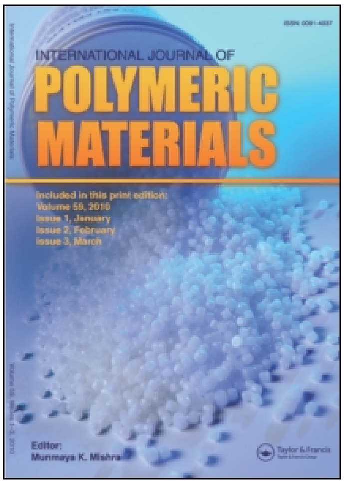

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Cure Characteristics of Short Polyester Fiber-Polyurethane Elastomer Composite with Interfacial Bonding Agents Based on Polymeric 4,4′-Diphenylmethanediisocyanate

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Cure characteristics of short polyester fiber-polyurethane composites with respect to different bonding agents (MD resins) based on 4, 4′ diphenylmethanediisocyanate (MDI) and various diols like propyleneglycol (PG), polypropyleneglycol (PPG) and glycerol (GL) were studied. Tmax. – Tmin. of composites having MD resin were found to be higher than the composite without MD resin. Minimum torque and Tmax. – Tmin., scorch time and optimum cure time were increased with the increase of MDI equivalence. Optimum ratio of MDI / – ol in the resin was found to be within the range of 1–1.5. It was observed from the cure characteristics that for getting better adhesion between short polyester fiber and the polyurethane matrix the best choice of MD resin was one based on MDI and 1:1 equivalent mixture of polypropyleneglycol and glycerol.

Keywords: Short fiber composites; elastomers; PET fibers; interfacial bonding; polyurethanes; isocyanates

1. INTRODUCTION

Advantages in processing, design flexibility, anisotropic properties and low cost favor the use of short fiber elastomer composites. A number

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of work has been reported regarding the various aspects of different short fiber elastomer composites. These include physical properties and the effect of fibers on the ultimate properties of composites [1–13]. The mechanical properties of composites mainly depend on the elastomer matrix, the nature of fiber, the distribution and orientation of fiber in the matrix and the interfacial bonding between the matrix and the fiber [2–3, 8, 14–17]. Of these the interfacial bonding becomes important because many of the properties of composites, in addition to strength, modulus and structural integrity, depend on this. For improving the fiber matrix adhesion a tricomponent dry bonding system based on Hydrated silica – Resorcinol – Hexamethylenetetramine has been successfully tried in many short fiber elastomer composites [2, 4, 18, 19].

However, for a polyurethane elastomer based short fiber composite it has been reported that the conventional HRH system was not effective [14, 20]. It, rather, resulted in the degradation of the matrix. In an earlier communication we have reported a new bonding agent (TP resin) based on polymeric toluenediisocyanate and polypropyleneglycol for short polyester fiber – millable polyurethane composite. In the present work, a number of urethane resins based on polymeric 4, 4′-diphenylmethanediisocyanate (MDI) and different diols have been evaluated as the interfacial bonding agent for short polyester fiber – polyurethane elastomer composites by studying its cure characteristics. A 20 phr short fiber loaded composite was selected for the study.

2. EXPERIMENTAL

Polyether based urethane rubber (Adiprene CM, Specific gravity 1.06, Mooney viscosity MS – 10 at 100° C approximately 60) used in this study was obtained form Uniroyal Chemical Co. Inc. USA. Caytur- 4: a zinc chloride – MBTS complex and catalyst for polyurethane vulcanisation was obtained from Uniroyal Chemical Co. Inc. USA. Short polyethyleneterephthalate (PET) cord chopped to approximately 4 mm length (fiber dia : 21 μm) was procured from Mudura Coats, India. MBTS (dibenzothiazyl disulphide) and MBT (2-Mercaptobenzothiazole) were supplied by Bayer India Ltd. Glycerol and propylene glycol were obtained from BDH, Bombay, India. Polypropyleneglycol (molecular weight – 2000) was a Fluka Chemie AG product. Table I

TABLE I Formulation of the Mixes

Ingredient	Mix No.													
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*	*M*	*N*
PG	–	1.5	1.1	0.8	0.6	–	–	–	–	–	–	–	–	–
PPG	–	–	–	–	–	4.6	4.4	4.2	3.9	–	–	–	–	2.2
GL	–	–	–	–	–	–	–	–	–	1.3	0.9	0.7	0.5	0.07
MDI	–	3.5	3.9	4.2	4.4	0.4	0.6	0.8	1.1	3.7	4.1	4.3	4.5	0.6

