

RHEOLOGICAL PROPERTIES OF SHORT POLYESTER FIBER-POLYURETHANE ELASTOMER COMPOSITE WITH DIFFERENT INTERFACIAL BONDING AGENTS

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Abstract

The rheological behavior of a short-polyester-fiber-filled polyurethane elastomer composite containing different bonding agents has been studied in the temperature range 120–160°C and in the shear rate range 63–608 s⁻¹. The composite with and without bonding agents showed a pseudoplastic behavior which decreased with the increase of temperature. Composites containing bonding agents based on polypropyleneglycol and 4,4'-diphenylmethane-diisocyanate showed the lowest viscosity values at a particular shear rate, whereas composites containing a glycerol- (GL) based bonding agent showed the highest viscosity. The viscosity of the composite decreased sharply after a particular temperature

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(140°C) and the fall was less drastic in the composite containing a GL-based bonding agent.

INTRODUCTION

Short-fiber-reinforced polymer composites are finding wide application areas because of its good processing characteristics and anisotropic mechanical properties [1-4]. As many of the processing steps, such as mixing, extrusion, calandering, and molding, in the modern polymer industry involve flow of the polymer, an understanding of the rheological characteristics of the composites is essential. The rheological behavior of polymer melts provides the choice of processing conditions and influences the morphology and mechanical properties of the final product. Brydson indicated the need for rheological studies and its importance in the selection of a processing condition and in the designing of processing equipments [5]. White and Tokita [6] and White [7,8] have reported the correlation between rheology and processing and the rheological properties and extrusion characteristics of polymer melts. Crowson et al. [9,10] studied the rheology of short-glass-fiber-reinforced thermoplastics and reported that the fiber orientation resulting from the convergent, divergent, and shear flows and the fiber alignment takes place only at a high rate of shear. Flow characteristics of the thermoset compounds filled with polyethyleneterephthalate (PET) fiber have been studied by Owen and Whybrew [11]. Several studies have been reported on the rheological characteristics of short-fiber-reinforced polymer melts [12-16]. Murty et al. [17] studied the rheological behavior of short-jute-fiber-filled natural rubber (NR) composites. The dependence of die swell on the L/D (length to diameter) ratio of the capillary has been studied by many workers and concluded that the die swell decreases with the increase of L/D ratio [18-21]. Kutty et al. [22] studied the rheological properties of a Kevlar fiber-filled thermoplastic polyurethane composite. Gupta and co-workers [23] have reported on the flow properties of the polypropylene-ethylene propylene diene monomer (PP-EPDM) blend filled with short glass fibers. Recently, rheological behavior of a short-sisal-fiber-reinforced NR composite has been studied by Varghese and co-workers who reported that the incorporation of a treated fiber increases the melt viscosity and decreases the melt elasticity [24]. The dependence of rheological properties of the staple polyester-fiber-filled polyurethane elastomer composite has

been reported [25]. This article deals with the rheological properties of a short-polyester-fiber-filled composite containing different bonding agents (MD resins) based on polypropyleneglycol (PPG) and glycerol (GL) with 4,4'-diphenylmethanediisocyanate (MDI) at 20 phr fiber loading.

EXPERIMENTAL

Materials

Adiprene, an ether-based millable polyurethane elastomer, was procured from Uniroyal Chemical Inc. Co. (USA), and polyester staple fiber, approximately 4 mm in length, was supplied by Madura Coats (India). All other ingredients are of commercial grade.

The formulation of the mixes is given in Table 1. The mixes were prepared in a Hake Rheomix, at a temperature of 60°C and at a rotor speed of 30 rpm for 4.5 min.

Rheological studies were carried out using the Monsanto Processability tester. A capillary of diameter 1.5 mm and $L/D = 30$ was used. The measurements were carried out at different shear rates ranging from 63 to 608 s^{-1} . The experiments were carried out at different shear

TABLE I
Formulation of the Mixes

Ingredients ^a	Mix no.			
	C	C1	C2	C3
Adiprene	100	100	100	100
PET fiber	20	20	20	20
Zinc stearate	0.5	0.5	0.5	0.5
Caytur-4	0.35	0.35	0.35	0.35
MBTS	4	4	4	4
MBT	1	1	1	1
PPG	—	4.44	—	2.22
GL	—	—	0.99	0.07
MDI	—	0.56	4.01	0.56

^a MBTS = dibenzothiazyl disulfide; MBT = 2-mercaptobenzothiazole; PPG = polypropyleneglycol; GL = glycerol; MDI = 4,4'-diphenylmethanediisocyanate.

rates obtained by moving the piston at different preselected speeds (0.05–0.25 in./mm). The true shear stress was calculated as [5]

$$\tau_w = \frac{PR}{2L}$$

where τ_w is the shear stress of the wall, P is the pressure drop, L is the length of the capillary, and R is the radius of the capillary.

