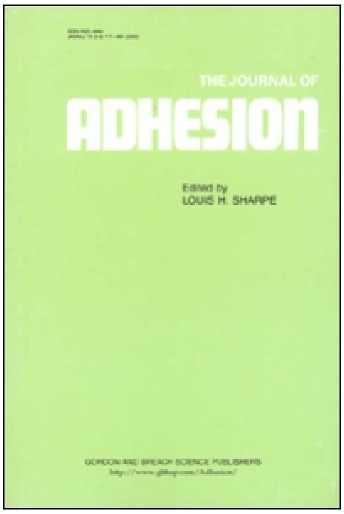

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Improved Adhesion Properties of Polyurethane Adhesive Containing Fumaric Acid

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Improved Adhesion Properties of Polyurethane Adhesive Containing Fumaric Acid*

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Different amounts (0.5–3 wt%) of fumaric acid (FA) were added to a solvent-based polyurethane (PU) adhesive. Addition of FA produced a decrease in viscosity and changed the rheological and viscoelastic properties of the liquid PU adhesive, which was more marked upon increasing the time after the adhesive was prepared and more noticeable for high amounts of FA. According to molecular weight distribution, differential scanning calorimetry, thermal mechanical analysis and thermogravimetry measurements, the addition of FA seemed to produce a reaction with the polyurethane (possibly an acid-catalyzed transesterification reaction) which resulted in chain cleavage, disruption of polyurethane crystallinity and a loss of physical properties. These modification in PU structure did not affect the surface energy value of the PU adhesive although the *T*-peel strength of roughened rubber/PU adhesive/roughened rubber joints increased when the PU adhesive contained FA. This improvement was due to the removal of antiadherent substances (zinc stearate, paraffin wax) from the rubber surface produced by migration of FA to the PU adhesive surface once the adhesive joint was formed. Therefore, the carboxylic acid seemed to act as a compatibilizer between the rubber surface and the PU/adhesive interface.

KEY WORDS: Polyurethane adhesive; fumaric acid; styrene-butadiene rubber; adhesion; zinc stearate; rheology; differential scanning calorimetry (DSC); gel permeation chromatography (GPC); thermogravimetry (TG); thermalmechanical analysis (TMA); contact angle measurements; FTIR; mechanical properties; T-peel tests.

INTRODUCTION

Solvent-based polyurethane adhesives (PU) are widely used to join a broad range of materials (leather, textiles, wood, porous synthetic materials, polymeric materials)[1]. Nevertheless, synthetic rubbers are not compatible with PU adhesives and a lack of

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adhesion between them is generally produced. Some compounds (antioxidants and/or mould release agents) in the formulation provide antiadherent properties to rubber, which may be responsible of its poor adhesion to PU adhesives.[2]

With respect to this concern, different procedures have been proposed to increase the adhesion between synthetic rubber and PU adhesive. Since it is not feasible to avoid the addition of antiadherent substances in the formulation of rubber, due to the increase in the production costs, a surface treatment should be used to produce strong and permanent adhesive joints[3]. The most common surface treatments for synthetic vulcanized rubber are abrasion[4] and halogenation[5–7]. In some rubber compounding, the most significant drawback of abrasion is the gradual migration of antiadherent substances to the surface once the adhesive bond is formed. On the other hand, halogenation of rubber, although in general very effective, is a time-consuming process and, in addition, causes problems of toxicity due to the formation of chlorine vapours.

Although a surface treatment of rubber enables adequate adhesive joints to be obtained, an additional modification of PU adhesives may help to increase the adhesion strength as well as the durability of the adhesive bond. Different procedures have been proposed to modify the properties of PU adhesives[8–10]. Through these studies, it has been determined that the viscosity and the rheological properties of PU adhesives can be modified by addition of silica or silicates[9,10], and tack can be provided by addition of cumarone-indene or phenolic resins[8], Furthermore, reactive isocyanates are known to improve the resistance of PU adhesive joints against moisture and temperature[8].

A few years ago, two patents[11,12] proposed the addition of carboxylic acids to increase the adhesion of liquid PU adhesives to synthetic vulcanized styrene-butadiene rubber (SBR). The organic acids used were of different chemical natures, the *trans*-1,2-ethylenedicarboxylic acid (fumaric acid, FA) providing one of the most noticeable increases in adhesion. Although the effectiveness of the addition of FA to liquid PU adhesive has been experimentally proved, the nature of the modifications produced leading to enhanced adhesion has not yet been explained. Because no fundamental studies dealing with this subject have been carried out, the main objective of this study is to establish the nature of the modifications produced by addition of FA to PU adhesives, which enhance their adhesion to a synthetic vulcanized SBR material.

EXPERIMENTAL

Materials

PU adhesives A polyester-urethane based on ε-polycaprolactone and diphenylmethane 4,4′-diisocyanate (MDI) (*Pearlstick 45-40/15* from Merquinsa S.A., Barcelona) was used in this study. This polyurethane has a medium thermoplasticity, very high crystalliazation rate and short open-time. PU adhesive solutions containing 18 wt% of polymer in 2-butanone were prepared in a laboratory mixer (1500 rpm), simultaneously adding amounts of FA (99 wt% minimum purity) between 0.5

and 3 wt% (with respect to the PU adhesive). The mixture was stirred for 2 hours at room temperature.

