

# Studies on the curing of short polyester fiber-polyurethane elastomer composite with different interfacial bonding agents

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(Received 2 November 1994; revised version received 5 February 1995; accepted 7 February 1995)

**Abstract:** The cure characteristics of polyester short fiber-polyurethane elastomer were studied with respect to different fiber-matrix bonding agents. A hexamethylenetetramine-resorcinol-hydrated silica based bonding agent was found to affect the stability of the composite. A new bonding agent, TP resin, based on polymeric toluenediisocyanate and polypropylene glycol has been developed. Cure characteristics of the composite with and without TP resin at different fiber loadings were also compared. Minimum torque, scorch time and optimum cure time increased with fiber content. Maximum torque was consistently higher with TP resin at all fiber loadings.

## 1 Introduction

Short-fiber reinforced elastomers have considerable importance because of their advantages in processing and good mechanical properties. Normally used fibers for reinforcement include cellulose, glass, nylon, aramid, polyester, jute, sisal and silk.<sup>1-10</sup> Several studies on the mechanical properties of the composites exploring the influence of fiber loading, fiber orientation and dispersion and fiber-matrix adhesion.<sup>1,5-7,10-14</sup> The mechanical properties of a short fiber-elastomer composite critically depend on the interfacial bonding between the fiber and the matrix. A bonding system based on Hydrated silica, Resorcinol and Hexamethylenetetramine (HRH) was found to improve the fiber-matrix adhesion in the case of composites involving NR-silk, NR-short jute fibers and carboxylated nitrile rubber-short jute fibers.<sup>1,5-8</sup> Recently, Kutty *et al.* studied the action of the HRH bonding system in a polyurethane elastomer-short fiber composite and found that HRH had a detrimental effect on the curing of the urethane elastomer.<sup>15,16</sup> The aim of the present study is to give a better insight into the action of HRH in the polyurethane matrix and to develop a better bonding

system for a polyurethane-short polyester fiber composite.

## 2 Experimental

### 2.1 Materials used

Adiprene CM: Polyether urethane rubber (Specific gravity 1.06, Mooney viscosity MS-10 at 100°C approximately 60), obtained from Uniroyal Chemical Co. Inc., USA, Caytur: -4: a zinc chloride-MBTS complex and catalyst for polyurethane vulcanization, obtained from Uniroyal Co. Inc., USA., Short polyethylene-terephthalate (PET) cord chopped to 4 mm length (fiber diameter: 21 μm) was procured from Madura Coats, India; MBTS: Dibenzothiazyl disulfide, obtained from Bayer India Ltd; MBT: 2-Mercaptobenzothiazole, obtained from Merck India; Silica: Vulcasil S, a Bayer AG product obtained from Bata India Ltd.

### 2.2 Processing

Formulations of the mixes are given in Table 1. These mixes were prepared as per ASTM D 3184 (1980) and ASTM D 3182 (1982) on a laboratory two-roll mill. Cure characteristics were determined

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**Table 1 Formulation of the mixes**

	Ingredient																		
	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	
Adiprene	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
TP resin	—	—	—	—	—	—	—	—	—	—	—	2	5	8	5	5	5	5	
Polyester fiber	—	5	10	20	30	10	—	—	—	—	—	—	—	—	—	5	20	30	
HMTA	—	—	—	—	—	5	5	—	—	5	5	—	—	—	—	—	—	—	
Resorcinol	—	—	—	—	—	2.5	2.5	—	—	2.5	2.5	—	—	—	—	—	—	—	
Silica	—	—	—	—	—	1.6	1.6	—	—	5	10	—	—	—	—	—	—	—	
CuSO <sub>4</sub> ·5H <sub>2</sub> O	—	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—	—	
CuSO <sub>4</sub> (anhydrous)	—	—	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—	

Zinc stearate, 0.5 phr; Caytur-4, 0.25 phr; MBTS, 1 phr; and Sulphur, 0.75 phr are common to all mixes. TP Resin was prepared by mixing molar proportions of polymeric, toluenediisocyanate and polypropylene glycol in the ratio 1:2.

by using a GOTTFFERT Elastograph Model 67.85 at 150°C. Scorch time was taken as the time for 10% rise in torque from minimum torque.

