

Elastomeric Polyurethanes Reinforced with Aramid Fibers

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Synopsis

Thermoplastic polyurethane is a relatively new development in the elastomers field, combining elastomeric behavior with thermoplastic processing characteristics. Thus, high production rates and reduced scrap can be achieved but, increased versatility for the incorporation of additives is also possible. In this work, thermoplastic polyurethane matrices were prepared and Kevlar pulp was dispersed as a reinforcing agent. Since good dispersion and appropriate filler volume fraction are critical factors for a reinforcing effect, special attention was paid to the optimization of these parameters. Thermoplastic polyurethanes were prepared by mixing a low melting polyol with a low melting diisocyanate and the subsequent addition of small amounts of a chain extender, namely, a low molecular weight diol such as 1,4 butanediol. The Kevlar pulp was added under stirring either in the polyol or the diisocyanate melt. This incorporation technique allows the dispersion of small fiber percentages. Thus, calendaring of the materials prepared was also performed and additional fibers were incorporated. Changes in the properties of the specimens prepared as a function of the filler volume fraction and the dispersion technique were determined, taking into consideration the possibilities of chemical interaction between fibers and matrix.

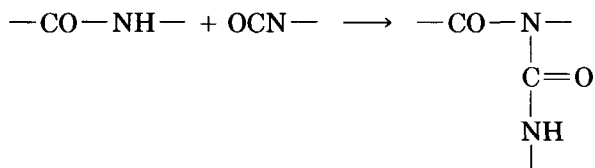
INTRODUCTION

It is well known that aramid fibers present exceptional physical and technical characteristics, therefore, they are used extensively as reinforcing agents nowadays. Thus, many researchers studied the properties and performance of aramid fibers as reinforcement not only for thermosetting,¹⁻³ but also for thermoplastic matrices.⁴⁻¹²

The composites based on thermosetting materials reinforced with aramid fibers have of course some limitations due to the brittleness of the matrix. Moreover, the preparation of such composites is often characterized by slow production cycles. These reasons mandated the introduction of thermoplastic matrices, leading to the production of composites with very important properties.

In thermosetting or thermoplastic polymers, adhesion of the fibers to the matrix is very critical. In fact, although aramid fibers could readily combine with most resins used in manufacture of composites, experience has shown that their poor interfacial adhesion to the resin matrix can lead to compressive breakdown. To fully utilize the excellent reinforcing properties of aramid fibers, obvious improvements must be made in the area of interlaminar adhesion.

Many previous attempts have been made to modify the aramid fiber surface and promote adhesion. Thus, commercial coupling agents,¹ boiling in water,⁶ chemical modification,⁷ bromine,¹³ or chloride^{14,15} treatment have been proposed. Furthermore, the reaction of aramid fibers with an isocyanate-linked polymer (according to the following scheme) is reported¹⁶ as an effective surface treatment.



In this work, an attempt was made to incorporate discontinuous aramid fibers in thermoplastic polyurethane matrices, following two different dispersion techniques. First, a conventional mixing of short fibers and liquid polyurethane matrix by mechanical stirring was carried out. Furthermore, a two-step mixing process was followed providing mechanical stirring and then calendering of the solidified mixture.

This study intends not only to provide information about the properties of such composites but also to evaluate the different incorporation techniques. Moreover, our study could constitute an approach to the possible fiber-matrix interactions, since the results obtained are strongly affected by this interrelation.

EXPERIMENTAL

Materials and Method

The two components of the thermoplastic polyurethane, namely diisocyanate and polyol, were Desmodur 44-MS and Desmophen 2000 M, respectively (Bayer AG). Kevlar pulp (Du Pont de Nemours & Co. Inc., nominal fiberlength 2 mm) was used as the reinforcement.