PU films were used to determine the properties of PU adhesives. These films were prepared by placing a small amount of PU adhesive solution in a polyethylene mould, in which it was spread by means of a glass slide. To avoid the formation of roughness or air-bubbles on the surface, the solvent was slowly removed. For this, the mould was placed into a desiccator saturated with 2-butanone for 18 hours and subsequently left to open air for 3 hours (to ensure the complete evaporation of solvent). PU films obtained were around 0.1 mm thick.

SBR materials Adhesion strength was obtained from T-peel tests of adhesive joints carried out between two identically surface-treated test pieces of SBR. This rubber had a °Shore A hardness of 77 and an oil and plasticizer content of 12 wt%. Sulphur was used as vulcanizing agent and the rubber formulation (Tab. I) included precipitated silica as filler as well as zinc stearate and a microcrystalline paraffin wax (antioxidant); these two compounds may cause lack of adhesion to solvent-based PU adhesives[13].

Experimental Methods

Rheology Flow curves (shear stress *vs.* shear rate) were obtained for PU adhesive solutions with and without FA. 100 ml of polyurethane adhesive were placed in the cup which was sealed with a solvent trap to avoid solvent evaporation during the experiments. Rotational experiments were performed under Control Shear Stress mode and the sample was run for 8 minutes at 200 Pa. The experimental measurements were obtained with a cylinder model SC4-27 (diameter = 11.76mm; length = 33.02mm) manufactured by Brookfield. A Brookfield DV III rheometer was used and all the measurements were carried out at 23°C. The influence of the time after addition of FA to PU adhesives was monitored.

TABLE I
Formulation of SBR

Component	percentage (phr)[a]
SBR 1502	100
Precipitated silica	42
Cumarone-indene resin	5
Sulphur	2
N-Cyclohexyl-2-benzothiazolesulphenamide	2
Dibenzothiazyl disulphide	2.5
Stearic acid	2.4
Zinc oxide	1.5
Phenolic antioxidant	0.5
Microcrystalline paraffin wax	0.8
Hexamethylene tetramine	1
Zinc stearate	5.4

[a] phr = parts per 100 parts of rubber.

Viscoelastic properties of liquid PU adhesives were determined at 10°C in a *Physica Rheolab MC100* instrument by using a Z2 DIN normalized cylinder. Oscillatory experiments were carried out to determine the viscoelastic properties (the elastic or storage modulus, G', and the viscous or loss modulus, G'') of the liquid PU adhesives. 100 ml of polyurethane adhesive were placed in the cup which was sealed with a solvent trap to avoid solvent evaporation during the experiments. Experiments were performed under Control Shear Stress mode and the sample was run for 5 minutes at 200 Pa. Deformation amplitude was selected to 20.3 mrad. G' and G'' were varied as a function of frequency (0.1–50Hz).

Differential Scanning Calorimetry (DSC) Glass transition temperature (T_g) of the PU adhesives were determined from DSC curves by manually tracing the tangent to the curve inflection corresponding to the glass transition. 6–9 mg of PU films were used. The experiments were carried out in a *Mettler-DC30* system in a range of temperature between −130 and 100°C, a heating rate of 10°C/min being used.

Gel Permeation Chromatography (GPC) Molecular weight distribution of the PU adhesives was obtained by means of GPC. Number-average (M_n) and weight-average (M_w) molecular weight, and polydispersity of the PU adhesives were measured. 20 μl of a solution of PU in tetrahydrofurane were introduced using a rate of 1 ml/min. The columns used had a pore size of $10^3, 10^4$ and 10^5 Å, the standard polymer employed being polystyrene ($M_w/M_n \leqslant 1.1$).

Thermogravimetry (TG) measurements Weight loss of the PU adhesives as a function of temperature was studied in inert atmosphere using a *Setaram TGDSC92-16,18* thermobalance. 10 mg of PU were used. Temperature was raised from 25°C to 200°C using a heating rate of 5°C/min, and then the temperature was increased from 200°C to 500°C using a heating rate of 20°C/min.

Thermomechanical Analysis (TMA) measurements The deformation experienced by the PU adhesives with and without FA was measured in a *Setaram TMA 92-16,18* apparatus. PU film test pieces 1 cm long and 1 cm wide were used. All experiments were carried out in compression mode using a constant force of 0.1 N produced by a hemispherical test probe. Temperature was maintained at 25°C for 1 minute and subsequently increased to 200°C using a heating rate of 5°C/min; at the last stage of measurement, the temperature was constantly maintained at 200°C for 10 minutes.

