Self adhesion of short Kevlar fibre–thermoplastic polyurethane composite

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Abstract—The self adhesion behaviour of thermoplastic polyurethane (TPU) in itself and its composite with short Kevlar fibre with respect to contact time, temperature, pressure, and fibre loading has been studied. The adhesion strength showed two linear increments of different slopes with respect to the square root of time: with temperature and pressure of contact, the adhesion strength was improved. The maximum strength was obtained with 20 phr of short fibre in only one of the mating substrates in the peel test sample. The duration for wetting and diffusion was shifted to longer time intervals with fibres loaded in both the substrates.

Keywords: Self adhesion; thermoplastic polyurethane; Kevlar staple fibre; joint strength.

1. INTRODUCTION

Adhesion between two similar polymeric substrates has been studied elaborately and it has been reported that the interfacial diffusion of macromolecules plays a critical role in self adhesion of polymers [1–6]. Bister *et al.* [3] reported a theoretical treatment of self adhesion of polymers. Self adhesion plays a decisive role in the processing of thermoplastic elastomers and their composites with short fibers, since the fabrication stages quite often involve consolidation of multiple layers of these composites. In the absence of a conventional vulcanization stage in these TPU composites, proper bonding between the layers at the joints is essential. Kurian *et al.* [7] have studied the self adhesion behaviour of high density polyethylene filled natural rubber vulcanizates and found that the self adhesion strength improved in the presence of high density polyethylene as compared to that with HAF black filled natural rubber vulcanizates.

Recently, the authors have reported on the mechanical and rheological properties of short Kevlar fibre–thermoplastic polyurethane composites [8–11]. The present investigation attempts to understand the self adhesion behaviour of thermoplastic polyurethane alone and short Kevlar fibre filled thermoplastic polyurethane. The effects of different parameters such as contact time, contact pressure, contact temperature and fibre content on the self adhesion of thermoplastic polyurethane have been studied.

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2. EXPERIMENTAL

2.1. Materials

Ether–based thermoplastic polyurethane (Estane 58311, Mw $= 1.5 \times 10^5$; T_g determined by DMA $= -21°C$) was procured from Urethane India Ltd, Madras. Uncoated short Kevlar staple fibre (T-970) having an average length of 6 mm and L/D 500 μm was procured from Du Pont Co., USA.

2.2. Processing

The formulation of the mixes are given in Table 1. The mixing of TPU with Kevlar fibre was carried out in a Brabender Plasticorder PLE 330 fitted with a cam type rotor head at 180°C and at 60 rpm rotor speed, after drying the ingredients in an air oven at 120°C for 2 h to drive out any moisture [9, 10]. The mixing sequence is given in Table 2. After the mixing, the material was sheeted out on a laboratory size (150 mm × 300 mm) open two-roll mill at a nip gap of 0.8 mm. Tensile sheets were moulded in a Labo press at 180°C and 45 kg cm^{-2} pressure for 3 min and subsequently cooled by passing cold water through the press platens. The surfaces of the sheets were protected by aluminium foils on either side within the mould cavity and this helped in easy demoulding. Adhesion samples of size 25 mm × 75 mm were cut out from the tensile sheets while the protective aluminium foil was kept intact. The aluminium foils were subsequently peeled off to allow the two virgin surfaces of the samples to come in contact with each other; a length of 25 mm at one end was left as lobes for gripping. This specimen was kept in the cavity of a special type mould and heated at different temperatures and pressures. On completion of the moulding time, the samples were removed immediately and cooled under constant load. Finally, the 180°

Table 1.
Formulation of the mixes

Ingredient	Mix no.				
	TP0	TP10	TP20	TP30	TP40
TPU^a	100	100	100	100	100
Kevlar^b	—	10	20	30	40

^{a}Thermoplastic polyurethane, Estane-58311, from Urethane India Ltd, Madras.
^{b}Untreated Kevlar aramid staple fibres (T-970) from Du Pont Co., USA.

Table 2.
Mixing sequence

Ingredient	Time in min	RPM	Ram
1/2 TPU	0	30	Up
Fibre	1.5	30	Up
1/2 TPU	3.0	60	Down
—	9.0	—	Dump

peel adhesion test was carried out at a crosshead speed of 50 mm min^{-1} in an Instron UTM, model 1195.