The pulp was added to the melted diisocyanate and stirred for 1 min. Then the appropriate amount of melted polyol was added and stirred for 2 min. Finally, the required amount of 1,4 butanediol was added under stirring. The compound was then poured on a glass plate, coated with a silicone release agent. The first series of samples includes the compounds so prepared with varying filler volume fraction. A second series is derived after calendering of the above compounds (see also Table I).

A laboratory roll mill (Scamia-France) was used for the calendering process. The roll temperature was adjusted at 80°C and the overall process duration was about 15 min. For the preparation of specimens, both series of the thermoplastic samples prepared were molded into plaques of about 3-mm thickness. A heated plate hydraulic press at 160–180°C was used for the molding.

TABLE I
Presentation and Composition of the Series of Specimens Prepared

Presentation		Composition			
Mechanical stirring	Calendering	Diisocyanate (g)	Polyol (g)	Pulp (g)	V_f (%)
P0	P0	15	40	0	0
P1	PC1	15	40	0.45	0.7
P2	PC2	15	40	0.9	1.3
P3	PC3	15	40	1.8	2.7
P4	PC4	15	40	3.6	5.2
	PC5	15	40	7	9.25

Testing and Measurements

Infrared Spectroscopy

The infrared (IR) spectra of Kevlar pulp as well as pulp treated with diisocyanate, were obtained to determine whether any changes could be induced by the treatment.¹⁶ KBr tablets containing 0.3% of finely cut aramid pulp were tested in a Perkin-Elmer 283 B Spectrophotometer.

Tensile Measurements

The ASTM D 412 designation¹⁷ was followed to determine changes of the tensile characteristics. The tensile specimens were cut from the molded plaques using a Zwick cutting machine. A JJ Instrument tensile machine was used to record the load-elongation curve. In all cases, grip separation speed was 100 mm/min.

Density Measurements

The densities of the samples prepared were determined by weighing in air and then in distilled water, using a Mettler analytical balance. The density value was calculated using the following formula¹⁸:

$$\rho_s = \frac{B_a \rho_w}{B_a - B_w}$$

where: ρ_s is the sample density, B_a is the weight in air, B_w is the weight in water, and ρ_w is the density of water.

Wear Resistance Measurements

The specimens used for the wear resistance tests had the form of discs of 13-mm diameter. A Zwick testing machine was used and the wear resistance was expressed by the volume loss.

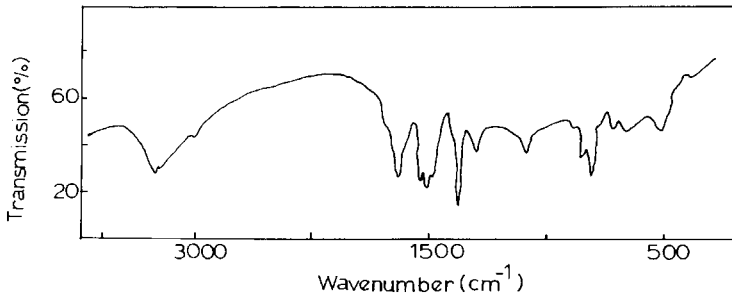


Fig. 1.

RESULTS AND DISCUSSIONS

The IR spectrum of Kevlar pulp is presented in Figure 1. This pattern is essentially the same with that of the treated Kevlar pulp. These results are perhaps evidence that no reaction between aramid and diisocyanate occurs, although the treated fibers obtain a dark brownish color.

The tensile strength of the two series of specimens as a function of the filler volume fraction is shown in Figure 2. The filler volume fraction (V_f) was calculated from the weight of matrix and filler using the equations:

$$V_p = \frac{d_f W_p}{d_p W_f + d_f W_p}$$

and

$$V_f = \frac{d_p W_f}{d_p W_f + d_f W_p}$$

where V , d , W , p , and f represent the volume fraction, density, weight fraction, polymer, and fiber, respectively.