Contact angle measurements Doubly distilled water drops were placed on the surface of PU adhesive films and contact angles (25°C) were measured. The PU films were placed in an hermetic, isothermal (25°C) and solvent-saturated chamber of a *Ramé Hart 100* goniometer, and the contact angle on both sides of the drops was measured. Single sessile drops of 2 μl of water were placed on the PU film surface, and the measurements were taken 10 minutes after the drops were placed on the film.

FTIR spectroscopy To obtain adequate IR spectra of the PU adhesive films, the adhesive solutions were diluted with 2-butanone (1 part by weight of liquid PU adhesive was mixed with 5 parts by weight of 2-butanone). A small amount of this solution was placed on a KBr window, and the solvent was removed by spontaneous evaporation for 2 hours. The measurements were carried out by transmission in a *Nicolet 510 FTIR* spectrometer. 80 scans per experiment were done and the sensitivity of the system was 2 cm^{-1}.

Measurements of mechanical properties of PU adhesive films The tensile strength and elongation at rupture of PU film were measured with an *Instron model 1121* test apparatus. All experiments were carried out with standard dog bone test samples, following the test procedure indicated in the ISO 37–77 standard; a rate of 0.1 m/min was used.

T-peel tests Adhesion were measured from T-peel tests of roughened SBR/PU adhesive/roughened SBR joints. The SBR surface was roughened by using sandpaper no. 60 (0.5 mm of the external surface was removed). Subsequently, 100 mg of PU adhesive was applied to each rubber surface to be joined, and left to dry for 30 minutes. The dried PU film was suddenly heated to 70°C using infrared radiation in order to facilitate the contact between the PU adhesive applied to the two SBR test pieces. The melted PU adhesive films were placed in contact and a pressure of 3 atm was applied immediately for 10 seconds to achieve a suitable joint. Test samples were kept at 23 ± 2°Cand50% relative humidity for 72 hours before the T-peel test was measured in an *Instron model 1121* (peel rate:0.1 m/min).

The modifications produced on the SBR surface through being in contact with the PU adhesives (after the *T*-peel test) were checked by FTIR spectroscopy. IR spectra of rubber surface were determined using a Multiple Attenuated Total Reflectance (ATR) technique, a crystal of thallium bromoiodide (KRS-5) being used.

RESULTS AND DISCUSSION

Figure 1 shows the flow curves of PU adhesives without and with 3 wt% FA as a function of time after their preparation. The slope of the flow curves provides the viscosity of the adhesives. The linear shape of the flow curves indicates that, in the range of shear stress studied, a Newtonian behaviour of solutions is obtained. PU adhesive without FA shows a progressive increase of viscosity with time after its preparation for up to 21 days, due probably to an entanglement of soft segments which gives rise to a more reticulated segmented PU structure. However, for PU adhesive with 3 wt% FA there is a initial increase of viscosity which, after 30 days from its preparation, is reduced to provide a smaller value than the original (1 day after preparation). Therefore, it is found that the addition of FA has a detrimental rheological effect on PU adhesives which may be associated with a chemical modification of the polyurethane structure.

Figure 2 shows the variation of storage modulus (G') and loss modulus (G'') as a function of the frequency for PU adhesives (one month after their preparation) with and without FA. Always G' is higher than G'' due to the predominant elastic properties in PU adhesives. Addition of FA to PU adhesive produces a decrease of both moduli (more noticeable for G'), which becomes more significant as the amount of FA added increases. Therefore, the addition of FA reduces the viscoelastic properties of PU adhesive due probably to a modification of the PU structure. For