3. RESULTS AND DISCUSSION

3.1. Effect of contact time on the self adhesion of TPU

According to Bothe and Rehage (6):

$$\sigma_H = k(\rho/M)^{2/3} D^{1/2} \cdot t^{1/2} + \sigma_A,$$

where k is the proportionality constant, ρ is the density, M is the molecular weight, D is the diffusion coefficient, and t is diffusion or contact time. The intercept σ_A signifies the adhesion strength at zero contact time and denotes the initial adhesion of the component phases. The adhesion strength varies linearly with $t^{1/2}$. Such a plot of adhesion force vs. square root of time for unfilled thermoplastic polyurethane is given in Fig. 1. It shows two distinct regions of different slopes. A behaviour of similar pattern has been discussed by Bothe and Rehage [6]. The joint strength between two surfaces in contact arises from two factors: (1) macroscopic accommodation of the contacting surfaces, thus increasing the contact area, hence improved adhesion strength, and (2) the interfacial diffusion of mobile chain ends. The first process takes place in a very short time span and it is not seen in the figure. The diffusion is the main process involved in Region I as shown in Fig. 1. In this region, the increase in adhesion strength is sharp with respect to time. The strength is controlled by the depth of penetration of chain ends and also the number of chain ends involved. At a given pressure and temperature the probable number of chain ends involved can be assumed to be constant. Therefore an increase in adhesion strength in Region I is mainly due to an increase in depth of penetration of the chain ends, which increases sharply with contact time. In Region II, the adhesion strength is higher but increases steadily and slowly with time. This is because another factor, the entanglement of the chains, plays a major role here. The breakage of the test
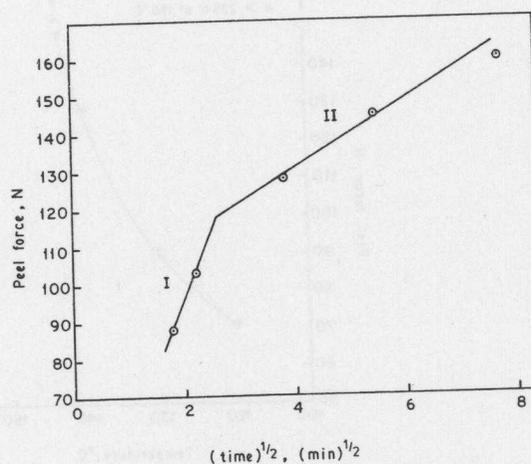

Figure 1. Effect of contact time on the self adhesion of TPU.

sample occurs by slipping past of the diffused chain ends in the contact plane as it is the weakest region in the system. Entanglement of chains cannot be easily undone under tensile strain which results in higher adhesion strength. The chain ends which diffuse across the interface and form interconnections or bridges with the other phase are fused in the network of its own phase, making the contact zone weakest. Similar observations have been reported in the case of acrylonitrile butadiene rubber by Bothe and Rehage [6].

3.2. Effect of contact temperature on the self adhesion of TPU

The effect of contact temperature on the self adhesion strength of TPU joints was studied, with the contact pressure being kept constant at 10 kg cm^{-2} and time of contact constant at 15 min. The temperature of contact was varied from 120 to 150°C. Figure 2 shows the variation of self adhesion strength of TPU with temperature of contact. It is evident from this figure that self adhesion strength increases with an increase in the temperature of contact, and the strength reaches an exorbitantly high value of 250 N at a temperature of 150°C. This may be attributed to the cohesive failure of the TPU matrix as contrasted with the interfacial failure occurring at a temperature of 140°C. This may be further explained as due to the increased plasticity of the TPU at a temperature higher than 140°C which resulted in rapid plastic flow at the interface between the two matrices. Consequently, the chain segments and chain ends interdiffuse rapidly at the interface, causing intermolecular locking. As per Campion [12] the presence of free space, both intra- and inter-molecular, helps in the diffusion process which increases the effective contact area between the chains. This enhances the interfacial strength of the polymer joints. Similarly, at a temperature of 150°C and a pressure of 50 kg cm^{-2}, the TPU joint fuses to a single matrix, thus facilitating peeling through the matrix rather than at the interface which no longer exists. This phenomenon is expected to also occur at temperatures higher than 150°C; hence, no studies at higher temperature were performed.
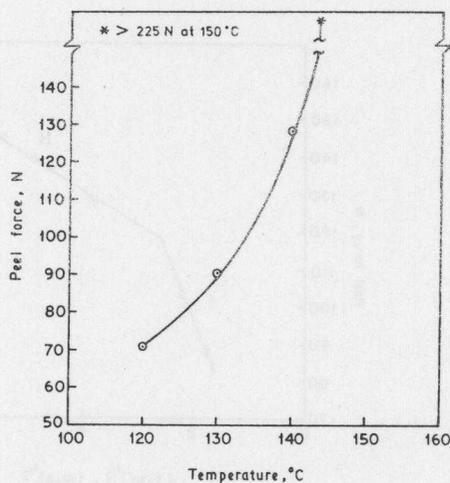