PG–Propyleneglycol, PPG–Polypropyleneglycol, GL–Glycerol and MDI–4,4′diphenylmethanediisocyanate. Base recipe: Adiprene 100, Short polyester fiber 20, Zinc stearate 0.5, Caytur–4 0.35, MBTS 4, MBT 1 and Sulphur 0.75. All values are expressed as parts per hundred rubber (phr).

shows the formulation of the mixes A–N. Except Mix A, all the mixes contain MD resin, based on different diols and polymeric MDI, as the bonding agent. In Mixes B–N the diol and isocyanate concentrations were so adjusted that the resin content was five parts per hundred rubber (phr) and the diol to isocyanate ratio varied from 1:0.67 to 1:2. Mixes B–E, F–I contain propyleneglycol, polypropyleneglycol as the diol and Mixes J–M contain a triol, glycerol. Mix N is a modified form of Mix G, where 50 parts by equivalence of polypropyleneglycol was replaced by glycerol.

The mixes were prepared as per ASTM D 3184 (1980) and ASTM D 2367 (1982), on a laboratory size two – roll mill. Cure characteristics of these mixes were found out using a GOETTFERT Elastograph Model 67.85 at 150°C.

Vr, the volume fraction of rubber, values of these mixes were also determined using tetrahydrofuran as the solvent.

3. RESULTS AND DISCUSSION

3.1. MDI – PG Resin

The cure curves of the Mix A and Mix B–E containing MDI and propyleneglycol in the equivalence ratio of 0.67:1, 1:1, 1.5:1 and 2:1 are shown in Figure 1. The cure characteristics of the mixes are shown in Table II. In Mix B, the MD resin formed was –ol terminated whereas in Mixes D and E the resin was isocyanate terminated.

5 phr of the MD resin in the matrix considerably alters the cure pattern of the polyurethane – short polyester fiber composite.

3.1.1. Minimum Torque and Tmax. – Tmin.

Figure 2 shows the variation of minimum torque and difference of maximum and minimum torque (Tmax. – Tmin.) with different MDI/diol ratios. The minimum torque shows only a marginal increase with increasing isocyanate concentration. This indicates that the processability of the composite is hardly affected by the incorporation of the urethane resin.

The Tmax. – Tmin. values show a major reduction when the MD resin formed is –ol terminated (Mix B), whereas for Mixes C and D

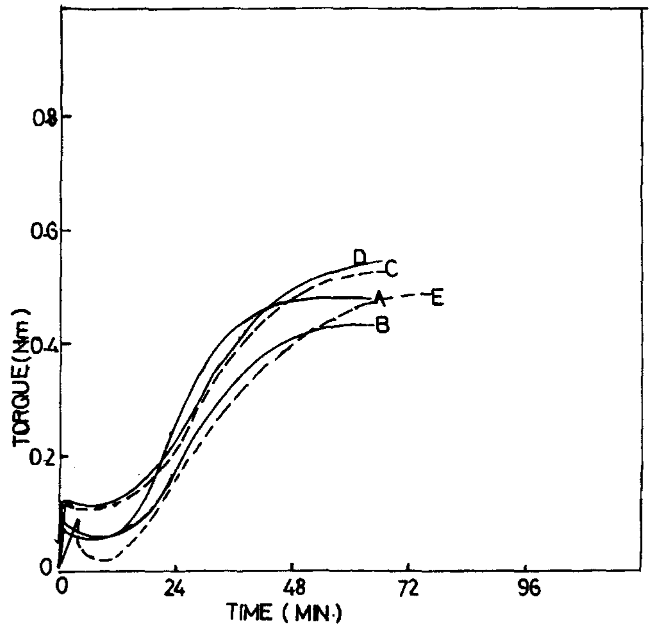

FIGURE 1 Rheographs of Mixes A – E.