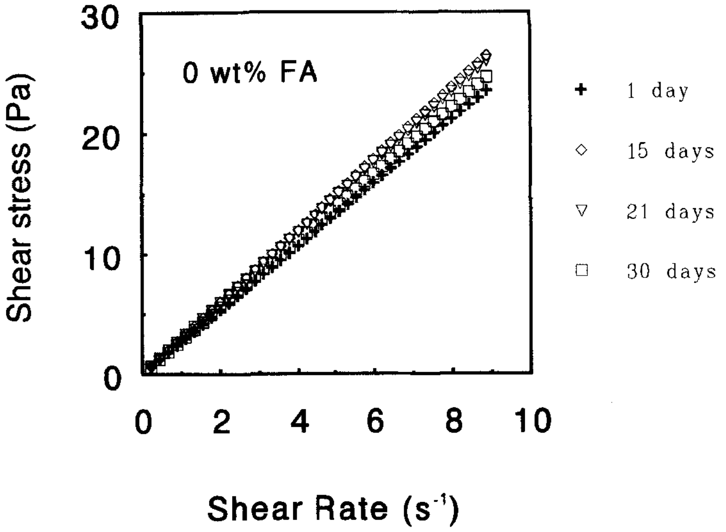


FIGURE 1a

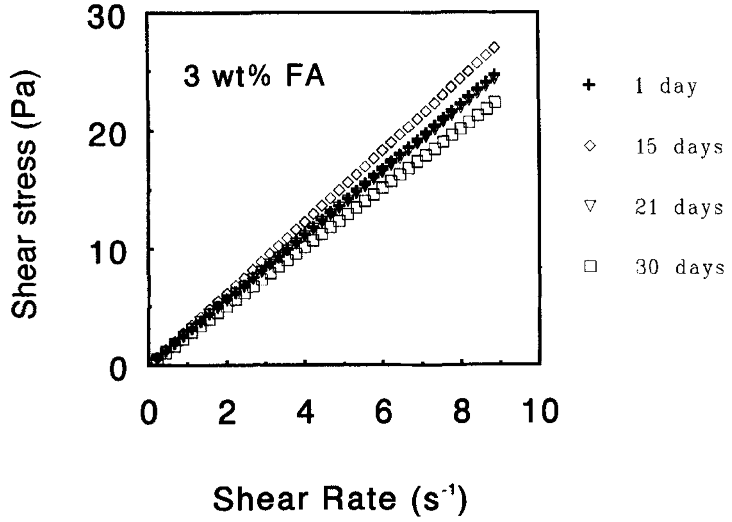


FIGURE 1 Flow curves (shear stress *vs.* shear rate) of PU adhesives a) without and b) with 3 wt% FA. Influence of time after preparation of adhesive.

frequency values lower than 1, there is a more noticeable decrease of G' in PU adhesive with 3 wt% FA which may be ascribed to a more marked decrease in the molecular weight of polyurethane.

Table II includes the glass transition temperature (T_g), the number-average (M_n) and weight-average (M_w) molecular weight, and the polydispersity of the PU adhesives without and with 3 wt% FA, one month after their preparation. Addition

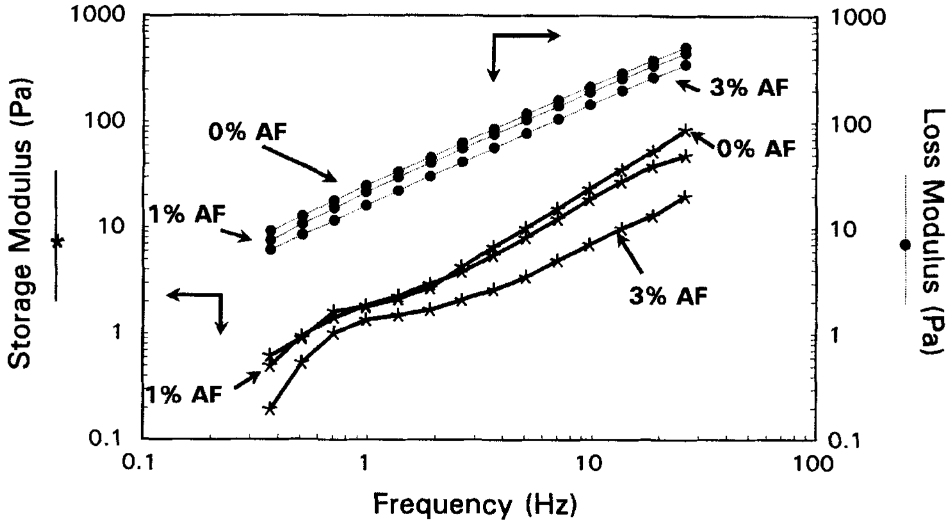


FIGURE 2 Variation of storage modulus and loss modulus as a function of frequency for PU adhesives with and without FA (one month after their preparation). Deformation amplitude = 20.3 mrad.

TABLE II
Properties of the PU adhesives containing 0 and 3 wt% FA (one month after their preparation)

wt%FA	T_g (°C)	M_n	M_w	M_w/M_n
0	−49	144513	249596	1.7
3	−54	102256	156443	1.5

of FA produces a slight decrease in T_g and a fall in the average molecular weights, as well as a narrowing in the molecular weight distribution (there is a drop in polydispersity) of the PU. Thus, the FA could react with the polyurethane to produce chain cleavage (probably caused by hydrolysis of the ester linkages of the polyurethane) and a decrease of the crystallinity of the polyurethane (which is associated with the decrease in T_g value). This is in agreement with the decrease in viscosity and detrimental rheological effect on PU adhesive with FA (Fig. 1 and 2).

Figure 3 shows the TMA curves of PU adhesives one month after their preparation. At around 50°C a deformation corresponding to the softening of the crystalline portion of the PU can be observed. Addition of FA reduces that degree of deformation of PU film at the softening temperature, according to the above proposed disruption of the crystalline segments in the polyurethane. At around 120°C (Fig. 4) another change in TMA curves is produced, probably due to a phase transition in the PU from an amorphous solid to a liquid. The addition of FA causes a fall in the temperature required for this transition-from 125°C (0 wt% FA) to 115°C (3 wt% FA)-, and a lower degree of deformation is produced (the PU adhesive becomes less elastic).