Figure 2. Effect of contact temperature on the self adheison of TPU.

3.3. Effect of contact pressure on the self adhesion of TPU

The effect of varying the contact pressure on the self adhesion of the TPU joints is illustrated in Fig. 3. The contact temperature was kept constant at 140°C and the time of contact was kept constant at 15 min. The pressure was varied from 0 to 50 kg cm^{-2}. Self adhesion strength measured by the 180° peel test was found to increase linearly with contact pressure. At 50 kg cm^{-2}, however, the failure was again cohesive, the sample tearing through the TPU matrix. Therefore, contact pressure ranges beyond 50 kg cm^{-2} were not tested. The increase in the peel adhesion strength of the TPU–TPU joints on increasing pressure is due to an increase in the total area of contact which have resulted in rapid and complete diffusion of the component phases.
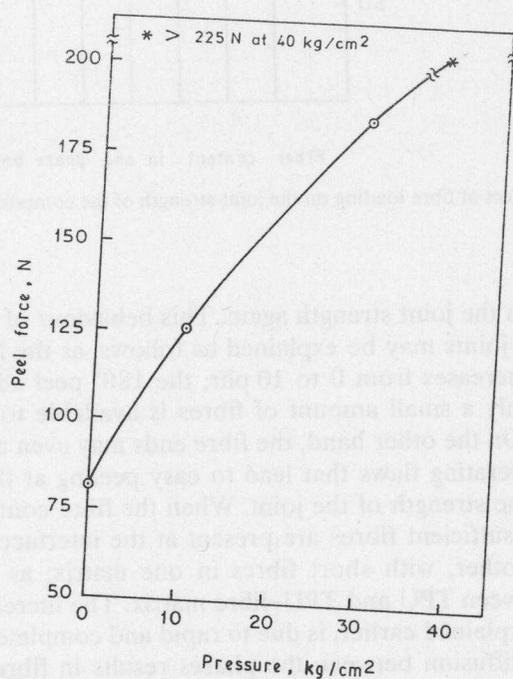

Figure 3. Effect of contact pressure on the self adhesion of TPU.

3.4. Effect of fibre loading in one phase

Since for neat TPU, a contact temperature of more than 140°C and a contact pressure of more than 40 kg cm^{-2} results in cohesive failure of the matrix, the effect of short Kevlar fibres on the composite joint strength was studied at a lower contact temperature and lower contact pressure. The fibre content in the composites was varied from 10 to 40 phr, while the contact temperature was kept constant at 140°C and the pressure at 10 kg cm^{-2}. Figure 4 shows the histogram of peel force vs. fibre content for TPU–short Kevlar fibre filled TPU joints. It shows that the joint strength decreases when the composite contains 10 phr of fibre content and increases to a maximum of 250 N at 20 phr of fibres. Increasing the fibre content further to 40 phr in one of the matrices led to a
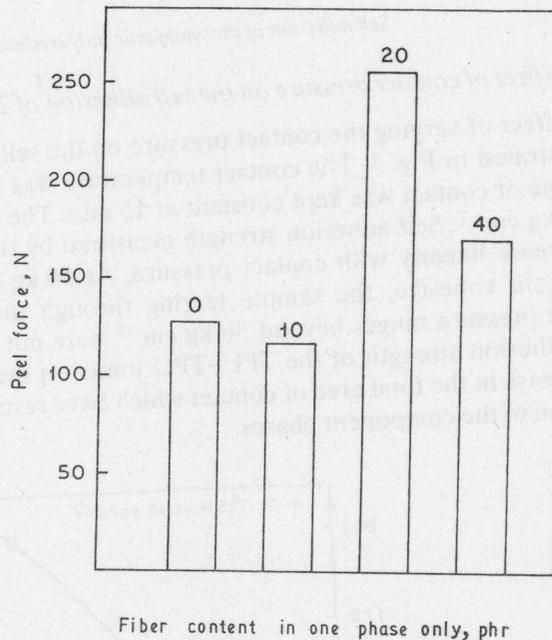
Figure 4. Effect of fibre loading on the joint strength of the composites, while fibres are in one phase only.