Apparent shear rate, shear rate at the wall, and viscosity were calculated using

$$\dot{r} = \frac{32Q}{\pi d_c^2}$$

$$\dot{r}_w = \frac{(3n' + 1)\dot{r}_a}{4n'}$$

$$\eta = \frac{\tau_w}{\dot{r}_w}$$

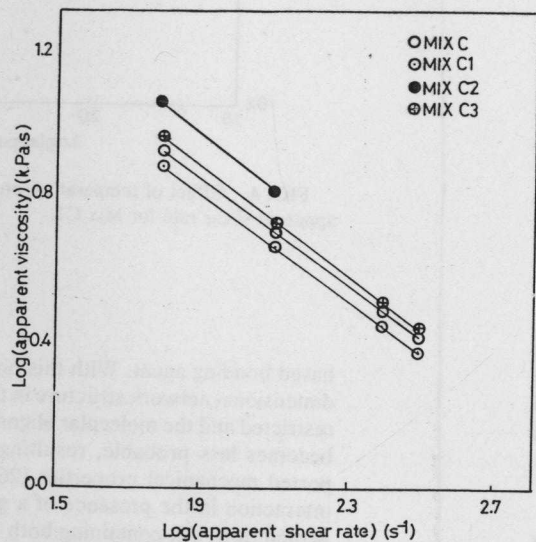


FIG. 1. Variation of apparent viscosity with apparent shear rate for Mixes C and C1–C3.

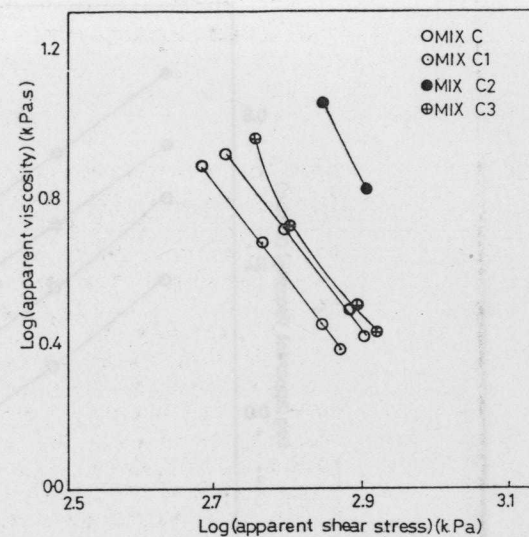


FIG. 2. Variation of apparent viscosity with apparent shear stress for Mixes C and C1–C3.

where \dot{r}_a is the apparent shear rate (s^{-1}), Q is the volume flow rate (mm^3/s), d_c is the diameter of the capillary (mm), \dot{r}_w is the shear rate at the wall (s^{-1}), n' is the flow behavior index, and η is the shear viscosity (kPa s). n' was calculated by linear regression from $\log \tau_w$ and $\log \dot{r}_a$.

RESULTS AND DISCUSSION

Figure 1 represents plot of $\log(\text{viscosity})$ versus $\log(\text{shear rate})$ at 120°C of the composites with and without bonding agents. It is evident from the figure that for all mixes, viscosity decreases with the increase

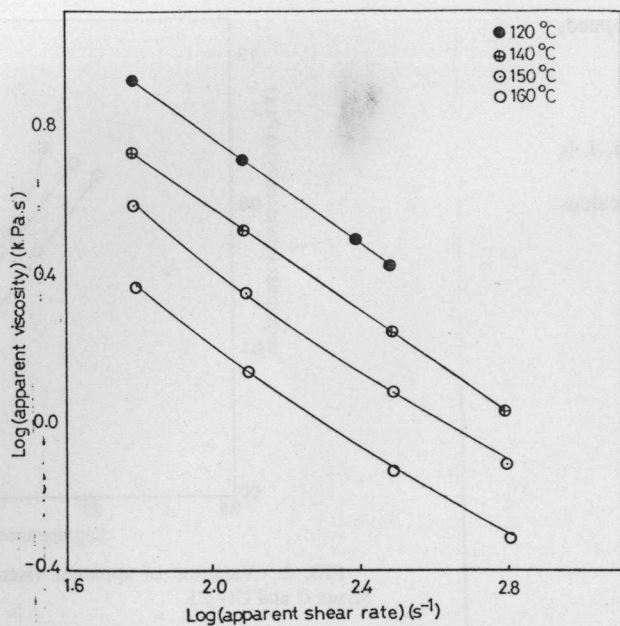


FIG. 3. Effect of temperature on the variation of apparent viscosity with apparent shear rate for Mix C.