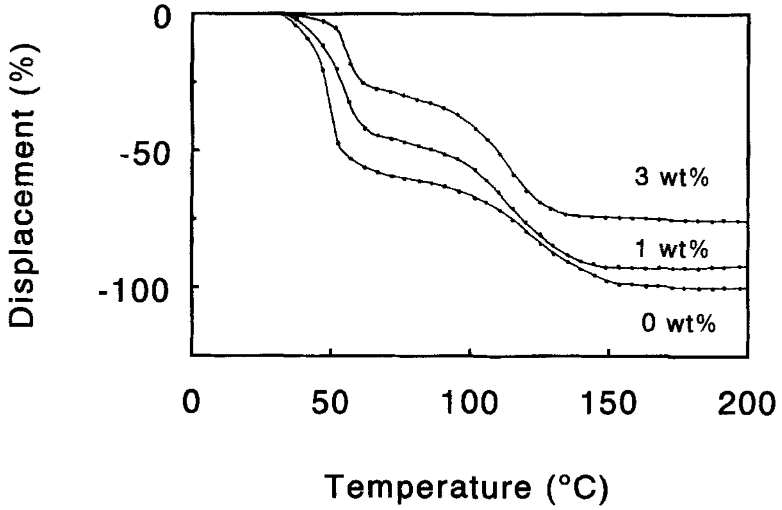


FIGURE 3 TMA curves of PU adhesives with 0, 1 and 3 wt% FA (one month after their preparation).

Figure 4 shows the TG curves of the PU adhesives. Whilst the PU without FA starts to decompose at 310°C, the addition of FA produces decomposition of the PU at a lower temperature (around 160°C); the higher the amount of FA added the more noticeable becomes the degree of decomposition at a lower temperature. Thus, before the complete decomposition of PU occurs, 1.3 wt% and 4 wt% of the PU adhesives containing 1 and 3 wt% FA, respectively, are lost. However, the sublimation of FA should contribute to the weight loss in the TG curves.

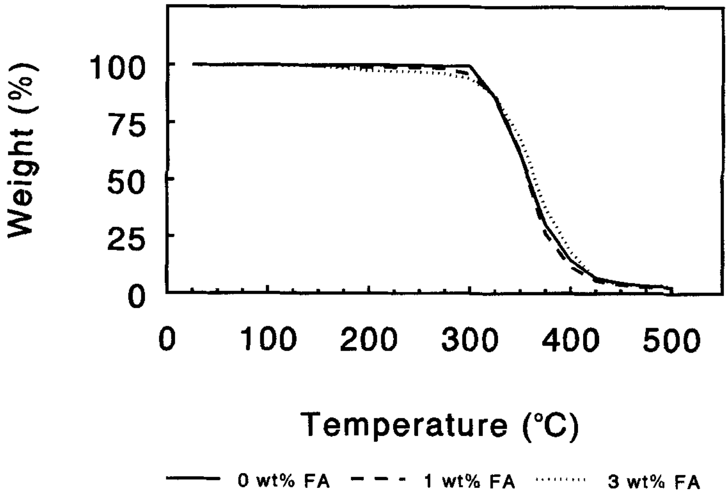


FIGURE 4 Thermogravimetry curves (TG) of PU adhesives with 0, 1 and 3wt% FA (one month after their preparation).

The IR spectra of PU adhesives obtained one day and one month after their preparation are included in Figure 5. The IR spectrum of the adhesive without FA (Fig. 5a) shows the characteristic bands of polyester-urethane[5,8]: C—O groups (1540, 1710 cm^{-1}), bands of polyester-urethane (1049, 1072, 1104 cm^{-1}), and aromatic ring of MDI (1598 cm^{-1}). The addition of FA to the adhesives (Fig. 5b) produces new slightly intense bands corresponding to FA (1273, 1673 cm^{-1}) in the IR spectrum, the intensity of which is greatly reduced one month after its addition to the adhesives (Figure 5c). Therefore, on increasing the time after addition of FA, the elimination of the carboxylic acid bands in the IR spectrum is produced due probably to a reaction with the PU segmented structure.

The mechanical properties (Tab. III) of the PU adhesives (one month after their preparation) shows that the addition of FA decreases the tensile strength and increases the elongation at rupture of the PU films. Because the addition of FA produces a reduction in the crystalline structure of the soft segments in the polyurethane, a loss of physical properties should be expected (more elastic and less hard material). Therefore, the mechanical properties measured are in agreement with above experimental results.