As the curves of Figure 2 indicate, in both cases, a decrease of the tensile strength is evident with increasing V_f up to 3–4% and thereafter an increase occurs, but the value always remains below the starting strength value. It is

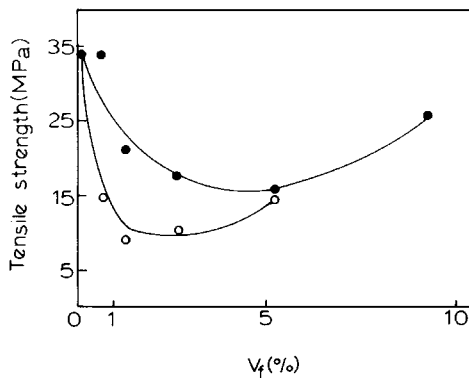


Fig. 2.

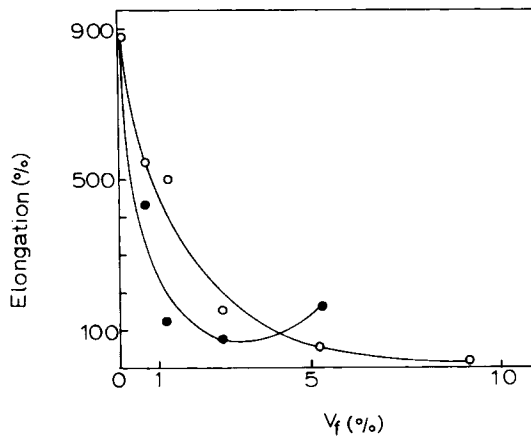


Fig. 3.

also clear that the strength of the calendered specimens is higher than that of the specimens of the first series.

The ultimate elongation as a function of V_f is presented in Figure 3. A decrease of the elongation with V_f is clear again, but the first series presents considerable deviations. This is due to the poor dispersion which leads to inhomogeneities. Finally, the Young's moduli of the two series of specimens versus V_f are presented in Figure 4. An increase of modulus with V_f is evident in both cases, but the higher increase corresponds to the calendered specimens.

The wear resistance and density measurements are shown in Table II. As the data of Table II indicate, there is a decrease of wear resistance with increasing V_f . The decrease in the case of the specimens prepared by mechanical stirring is considerably higher, due to the poor dispersion mentioned above. The same applies for the densities where some deviations are clearly apparent.

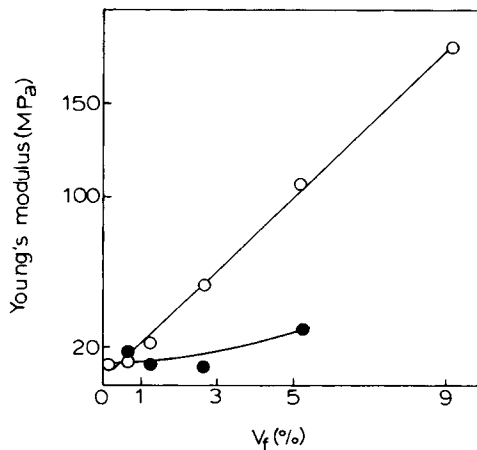


Fig. 4.

TABLE II
Wear Resistance and Density of the Two Series of Specimens

Specimen	Volume loss (mm ³)	Density (g/cm ³)
P0	57.5	1.236
P1/PC1	180/78	1.23/1.24
P2/PC2	271/112	1.19/1.253
P3/PC3	336/127	1.26/1.266
P4/PC4	264/132	1.25/1.273
P5	150	1.27

CONCLUSIONS

The above results can lead to the following conclusions:

1. The incorporation technique providing calendering is more efficient for a proper fiber dispersion in the thermoplastic matrix.
2. Reinforcing of thermoplastic polyurethanes with Kevlar pulp generally reduces tensile strength and elongation, but increases the elasticity modulus. In the area of low V_f (0.5–1%) the decrease in strength is not severe for the calendered samples.
3. The above behavior of the reinforced specimens indicates poor fiber–matrix adhesion. This is in agreement with the IR spectrum of the diisocyanate-treated aramid pulp.

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