of shear rate, indicating a pseudoplastic nature. Similar results have been reported earlier [22]. Over the whole shear rate range studied, the viscosity of the Mix C1, containing a bonding agent based on PPG and MDI, shows a lower viscosity than that of Mix C, with no bonding agent. This indicates a probable plasticizing effect of the bonding agent used. The observed mechanical properties of the composites also support this view [26].

The viscosity values of Mix C2 suggest a more restrained matrix indicating a better fiber-matrix interaction in the presence of a glycerol-

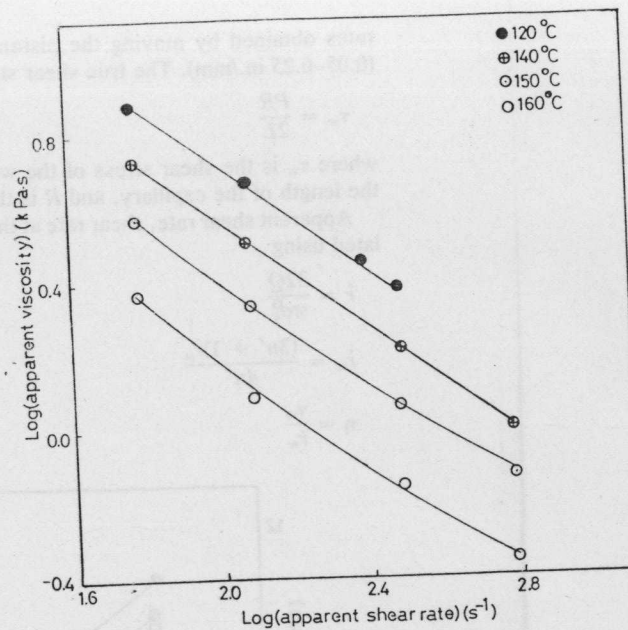


FIG. 4. Effect of temperature on the variation of apparent viscosity with apparent shear rate for Mix C1.

based bonding agent. With this bonding agent, the resin forms a three-dimensional network structure in the matrix and the flow becomes more restricted and the molecular alignment in the flow direction under shear becomes less probable, resulting in higher viscosity values. The reported mechanical properties [26] also suggested better fiber-matrix interaction in the presence of a glycerol-based bonding agent. As expected, Mix C3, containing both PPG and GL, shows viscosity values in between that of Mix C1 and C2. The presence of PPG seems to

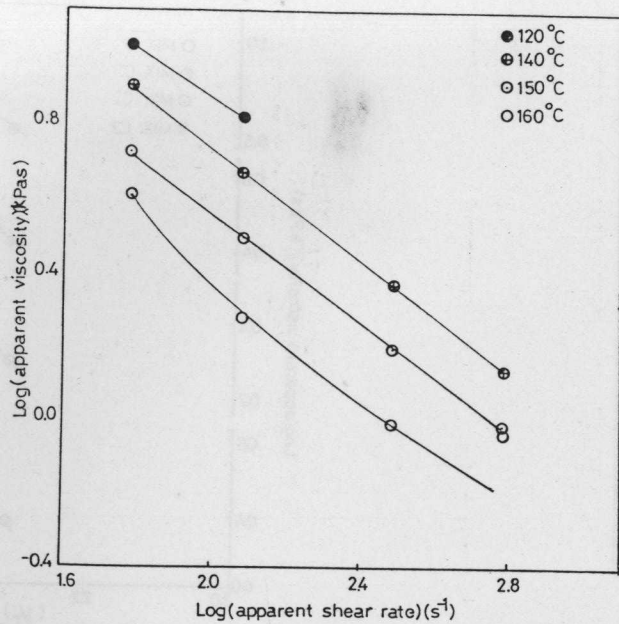


FIG. 5. Effect of temperature on the variation of apparent viscosity with apparent shear rate for Mix C2.

compensate for any restriction to flow due to glycerol; hence, Mix C3 shows the viscosity values almost equal to those of Mix C.