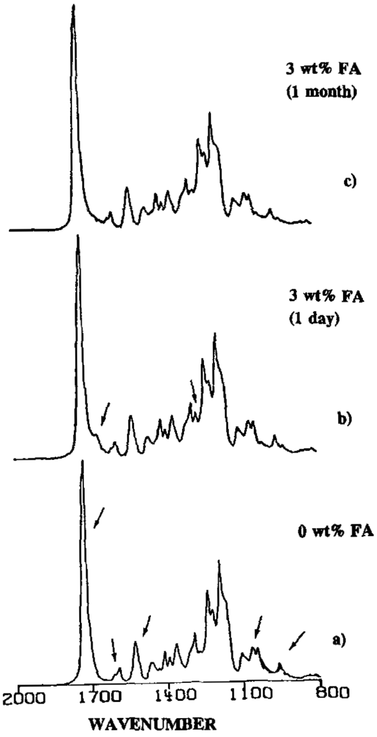


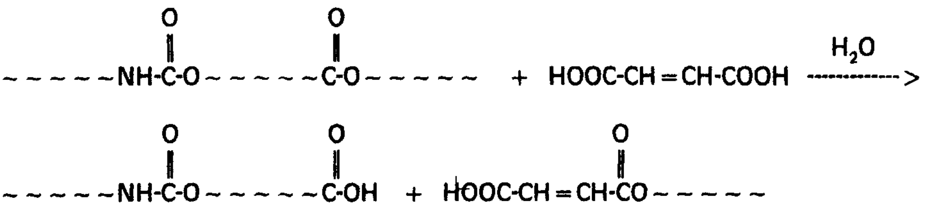
FIGURE 5 IR spectra of PU adhesives containing FA: a) 0 wt% FA (1 day after PU adhesive preparation); b) 3 wt% FA (1 day after PU adhesive preparation); c) 3 wt% FA (one month after PU adhesive preparation).

TABLE III
Mechanical properties of PU adhesive films

wt% FA	Tensile strength at rupture $(N/m^2) \cdot 10^6$	Elongation at rupture%
0	50	810
1	49.3	835
3	26	870

Figure 6 includes the water contact angles on PU films, obtained at different times after their preparation. There are no significant changes in contact angles of the films on increasing the amount of FA or increasing the time after their preparation. Thus, the structural modifications which result from the addition of FA do not affect the surface free energy of the PU films.

Considering all the experimental results given above, it is possible to explain the modifications produced in the polyurethane structure by incorporating FA in the liquid adhesive. The polyester urethane used in this study undergoes a transesterification reaction which is catalyzed by fumaric acid in the presence of a slight amount of water:



$$\sim\sim\sim\sim\sim NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\sim\sim\sim\sim\sim\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\sim\sim\sim\sim\sim + HOOC\text{-}CH{=}CH\text{-}COOH \xrightarrow{H_2O}$$

$$\sim\sim\sim\sim\sim NH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}O\sim\sim\sim\sim\sim\overset{\overset{\displaystyle O}{\|}}{C}\text{-}OH + HOOC\text{-}CH{=}CH\text{-}\overset{\overset{\displaystyle O}{\|}}{C}O\sim\sim\sim\sim\sim$$

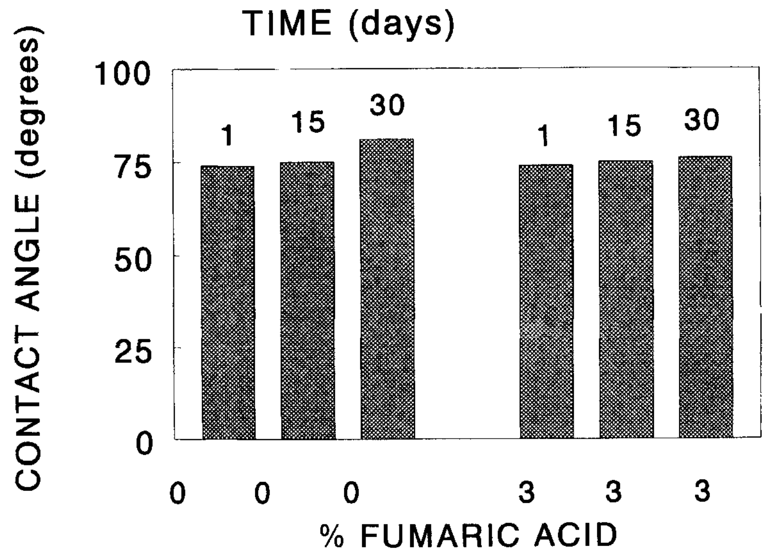


FIGURE 6 Water contact angles (25°C) of PU adhesive films containing different amounts of FA. Influence of time after preparation of PU adhesives.

This reaction would result in chain cleavage and in loss of physical properties, in such a way that the resulting chain ends may cause a disruption of the crystallinity of the polyurethane. The acid-catalyzed hydrolysis of polyester urethanes is well known and documented in the literature[14-16]. In our PU adhesives, the acid hydrolysis would not be expected to proceed quickly since there was no added water.

T-peel strengths of roughened SBR/PU adhesive/roughened SBR joints are given in Figure 7. The addition of amounts higher than 2 wt% FA to the PU adhesive produces a noticeable increase in T-peel strength. Figure 8 includes the T-peel strengths of roughened SBR/PU adhesive/roughened SBR joints as a function of the time after the adhesive preparation. Although a slight decrease in T-peel strength is produced, probably due to the chain cleavage and disruption of crystallinity in the PU structure, the improved adhesion between SBR and PU adhesives containing FA is maintained. This improvement cannot be easily understood because the addition of FA causes a modification of the segmented structure of PU, its mechanical, physical and thermal properties are reduced and there is no increase in the surface free energy of the PU films. This might be explained as a diffusion of fumaric acid to the interface, the diffusion process being expected to be much quicker than the hydrolysis reaction of the polyurethane chains. A higher concentration of FA on the surface would help to maintain the surface energy and the improved T-peel strengths observed even one month after the addition of FA to the PU adhesive.