### 3 Results and discussion

#### 3.1 Effect of fiber loading

Figure 1 shows the cure pattern of Mixes A-F, containing 0–30 phr of polyester short fibers. In the presence of short fibers the cure behaviour of polyurethane elastomer is greatly altered.

The minimum torque shows a linear increase with increase in fiber loading, as shown in Fig. 2a. However, the maximum torque remains more or less constant. A similar result in the case of polyurethane–short Kevlar fiber composite has been reported earlier.<sup>16</sup>

The scorch time and the cure time are found to increase with increase in fiber content (Fig. 2b). Scorch time is increased from 13.4 min at 0 phr fiber loading to 32.8 min at 30 phr fiber loading. Correspondingly, the cure time is increased from 31.6 min to 90.8 min. This, coupled with a constant maximum torque at all fiber loadings indicates a reversible adsorption of curatives by the fibers.<sup>16</sup>

#### 3.2 HRH bonding system

The curing of 10 phr polyester fiber-filled polyurethane elastomer in the presence of HRH bonding system was studied and the cure curve (Fig. 1) shows that the system undergoes degradation instead of curing, after about 6 min.

The cure behaviour was further studied in the absence of short fibers. Figure 3 gives the cure characteristics of the Mixes A&G. Mix A with normal curatives shows a good cure, where as Mix G containing the HRH bonding agent fails to cure. The torque shows a distinct fall beyond the plastic flow

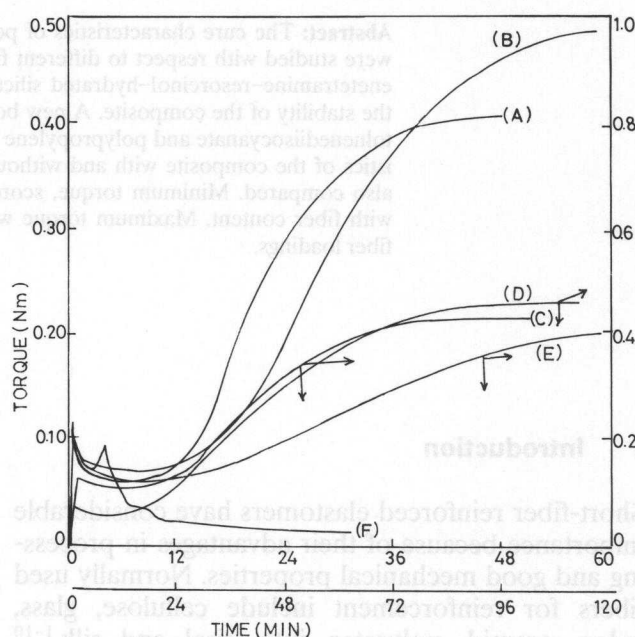


Fig. 1 Rheographs of Mixes A-F. For Mixes D, C and E the lower X-axis is to be taken.

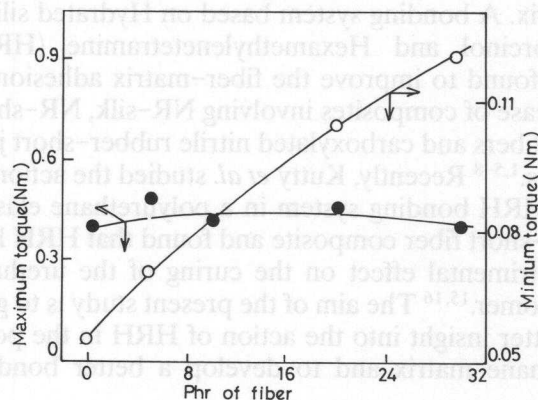


Fig. 2a Variation of maximum torque and minimum torque with fiber loading.