A similar pattern of behavior is observed in Fig. 2 where $\log(\text{viscosity})$ is plotted against $\log(\text{shear stress})$, at 120°C. The difference between viscosity values of different mixes seems to be more significant in this figure. This suggests that the log-log plot of viscosity and shear stress will be a better tool to study the effect of interfacial bonding agents on the flow properties.

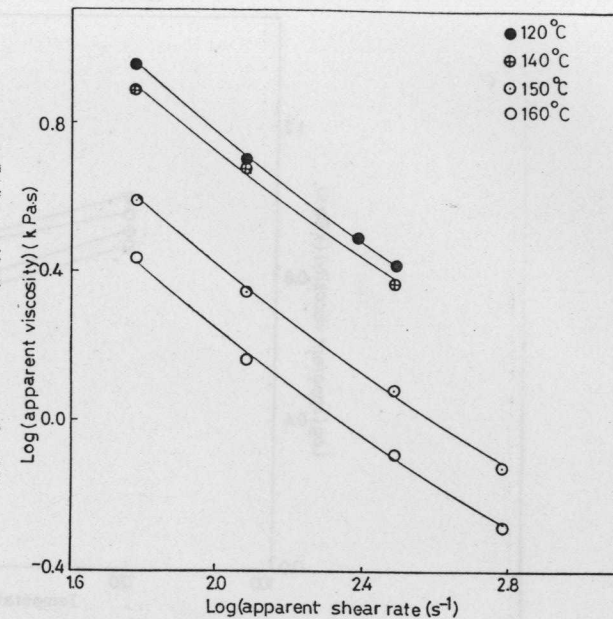


FIG. 6. Effect of temperature on the variation of apparent viscosity with apparent shear rate for Mix C3.

Effect of Temperature

In the shear rate range studied, the viscosity is found to decrease with increasing temperature (Fig. 3). A similar trend is also observed in the case of composites containing different bonding agents (Figs. 4–6). However, the variation in viscosity with temperature at a given shear rate is found to be different for different mixes. Figure 7 shows a plot of viscosity versus temperature at a shear rate of $61.3 s^{-1}$ for different mixes. It shows that beyond a temperature of 140°C, the viscosity of

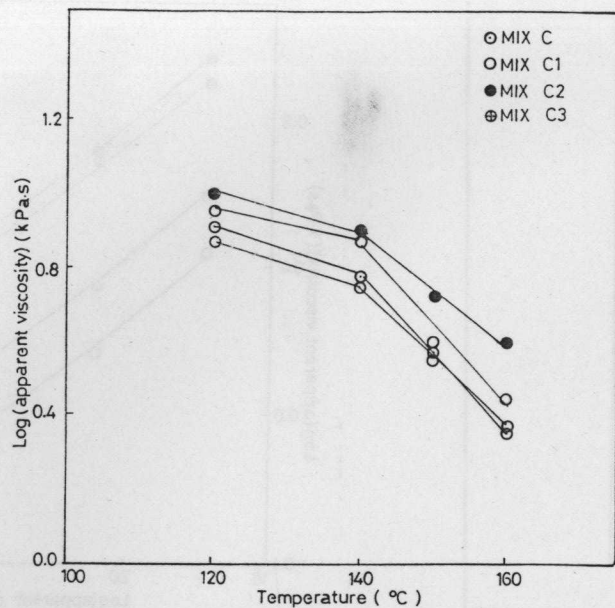


FIG. 7. Variation of viscosity of Mixes C and C1-C3 with temperature at a shear rate of 63.1 s^{-1} .

different composites falls very sharply. The fall is less drastic in case of Mix C2 containing a glycerol-based bonding agent when compared to Mix C1 and Mix C3. Between 120°C and 140°C , the reduction in viscosity is less significant.