The IR spectra of SBR surfaces after T-peel tests are given in Figure 9. The IR spectrum of the SBR joined with PU adhesive containing 2 wt% FA shows that a removal of ester groups (1535 cm^{-1}) and a noticeable decrease in the intensity of the

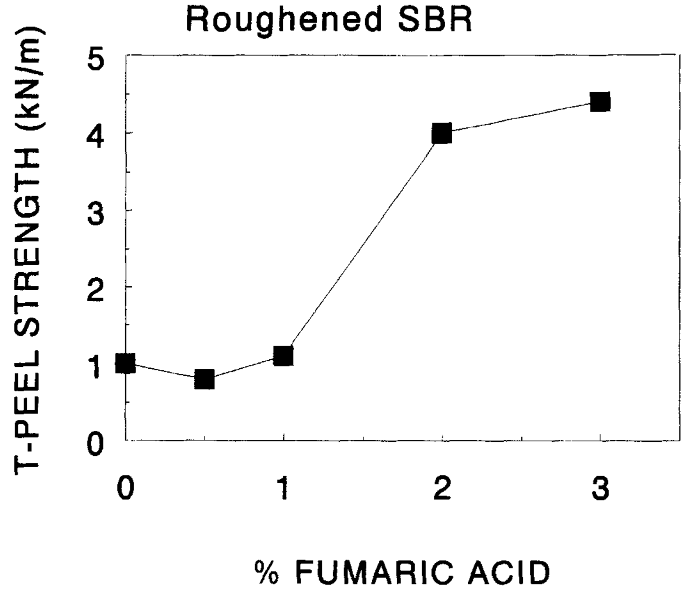


FIGURE 7 T-peel strength of roughened SBR/PU adhesives with FA/roughened SBR joints.

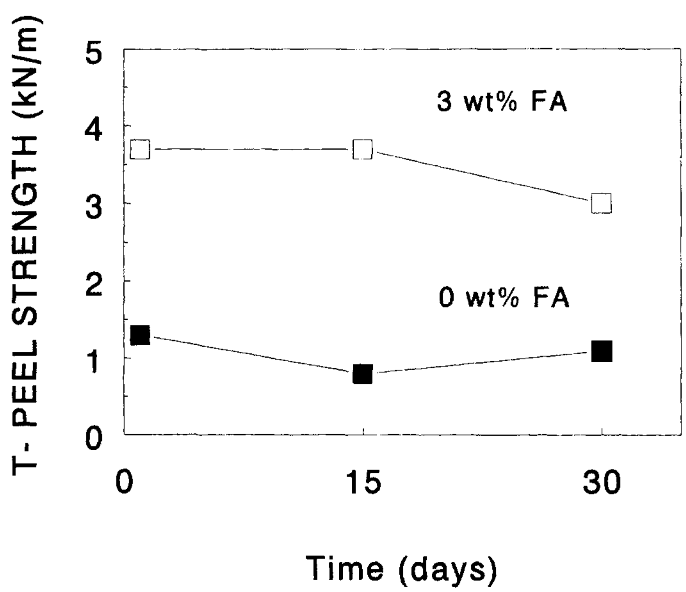


FIGURE 8 T-peel strength of roughened SBR/PU adhesives with FA/roughened SBR joints. Influence of time after preparation of Pu adhesives.

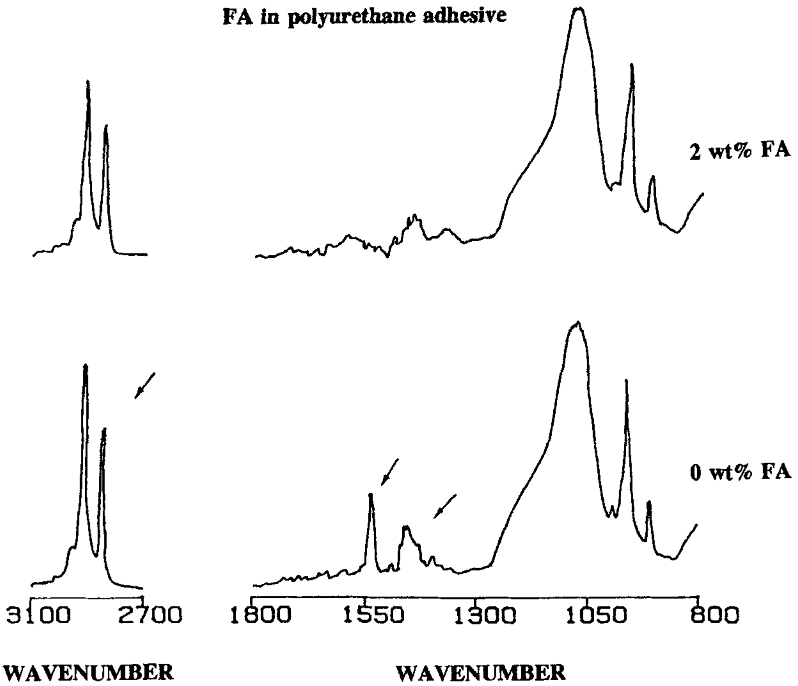


FIGURE 9 IR spectra of SBR rubber surfaces joined with PU adhesives containing 2 wt% FA (after T-peel test).