decrease in the joint strength again. This behaviour of the TPU and TPU–Kevlar composite joints may be explained as follows: as the fibre content in one of the matrices increases from 0 to 10 phr, the 180° peel adhesion strength decreases because only a small amount of fibres is available to diffuse and bridge at the interface. On the other hand, the fibre ends may even act as stress raisers at local points, generating flaws that lead to easy peeling at the interface and therefore reducing the strength of the joint. When the fibre content in the matrix is raised to 20 phr, sufficient fibres are present at the interface, and the matrices diffuse into each other, with short fibres in one matrix; as a result, good anchoring occurs between TPU and TPU–fibre matrix. The increased adhesion strength, as has been explained earlier, is due to rapid and complete diffusion at the interface. This interdiffusion between the phases results in fibre bridges which obstructs the peeling through the interface. This has been evidenced from the optical photomicrograph of the peeled surface of neat TPU, which shows the presence of embedded fibers on the surface (Fig. 5a and 5b). Although the initial length of the short Kevlar fibres is approximately 6 mm, it breaks down to approximately 1 mm during mixing in the Brabender Plasticorder. This reduction in length facilitates the interdiffusion process at the interface and this in turn results in an increase in the modulus of the interface due to stiffening. Thus, the combined strength is enhanced. When the fibre content was further increased to 40 phr again, the peel adhesion strength was reduced because more short fibres at the interface and less fibre–fibre adhesion resulted in a dilution of the matrix. The failure occurred between fibres with less interdiffusion of the matrix, making peeling easier. Therefore, the combined strength was lowered.
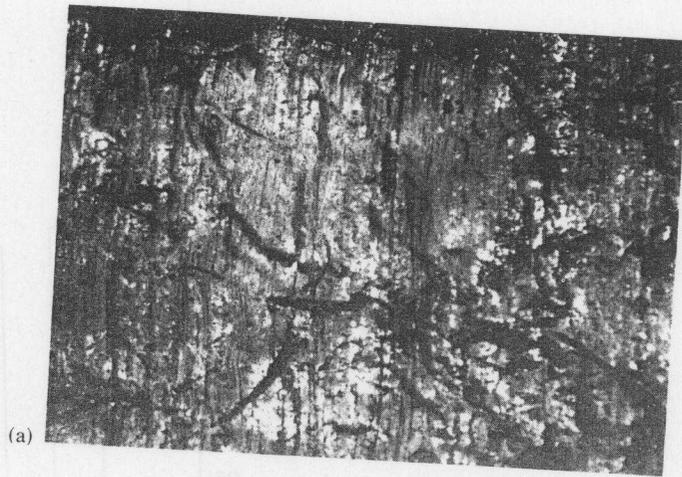
(a)
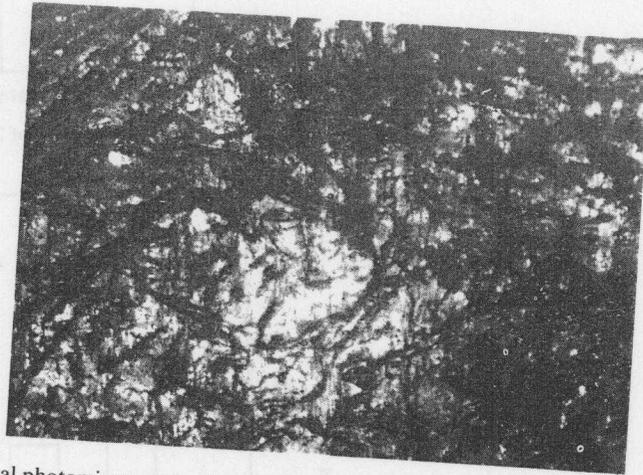
(b)

Figure 5. (a) Optical photomicrograph of TPU surface (peeled from 10 phr fibre filled TPU)— ×100. (b) Optical photomicrograph of TPU surface (peeled from 40 phr fibre filled TPU)— ×100.