TABLE II Cure characteristics of Mixes A – E

Mix No.	*Min. torque (N.m)*	*Max. torque (N.m)*	*Scorch time (minutes)*	*Opt. cure time (minutes)*
A	0.061	0.486	15.2	36.8
B	0.064	0.435	18.0	45.2
C	0.097	0.532	16.8	47.6
D	0.108	0.547	17.6	47.6
E	0.104	0.481	18.4	54.0

torque values are higher than that of Mix A. At still higher MDI/diol ratio (Mix E) torque is reduced significantly indicating that the optimum –NCO/–ol ratio is found to be around one. Also, Vr values of these mixes (Tab. III) do not show much variation. The high values of Tmax. – Tmin. and almost constant Vr values of short fiber composite in the presence of MD resin points to a more restrained matrix resulting from a better fiber – matrix bonding [14]. The low values of

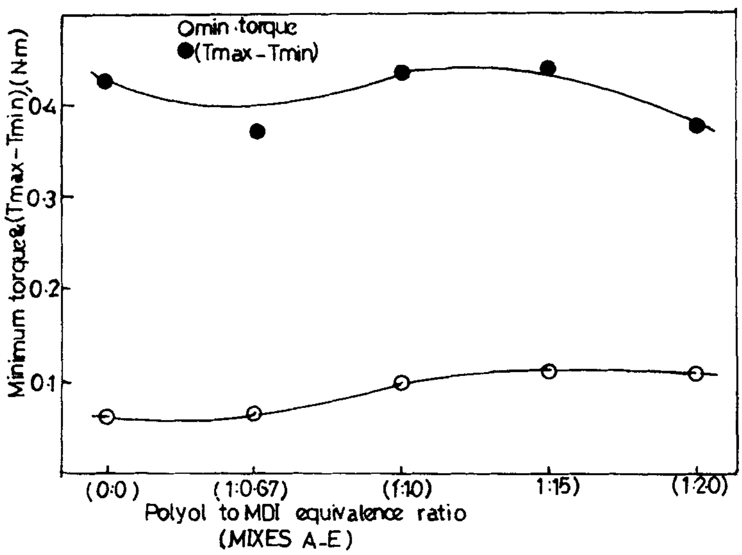

FIGURE 2 Variation of minimum torque and Tmax. – Tmin. of Mixes A – E with MDI equivalence.

TABLE III Volume fraction of the rubber (Vr) value of mixes A – N

Mix No.	*A*	*B*	*C*	*D*	*E*	*F*	*G*	*H*	*I*	*J*	*K*	*L*	*M*	*N*
Vr	0.180	0.176	0.193	0.217	0.203	0.183	0.183	0.177	0.172	0.197	0.197	0.216	0.196	0.197

Tmax. – Tmin. at very low and very high equivalence ratios is because of the less effective utilisation of the monomer functionalities. Since the MD resin components are adjusted to be 5 phr in all the mixes, at equivalence ratio other than one, the resin formation will not be optimum.

3.1.2. Scorch Time and Cure Time

Scorch time and optimum cure time increase as –NCO/–OH equivalence ratio increases (Fig. 3). The optimum cure time registeres an increase at an equivalence ratio of 2 (Mix E) and there is a corresponding reduction in the cure rate. Figure 4 shows the variation of cure rate with the equivalence of MDI in the composite. The cure rate

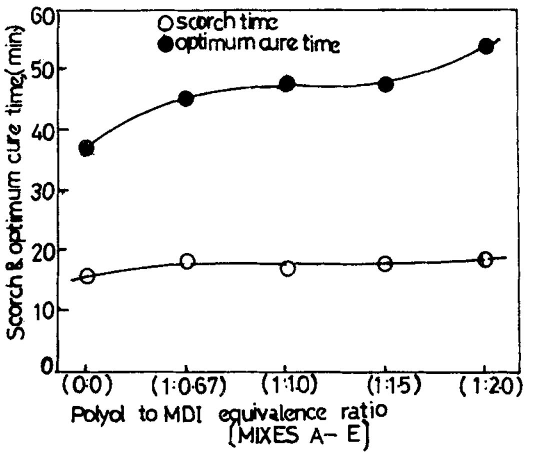

FIGURE 3 Variation of scorch and optimum cure time with MDI equivalence.

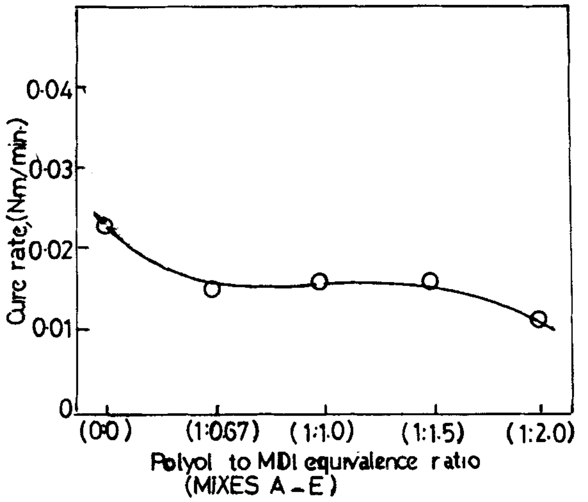

FIGURE 4 Variation of cure rate of Mixes A – E with MDI equivalence.

of all mixes containing MD resin is considerably lower than that of Mix A, the minimum being shown by Mix E. This suggests that the presence of MD resin, especially those containing excess isocyanate interferes with the sulphur curing of polyurethane. This is in agreement with the low value of Tmax. – Tmin. exhibited by Mix E.