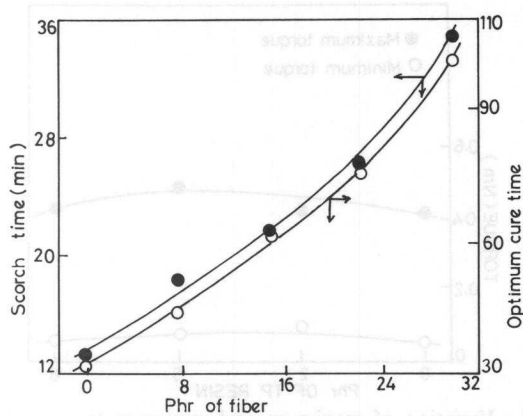


Fig. 2b Variation of scorch and optimum cure time with fiber loading.

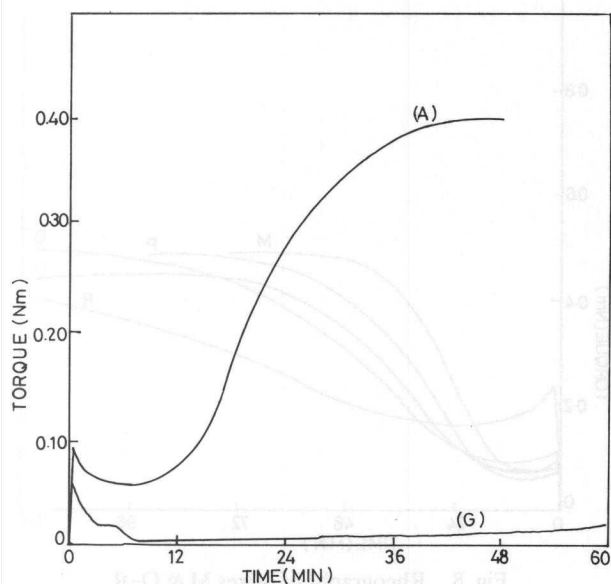


Fig. 3 Rheographs of Mixes A & G.

region. At about 6 min of cure the torque drops from 0.021 Nm to 0.006 Nm and then shows only a marginal increase. The very low final torque indicates an extensive molecular chain breakage instead of crosslinking. The molecular breakdown in the presence of HRH dry bonding system may be attributed to the hydrolysis of the urethane linkages of the elastomer. The resorcinol and hexamethylenetetramine at the curing temperature react to form water molecules which can hydrolyse the -NCO linkages.

This is further confirmed by studying the curing reaction with another water source that liberates water at elevated temperature.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was selected as a water donor and was incorporated at a level of 5 phr (Mix H). The cure behaviour is shown in Fig. 4. This also shows a cure pattern similar to that of Mix G. The torque is reduced from 0.042 Nm to 0.010 Nm at about 6 min curing. The pro-oxidant effect of copper has been checked by

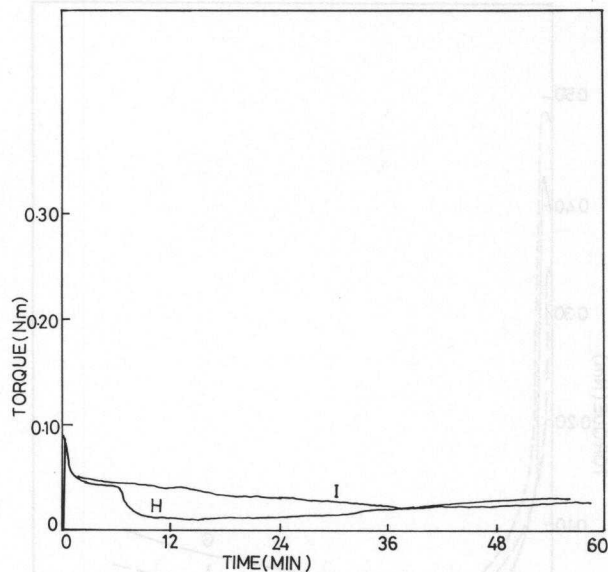


Fig. 4 Rheographs of Mixes H & I.

studying another sample with anhydrous  $\text{CuSO}_4$  (Mix I) and the cure curve is shown in Fig. 4. The torque shows a gradual and almost linear reduction with time. There is, however, no abrupt change in torque at 6 min. This indicates that the sudden change in viscosity of polyurethane in the presence of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is due to the hydrolysis of urethane by the water liberated by  $\text{CuSO}_4$ . This clearly confirms that the degradation of polyurethane in the presence of HRH dry bonding system is due to the water formed during resorcinol-formaldehyde resin formation.