Figure 5a and 5b (×100) show the peeled surfaces of neat TPU bonded to 10 and 40 phr fibre filled TPU samples, respectively. For a given contact time, temperature and pressure, the amount of fibre diffused (seen on the TPU surface in the figure) is a function of fibre content in one phase only. Figure 5b shows a higher amount of fibre adhering to the surface than Fig. 5a which is the peeled surface of 10 phr fibre filled TPU. With 40 phr fibre in one phase only, less matrix is available for interdiffusion and flow across the interphase, resulting in a reduction in adhesion strength. It shows that a 20 phr fibre loading in one phase only is optimum for improved adhesion strength.

3.5. *Effect of contact time on the self adhesion of short Kevlar–TPU composite*

The effect of contact time on the self adhesion of 20 phr fibre filled TPU is shown in Fig. 6. The maximum peel adhesion strength was obtained at 15 min contact time. At lower contact times of 3 and 5 min, the adhesion strength
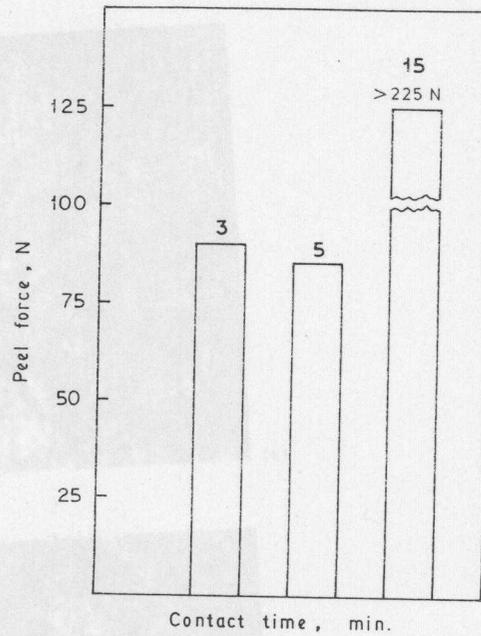
Figure 6. Effect of contact time on the self adhesion of 20 phr short Kevlar fibre–TPU composite.
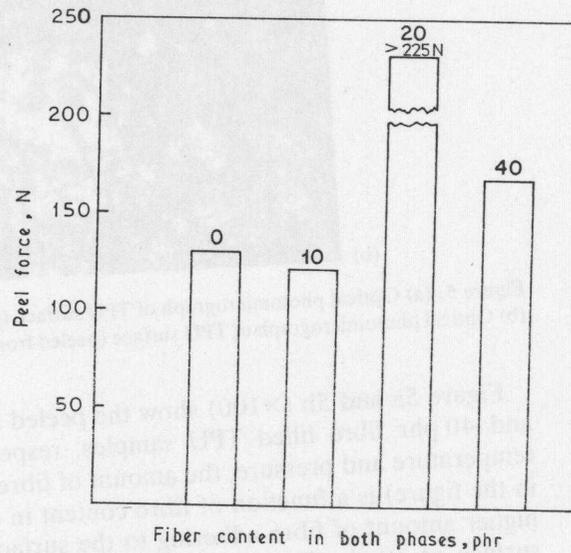

Figure 7. Effect of varying fibre content on the self adhesion of short Kevlar fibre–TPU composite.

remained almost the same. This reveals that in the presence of short fibres, the diffusion of chain segments and free chain ends is delayed.

3.6. Effect of fibre loading in both phases

The effect of incorporating short fibre in both phases on the self adhesion of TPU is shown in Fig. 7. Fibre loading was increased from 10 to 40 in both

phases. Temperature of contact was 140°C under a pressure of 10 kg cm^{-2} for 15 min. It is seen that the adhesion strength increased for a TP20/TP20 joint and also for a TP40/TP40 joint. The strength for the latter was lower than that for TP20/TP20 but higher than that of the neat TPU/TPU joint. For TP20/TP20 joint, the failure was cohesive but not interfacial since the failure propagates from the interface to one of the adherends during peeling thus leaving a thin layer of one substrate attached to the other substrate or component phase.

4. CONCLUSION

The following conclusions can be drawn from this study: The self adhesion of thermoplastic polyurethane and its short Kevlar fibre composite is dependent on contact time, pressure and temperature. Adhesion strength shows a two step dependence on the square root of the contact time. The presence of 20 phr of short fibre in one adhering phase only gives the maximum joint strength of the TPU matrix.

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