Activation Energy

Activation energies of composites C and C1-C3 are calculated from the plots of $\log(\text{apparent viscosity})$ versus $1/T$ (Fig. 8). Table 2 gives the values of activation energies at three different shear rates. The more or less same values of activation energies of the composites indicate

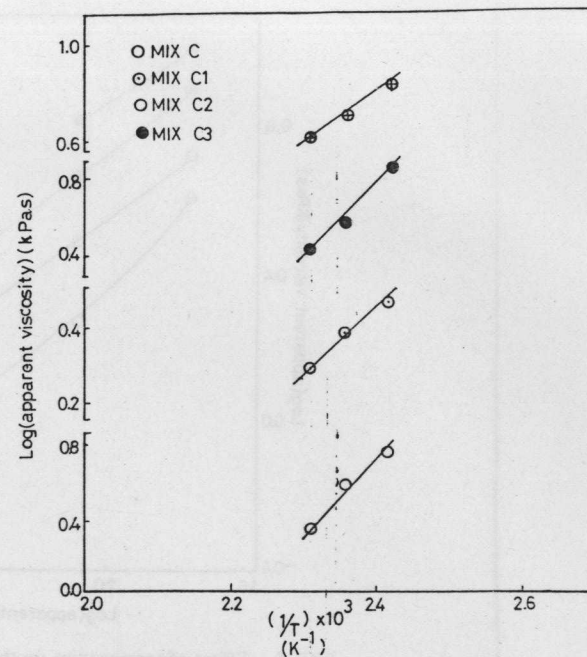


FIG. 8. Variation of apparent viscosity with $1/T$ at a shear rate of 61.3 s^{-1} .

that the temperature sensitivity of the composites remains unaffected with the rate of shear in the shear rate range studied. Similarly, there is not much change in the activation energies of the composites containing different bonding agents. This again shows that the presence of bonding agents also does not alter the temperature sensitivity of the composite.

Flow Behavior Index

Figure 9 shows the flow behavior index, n' , of composites C and C1-C3, with and without bonding agents, at different temperatures.

TABLE 2
Activation Energies (kcal) of Mixes C and C1-C3 at Different Shear Rates

Mix no.	Activation energy at different shear rates (kcal)		
	Shear rate (s^{-1})		
	61.3	122.6	306.5
C	15.39	15.56	15.81
C1	15.25	15.61	16.20
C3	17.43	17.73	15.25
C4	18.30	19.75	18.95

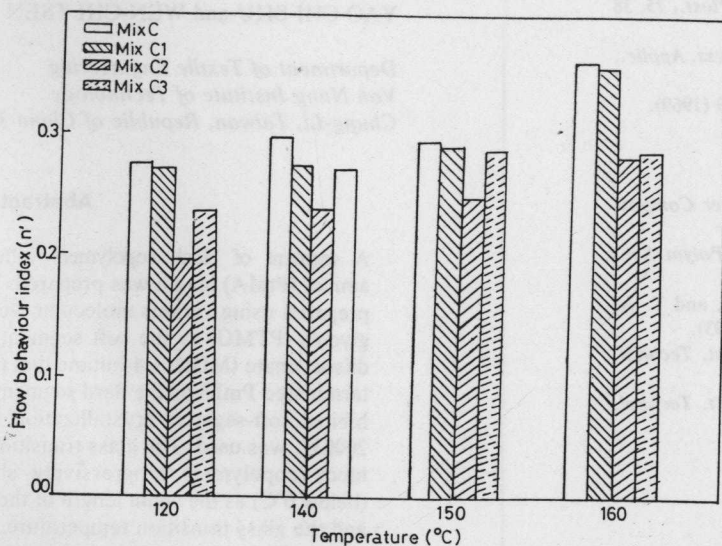


FIG. 9. Variation of flow behavior indices of Mixes C and C1-C3 with temperature.

The magnitude of n' indicates the extent of non-Newtonian behavior of the composite. It is clear from the figure that for all composites, n' increases with the increase of temperature, showing that as the temperature increases, the melt becomes more Newtonian in nature. Composites with a PPG-based bonding agent show the more or less same values of n' as that of the composite without a bonding agent, whereas composites with GL and PPG-GL mixture-based bonding agents show lower values of n' . This indicates that the bonding agent formed from GL and PPG-GL with MDI increases the pseudoplasticity of the composite.

CONCLUSIONS

From the above study, the following conclusions can be drawn:

Short-polyester-fiber-reinforced polyurethane elastomer composites with and without bonding agents exhibit pseudoplasticity which decreases with temperature.

Composites with a PPG-MDI-based bonding agent shows lower shear viscosity at a particular shear rate than that of the composite without a bonding agent, whereas composites with a GL-MDI-based bonding agent show the highest viscosity, indicating a better interaction between the fiber and the matrix.