Silica is incorporated as a modifier for resorcinol-formaldehyde resin formation.<sup>3,16</sup> The surface hydroxyl groups may have an effect on the urethane curing reaction. This was studied by changing the silica concentration from 1.6 to 10 phr (Mixes G, J, K). The cure behaviour of these mixes are shown in Fig. 5. As expected, the final torque values decrease with increase in silica content. Increasing the acidic -OH concentration in the medium increases the changes of urethane breakage.

A resin system (TP) based on polymeric toluenediisocyanate and polypropylene glycol which does not form water as a biproduct was used as a bonding agent. Figure 6 shows the cure behaviour of polyurethane-polyester composite containing polymeric toluenediisocyanate and polypropylene glycol corresponding to 2, 5 and 8 phr of TP resin (Mixes L, M, N). With increasing TP resin content the minimum torque and the maximum torque values show a marginal increase with a maximum at 5 phr of TP resin (Fig. 7) indicating an improved fiber-matrix interfacial bonding. A 5 phr loading of TP resin was selected for further studies.

Figure 8 shows the cure behaviour of mixes containing 0-30 phr fiber with 5 phr TP resin (Mixes M,

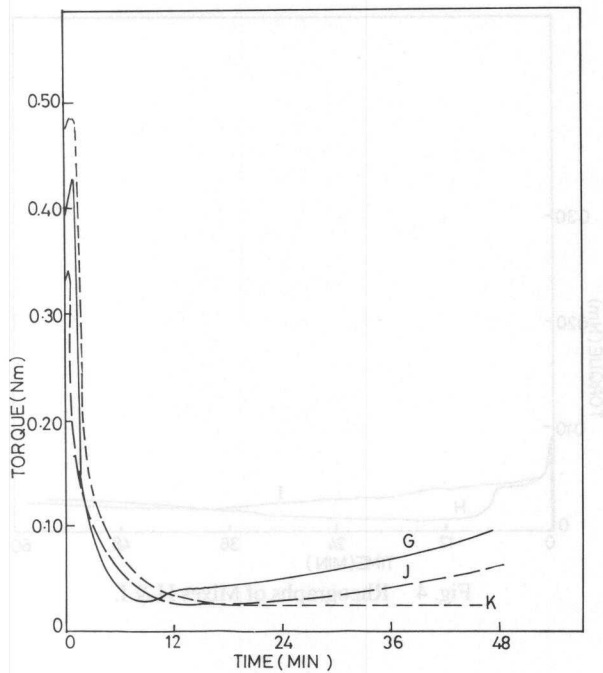


Fig. 5 Rheographs of Mixes G, J & K.

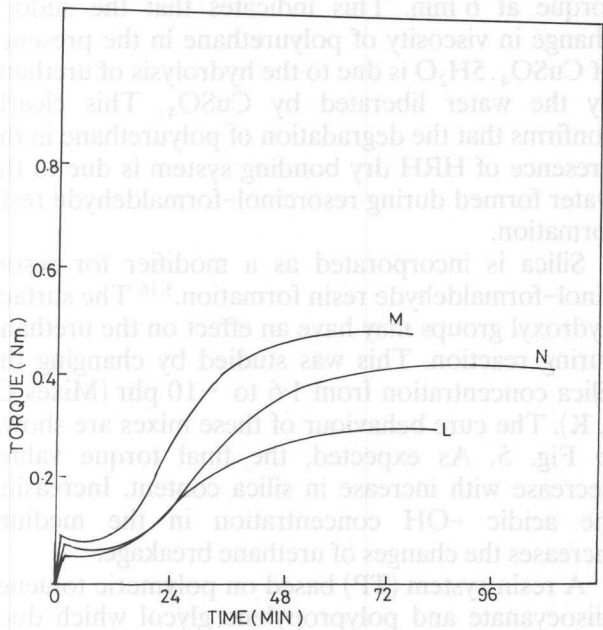


Fig. 6 Rheographs of Mixes L, M & N.