3.2. MDI - PPG Resin

Cure curves of the composites containing polypropyleneglycol based urethane resin (Mixes F – I) are shown in Figure 5. The variation of the minimum torque and the Tmax. – Tmin. with MDI/diol ratio is shown in Figure 6. The minimum torque values show a trend similar to that of MDI/PG based composite. Tmax. – Tmin. shows an increase as the MDI/diol ratio increases till the MDI equivalence ratio is 1.5 and thereafter remains more or less constant. Here also the Vr values show not much variation (Tab. III). The scorch time and cure time are increased in the presence of the MD resin (Fig. 7).

3.3. MDI - Glycerol Resin

The cure characteristics of Mixes J – M (Fig. 8) show a trend similar to that of the propyleneglycol based mixes (Mixes B – E). The minimum torque and Tmax. – Tmin. at different MDI/ – ol equivalence ratios are shown in Figure 9. The minimum torque shows a marginal

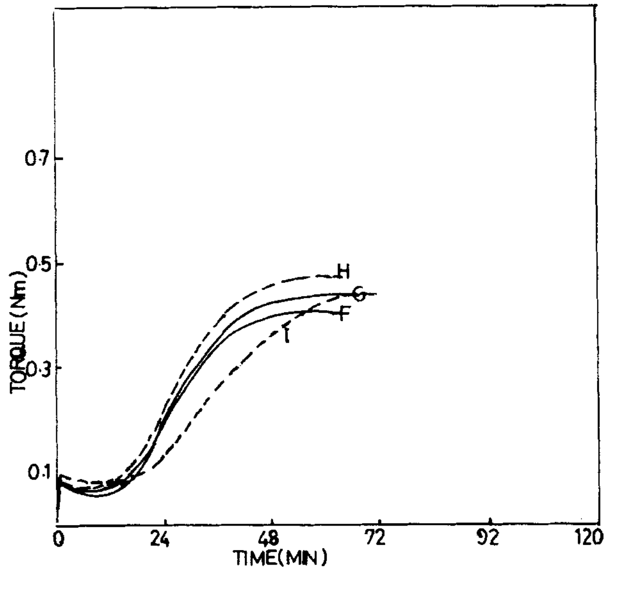

FIGURE 5 Rheographs of Mixes F – I.

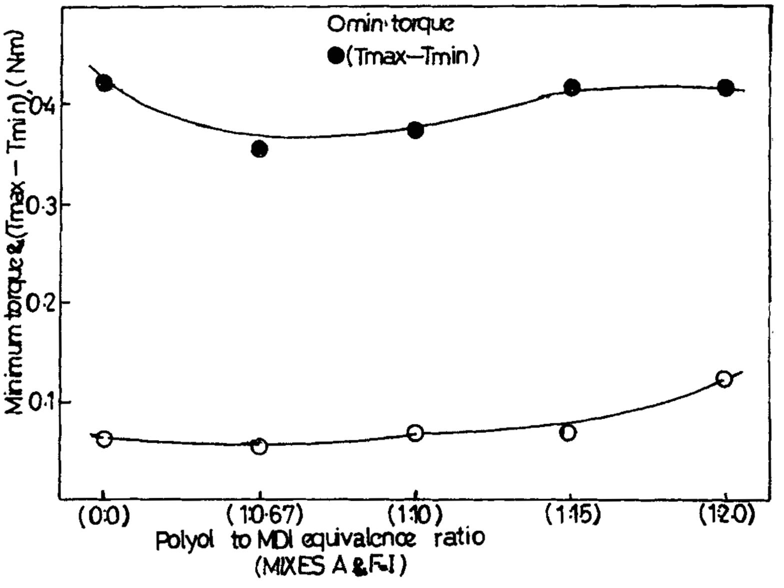

FIGURE 6 Variation of minimum torque and Tmax. – Tmin. of Mixes A and F – I with MDI equivalence.

