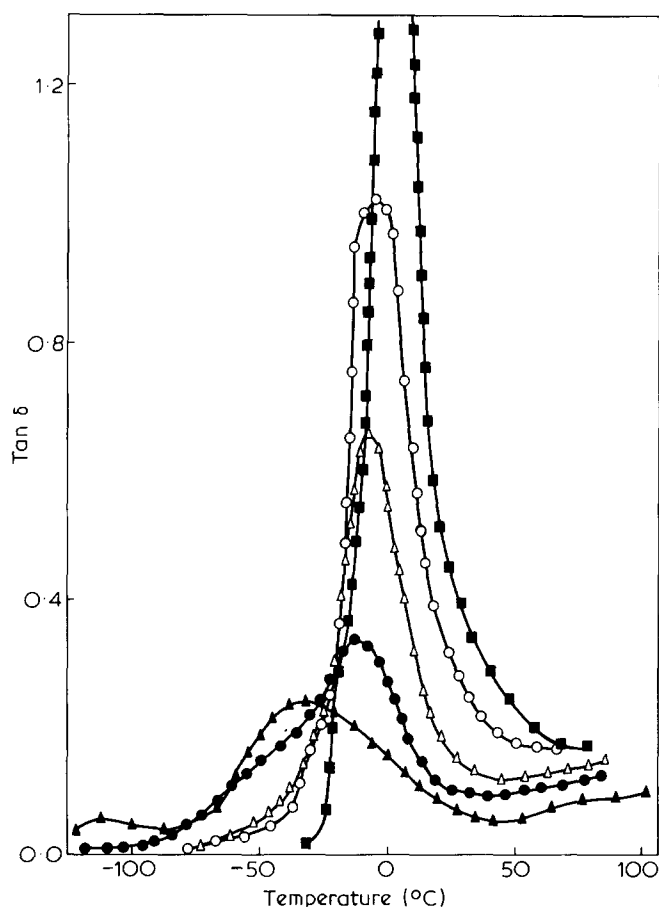


Figure 1 Tan δ versus temperature plots of the polyether ester (▲), nitrile rubber (■) and blends containing respectively 25 (○), 50 (△) and 75% (●) by wt of the polyether ester. Frequency, 110 Hz

totally incompatible the polyether ester transition would be small. Further, the glass transition regions of the constituent polymers overlap significantly resulting in the polyether ester transition appearing only as a shoulder. The consequence is that it is difficult to obtain a quantitative idea of the extent of immiscibility from Figure 1. However, the fact that the main transition moves steadily to lower temperatures as the polyether ester content increases indicates that some mixing is occurring.

Figures 2 and 3 show the dynamic storage (E') and dynamic loss (E'') moduli versus temperature plots for the blends and for the constituent polymers. The E' curves show only one relaxation region for the blends which becomes broader as the polyether ester level is increased. The glassy moduli of the blends are intermediate between those of the homopolymers, but in some cases the experiments were not carried to low enough temperatures to show whether the variations in modulus are systematic. The low value of the glassy modulus of the nitrile rubber is probably the result of some sample distortion in the Rheovibron clamps. This does not influence the interpretation of the observed trends in the transition region. The blends all exhibit a distinct rubbery plateau which increases in modulus, as expected, with increasing levels of the polyether ester. This reflects the increasing concentration of tetramethylene terephthalate segments which may crystallize to form a three-dimensional network^{2,5,7,8}.

The E'' versus temperature dispersions for the blends are broad. The 25% by wt polyether ester blend shows two maxima, one at a temperature which is within experimental error the same as that for the polyether ester and the other about 6°C below the nitrile rubber glass transition. The transition for the 50% by wt blend is broad and has a single maximum at a temperature 7°C lower than that of the glass transition of the nitrile rubber. Again, the transition for the 75% by wt polyether ester blend shows only one maximum, this time located at the polyether ester glass transition. It also shows, however, a distinct slope change at about 13°C below the nitrile rubber glass transition. This blend is the only one which shows the previously reported^{7,8,16,17} secondary polyether ester relaxation at -115°C.