O-R). Unlike in the case of HRH based compounds these mixes are found to give a perfect cure. A comparison of the cure parameters of the composite with and without TP resin (Fig. 9) shows that the maximum torque developed is higher for the TP resin containing composite. This suggests that TP resin at a concentration of 5 phr is a good choice for improving the properties of polyurethane-polyester short fiber composites.

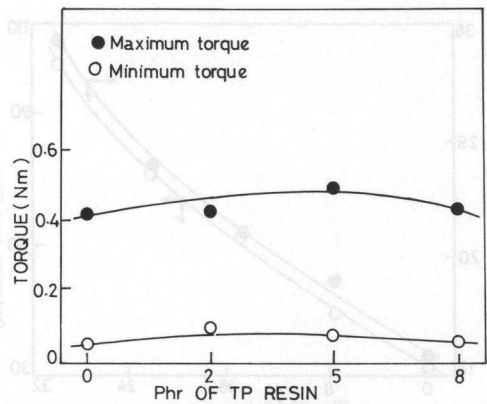


Fig. 7 Variation of maximum and minimum torque with TP resin.

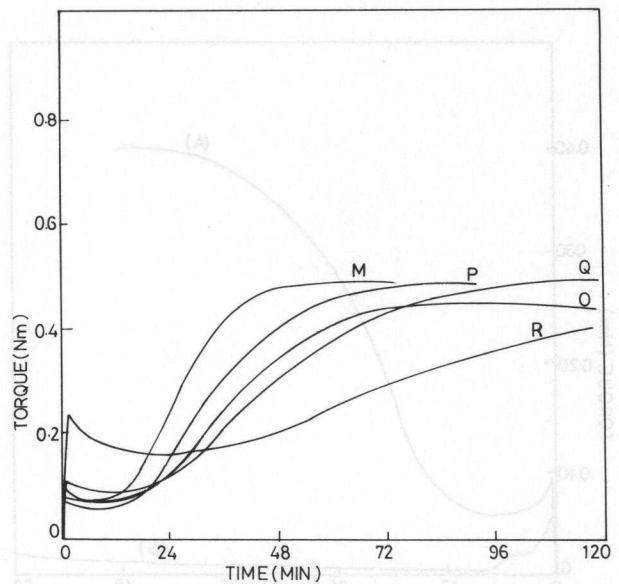


Fig. 8 Rheographs of Mixes M & O-R.

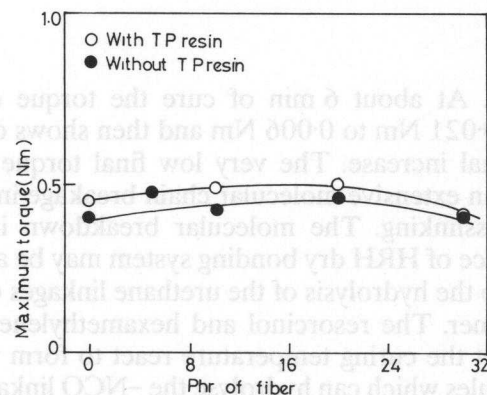


Fig. 9 Variation of maximum torque of the composite containing TP resin with fiber loading.

#### 4 Conclusions

From the above study the following conclusions can be drawn for polyurethane-polyester short fiber composites.

- (1) The cure characteristics such as minimum torque, scorch time and optimum cure time of the composite show a linear increase with increase in fiber loading, while maximum torque remains more or less constant.
- (2) The HRH dry bonding system is found to be ineffective.
- (3) A TP resin based on polymeric toluenediisocyanate and polypropylene glycol can be used as a better bonding agent in polyester short fiber composite.
- (4) The optimum level of TP resin in the composite is found to be 5 phr.
- (5) The cure characteristics of the composites are improved by incorporating TP resin.

### Acknowledgement

One of the authors (F. Suhara) would like to acknowledge the financial assistance given by CSIR, India.

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