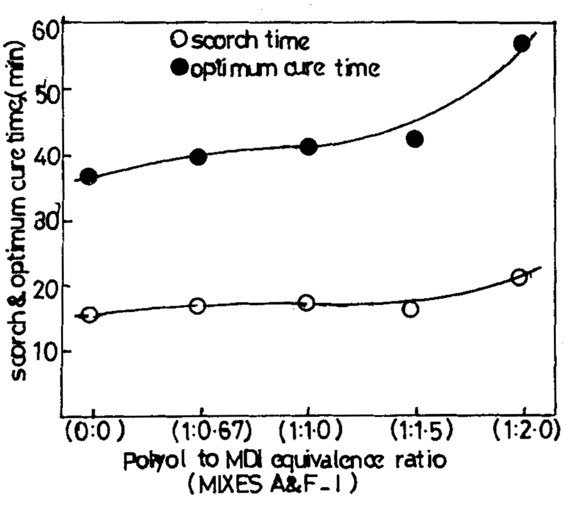

FIGURE 7 Variation of scorch and optimum care time of Mixes A and F – I with MDI equivalence.

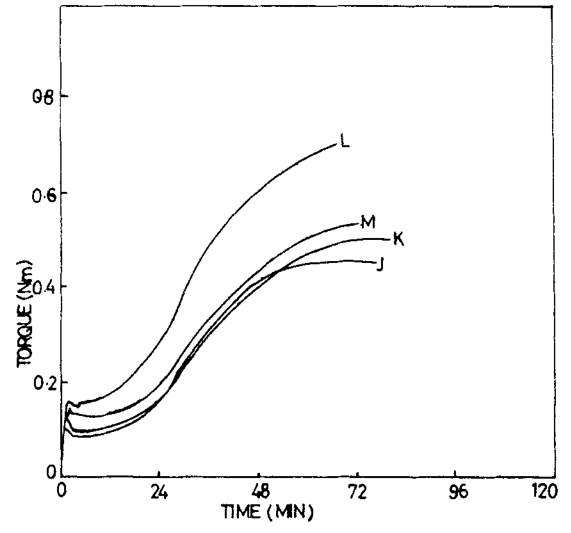

FIGURE 8 Rheographs of Mixes J – M.

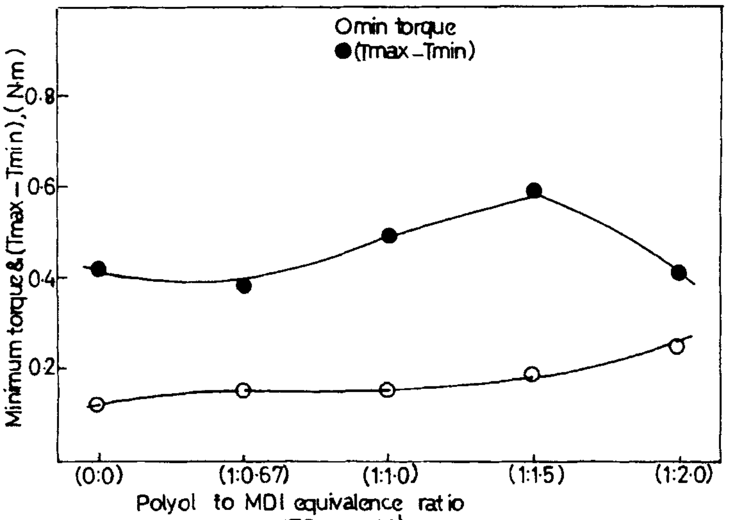

FIGURE 9 Variation of minimum torque and Tmax. – Tmin. of Mixes A and J – M with MDI equivalence.

increase with increasing MDI equivalence ratio. Tmax. – Tmin. attains a maximum at MDI equivalence ratio of 1.5, after which it drops drastically indicating that the resin formation is optimum when the MDI/–ol ratio is 1.5.

Cure time and scorch time (Fig. 10) show a trend as in the cases of MDI/PG and MDI/PPG based composites.