Shear viscosity of the composites at a particular shear rate decreases sharply beyond 140°C, and the fall is less drastic in the case of composites containing a GL-based bonding agent.

The presence of a bonding agent and the increase of shear rate do not change the activation energy of the composites.

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REFERENCES

1. S. R. Moghe, *Rubber Chem. Technol.*, **47**, 1074 (1974).
2. P. Hamed and A. Y. Coran, *Additives for Plastics*, Academic Press, New York, 1978, Vol. 1, p. 29.

3. M. Ashida, *Int. Polym. Sci. Technol.*, **12**, T/47 (1985).
4. A. K. Senapati, S. K. N. Kutty, and G. B. Nando, *Int. J. Polym. Mater.*, **12**, 73 (1989).
5. J. A. Brydson, *Flow Properties of Polymer Melts*, 2nd ed., George Godwin, London, 1981.
6. J. L. White and N. Tokita, *J. Appl. Polym. Sci.*, **11**, 321 (1967).
7. J. L. White, *Rubber Chem. Technol.*, **42**, 257 (1969).
8. J. L. White, *Rubber Chem. Technol.*, **50**, 163 (1977).
9. J. Crowson and N. J. Folkes, *Polym. Eng. Sci.*, **20**, 934 (1980).
10. J. Crowson, N. J. Folkes, and P. F. Bright, *Polym. Eng. Sci.*, **20**, 925 (1980).
11. M. J. Owen and K. Whybrew, *Plast. Rubber*, **1**, 231 (1976).
12. L. A. Goettler, A. J. Lambright, R. I. Leib, and P. J. Dimauro, *Rubber Chem. Technol.*, **54**, 277 (1981).
13. S. Wu, *Polym. Eng. Sci.*, **19**, 638 (1979).
14. Y. Chan, J. L. White, and Y. Oyanagi, *Polym. Eng. Sci.*, **18**, 268 (1978).
15. D. K. Setua, *Int. J. Polym. Mater.*, **11**, 67 (1985).
16. D. Roy, A. K. Bhattacharya, and B. R. Gupta, *J. Elastom. Plast.*, **25**, 38 (1993).
17. V. M. Murty, B. R. Gupta, and S. K. De, *Plast. Rubber Process. Applic.*, **5**, 307 (1985).
18. C. McLukie and M. J. Roger, *J. Appl. Polym. Sci.*, **13**, 1049 (1969).
19. M. J. Rogers, *J. Appl. Polym. Sci.*, **14**, 1679 (1970).
20. T. Arai and H. Aoyama, *Trans. Soc. Rheol.*, **7**, 333 (1963).
21. B. R. Gupta, *Indian. J. Rubber Res.*, **2**, 38 (1989).
22. S. K. N. Kutty, P. P. De, and G. B. Nando, *Plast. Rubber Compos. Process. Applic.*, **15**, 23 (1991).
23. A. K. Gupta, P. Kumar Krishna, and B. R. Ratnam, *J. Appl. Polym. Sci.*, **42**, 2595 (1991).
24. S. Varghese, B. Kuriakose, S. Thomas, C. K. Premalatha, and T. A. Koshy, *Plast. Rubber Compos. Process. Applic.*, **20**, 93 (1993).
25. F. Suhara, S. K. N. Kutty, and G. B. Nando, *Polym.-Plast. Technol. Eng.* **36**, 399 (1997).
26. F. Suhara, S. K. N. Kutty, and G. B. Nando, *Polym.-Plast. Technol. Eng.* (in press).

PHYSICAL PROPERTIES OF POLYURETHANE MODIFIED WITH POLY(*m*-PHENYLENE ISOPHTHALAMIDE)

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Abstract

A segment of block copolymers with poly(*m*-phenylene isophthalamide) (PmIA) length was prepared. The block copolymers were prepared using various molecular weights of polytetramethylene glycols (PTMG) as the soft segment, and 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butane diol (BD), and aromatic diamine-terminated PmIA as the hard segment. The block copolymers exhibited soft-segment crystallization when a PTMG greater than 2000 M_n was used. The glass transition temperature, T_{gs} , of these block copolymers progressively shift to lower temperatures (below 0°C) as the chain length of the soft segment was increased and the glass transition temperature, T_{gh} , of these block copolymers shift to higher temperatures (up 0°C) as the chain length of hard segment was increased. The stress-strain and stress-relaxa-