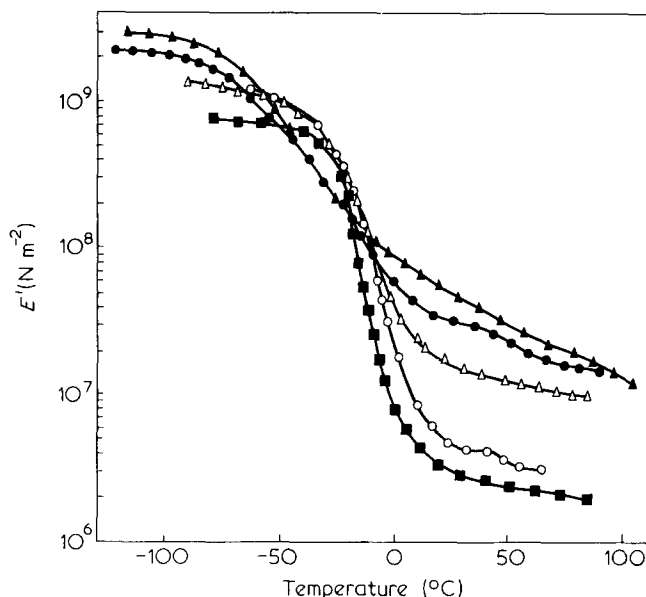


Figure 2 Dynamic storage modulus (E') versus temperature plots of the polyether ester (▲), nitrile rubber (■) and blends containing respectively 25 (○), 50 (△) and 75% (●) by wt of the polyether ester. Frequency, 110 Hz

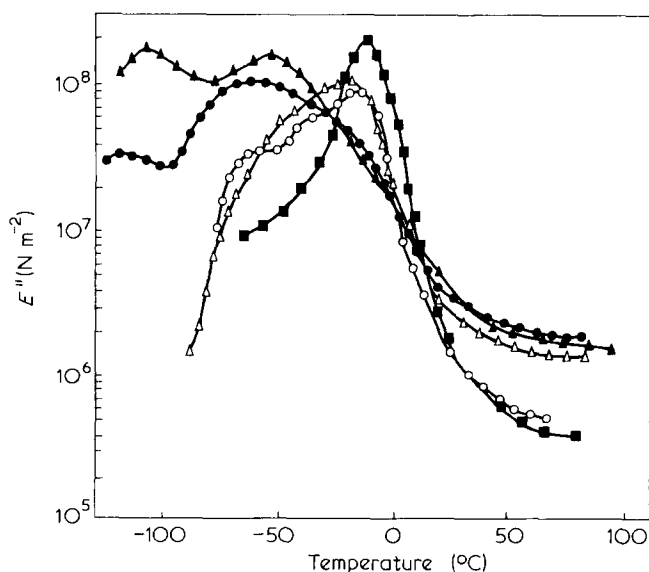


Figure 3 Dynamic loss modulus (E'') versus temperature plots of the polyether ester (▲), nitrile rubber (■) and blends containing respectively 25 (○), 50 (△) and 75% (●) by wt of the polyether ester. Frequency, 110 Hz

Figure 4 shows a plot of the glass transition temperatures from $\tan \delta$ data versus wt% nitrile rubber. It is clear that there is not a simple linear relation between the glass transition temperature and composition. It must, however, be kept in mind that some of the tetramethylene terephthalate segments are involved in crystallites, and, hence, are not available to mix with the nitrile rubber. If the data are replotted assuming that only the poly(tetramethylene ether) glycol terephthalate segments, which are present in the polyether ester at a level of about 50 wt%, are available for blending, it is found that the data points lie much closer to the straight line joining the glass transition temperatures of the constituent polymers. However, as the polyether ester transition at -32°C is assigned¹⁶ to the poly(tetramethylene ether) glycol terephthalate segments, it is clear from Figures 1 and 3 that all these segments are not blended with the nitrile rubber.

Taken together these observations indicate that there is some mixing of the polyether ester and the nitrile rubber. At high levels of polyether ester it is likely that a significant fraction of the tetramethylene terephthalate segments crystallize, but some of the poly(tetramethylene ether) glycol terephthalate segments do mix with the nitrile rubber in all three blends. However, it is not clear at any of the polyether ester concentrations if any of the amorphous tetramethylene terephthalate segments mix with the nitrile rubber.