3.4. MD Resin Based on Different Diols and Triol

3.4.1. Minimum Torque and Tmax. – Tmin.

Figure 11 gives the minimum torque and Tmax. – Tmin. of the composites containing MD resin with 1:1 equivalence of MDI and different –ols and also that of the composite containing no resin. The higher value of the Tmax. – Tmin. is exhibited by the composite containing glycerol based MD resin (Mix K). This may be attributed to the trifunctionality of the glycerol. With MDI the glycerol forms a three dimensional network structure leading to a more restrained matrix and improved fiber – matrix interactions. PPG/MDI resin based composite (Mix G) exhibits the lowest Tmax. – Tmin. and minimum torque values, indicating a low level of crosslinking coupled with better processability. MDI/PG resin based composite shows a Tmax. – Tmin. that is in

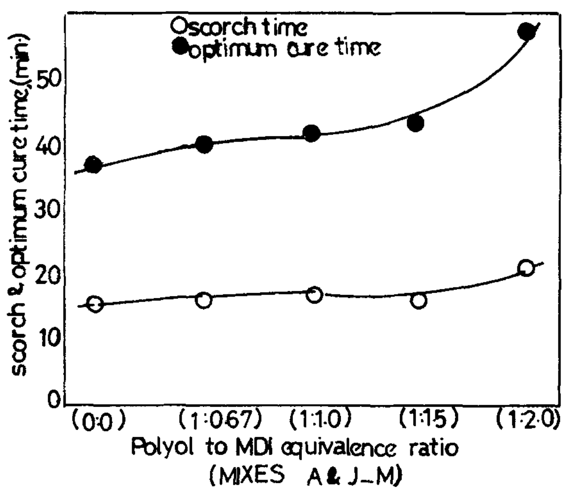

FIGURE 10 Variation of scorch and optimum care time of Mixes A and J – M with MDI equivalence.

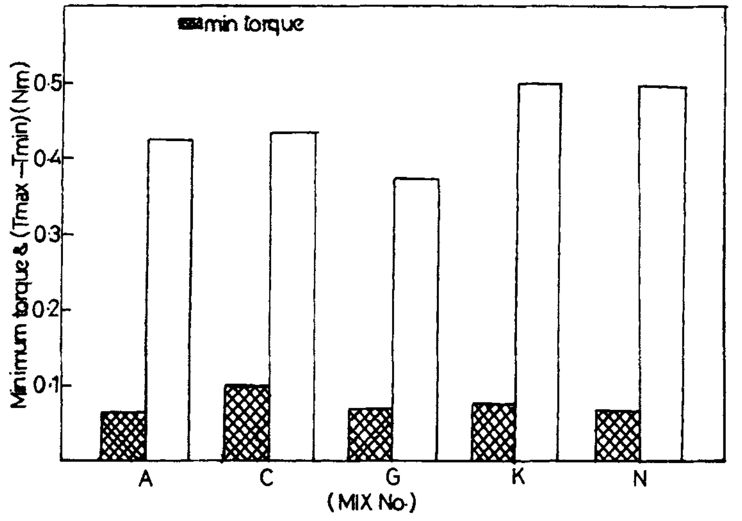

FIGURE 11 Minimum torque and Tmax. – Tmin. of Mixes A, C, G, K and N.

between that of Mixes G and K and the highest minimum torque. Substituting 50 parts by equivalence of the PPG by glycerol (Mix N) has a favourable effect on the extent of crosslinking, as indicated by the higher Tmax. – Tmin. values. At the same time, the minimum torque values show that processibility is not hampered significantly.

3.4.2. Scorch Time, Cure Time and Rate of Cure

Table IV gives the scorch time, optimum cure time and rate of cure of the composites containing MD resin with 1:1 equivalence of MDI and different –ols and that of composite without MD resin. Mixes, C, G and K require more cure time while Mix N shows a low cure time

TABLE IV Cure characteristics of Mixes A, C, G, K and N

Mix No.	*Scorch Time (minutes)*	*Cure Time (minutes)*	*Cure Rate (Nm/minute)*
A	15.2	36.8	0.023
B	16.8	47.6	0.016
G	17.2	41.6	0.017
K	15.2	57.6	0.014
N	13.6	34.8	0.027

compared to that of Mix A. Also, Mix N shows a high rate of cure and a comparatively lower scorch time.

4. CONCLUSIONS

From this study the following conclusions may be drawn: Urethane resins based on polymeric MDI with glycols and glycerol are effective in improving the fiber – matrix interaction in a short polyesterfiber – polyurethane elastomer composite. MDI/glycerol resin imparts a higher rate of cure and lower processibility to the composite than the MDI/polypropyleneglycol. A MDI/PPG/Glycerol resin gives an optimum scorch time, high rate of cure and good processibility.

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