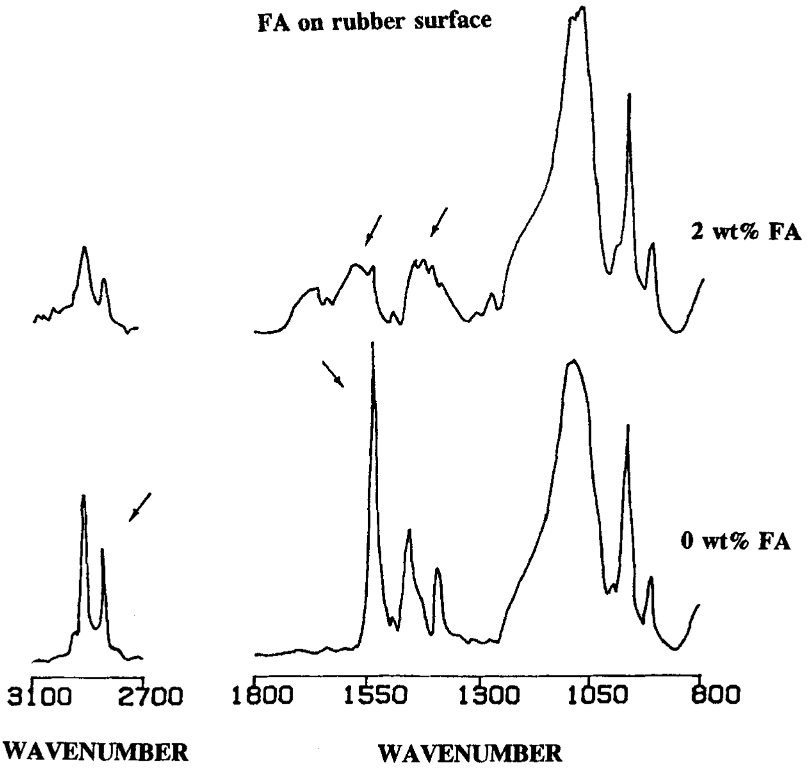


FIGURE 10 IR spectra of surface-treated SBR with and without solutions containing 2 wt% FA joined with PU adhesive without FA (after T-peel test).

bands of CH_2 and CH_3 groups (1394, 1462, 2849, 2918 cm^{-1}) is produced, which may correspond to the zinc stearate and paraffin wax on the SBR surface. The modifications on the SBR surface shown in Figure 9 can be explained by a diffusion of the FA molecules through the PU surface, which at the interfacial region could facilitate the interaction of the FA with the SBR surface. In other words, the FA acts as a compatibilizer of the SBR and PU surfaces and, thus, the decrease of intensity in the IR spectrum of Figure 9 corresponds to the creation of a new structure at the interface, instead of a removal of antiadherent compounds on the SBR surface. This same kind of explanation has been previously given to justify the improvement of the adhesion of aluminum to modified polyethylene by the addition of acrylic acid[17], and the improved adhesion of aluminum to modified polypropylene with maleic anhydride.

The proposed explanation related to the diffusion of FA molecules at the interfacial region was confirmed when the SBR surface was rubbed with a solution of 2-butanone-ethanol (1:1 in volume) containing 2 wt% FA, and an adhesive joint was made with the PU adhesive without FA. Figure 10 shows the IR spectrum of the surface treated SBR after the T-peel test was carried out. There is a considerable decrease of the intensity of the bands corresponding to CH_2 and CH_3 groups and zinc stearate is removed. Therefore, a migration of FA to the interfacial rubber/adhesive region should be produced, once the adhesive joint is achieved. In this way, FA seems to act as a compatibilizer of SBR and PU adhesive surfaces at the interfacial region.

CONCLUSIONS

1. The addition of FA causes a modification of the segmented structure of PU, which is more noticeable as the time after the adhesive preparation increases. The nature of the modification produced in the PU structure seems to be an acid-catalyzed hydrolysis of the ester groups, which has been evidenced through several experimental techniques. That reaction results in chain cleavage, loss of physical properties and disruption of the crystallinity of the polyurethane.
2. Although the addition of FA reduces the rheological and viscoelastic properties of adhesives due to a modification of the PU structure, and no modification of surface energy is produced, the adhesion of PU adhesives to SBR is increased. This suggests that after formation of the adhesive joint, a diffusion of the FA to the rubber-PU adhesive interfacial region probably occurs, which produces a decrease in the zinc stearate and paraffin wax concentrations at the interface.

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