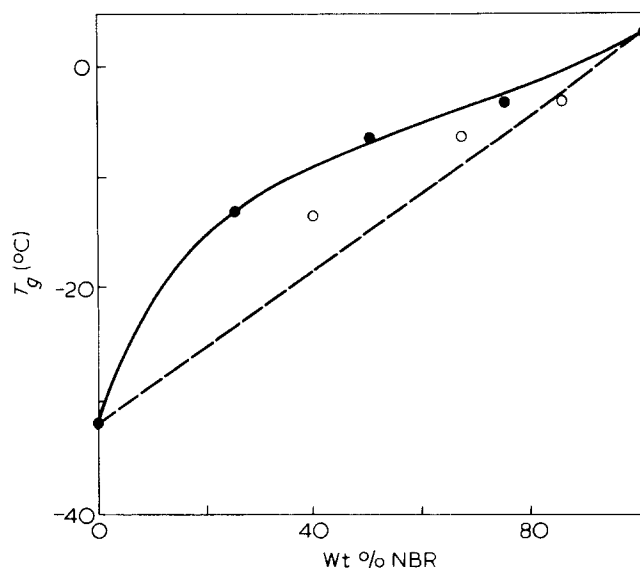


Figure 4 Glass transition temperatures (T_g) of the constituent polymers and the blends versus wt % nitrile rubber. The symbol (○) refers to the case where only the poly(tetramethylene ether) glycol terephthalate segments are considered

REFERENCES

- Witsiepe, W. K. *Adv. Chem. Ser.* 1973, **129**, 39
- Cella, R. J. *J. Polym. Sci. (Polym. Symp.)* 1973, **42**, 727
- Buck, W. H. and Cella, R. J. *Polym. Prepr.* 1973, **14**, 98
- Buck, W. H., Cella, R. J., Gladding E. K. and Wolfe, J. R. *J. Polym. Sci. (Polym. Symp.)* 1974, **48**, 47
- Nishi, T., Kwei, T. K. and Wang, T. T. *J. Appl. Phys.* 1975, **46**, 4157
- Nishi, T. and Kwei, T. K. *J. Appl. Polym. Sci.* 1976, **20**, 1331
- Hourston, D. J. and Hughes, I. D. *J. Appl. Polym. Sci.* 1977, **21**, 3099
- Hourston, D. J. and Hughes, I. D. *Polymer* 1979, **20**, 823
- Matsuo, M. *Jpn Plast.* 1968, **2**, 6
- Takayanagi, M. *Mem. Fac. Eng., Kyushu Univ.* 1963, **23**, 11
- Zakrzewski, G. A. *Polymer* 1973, **14**, 347
- Nielsen, L. E. *J. Am. Chem. Soc.* 1953, **75**, 1453
- Matsuo, M., Nozaki, C. and Jyo, Y. *Polym. Eng. Sci.* 1969, **9**, 197
- Kato, K. *Jpn Plast.* 1968, **2**, 6
- Stoelting, J., Karasz, F. E. and McKnight, W. J. *Polym. Eng. Sci.* 1970, **10**, 133
- Shen, M., Mehra, V., Niinomi, N., Koberstein, J. T. and Cooper, S. L. *J. Appl. Phys.* 1974, **45**, 4182
- Wetton, R. and Williams, G. *Trans. Faraday Soc.* 1965, **61**, 2123

Charge transfer complex between maleic anhydride and pyridine

J. A. Chamizo*, G. Mendoza-Díaz and J. L. Gázquez

Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México 20, D.F.

(Received 3 March 1980; revised 21 April 1980)

Charge transfer complexes (CTC) play an important role in the understanding of many chemical phenomena, such as hormone action¹, carcinogenic activity², and solvent-solute interactions³. Recent work has proved that they appear as intermediates in various organic reactions⁴.

In a recent publication Wurm, Regel and Hallensleben⁵ (WRH) discuss the formation of a 2:1 maleic anhydride (MAH):pyridine (Py) compound as a polymerization reaction intermediate. Their first step in this mechanism is the formation of a CTC between one molecule of Py and one of MAH. The purpose of the present work is to show, from a theoretical calculations, that there is a more stable configuration⁶ than the one proposed by WRH.

The calculations were performed within a modified

CNDO version⁷ of the all-valence electron SCF-MO approach. The method has been employed in previous successful investigations of catalytic systems because the parametrization has been designed to treat large distance molecular interactions. In particular, good results have been obtained for charge transfer and bond order⁸.

The first step consisted of the evaluation of the charge distribution, the ionization potential and the electron affinity of the isolated molecules⁹. These results together with the values of the *IEMO* and *HOMO* predict that Py acts like an acceptor and MAH acts like a donor of charge (see Table 1).

To evaluate the equilibrium distance, the charge transferred and the charge distribution in the molecules of the CTC we have allowed MAH to approach Py in two different ways, keeping both molecules rigid (see Figure 1). Notice that path A corresponds to the one proposed by WRH and that the charge distribution is slightly different.

* This paper comprises a portion of a dissertation which will be submitted by J. A. Chamizo in partial fulfillment for the Master's Degree UNAM