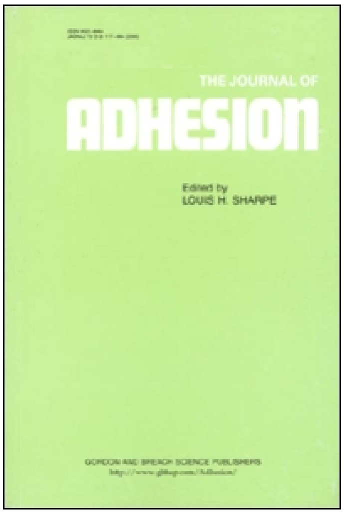

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Weak Boundary Layers in Styrene-Butadiene Rubber

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In this paper two kinds of weak boundary layers (WBL) in synthetic vulcanized styrene-butadiene rubber are described.

i) WBL produced by the presence of antiadhesion compounds of the rubber formulation (zinc stearate, microcrystalline paraffin wax). These WBL cannot be effectively removed by solvent wiping, whether followed by washing with an ethanol/water mix or not. Although this treatment allowed a significant removal of zinc stearate, the paraffin wax concentration on the surface was not greatly reduced, thus, poor adhesion of rubber was obtained. Chlorination with small amounts of ethyl acetate (EA) solutions of trichloro isocyanuric acid (0.5-5 wt% TCI/EA) and/or an extended halogenation treatment increased the adhesion strength and effectively eliminated the zinc stearate from the rubber surface. If an additional heat treatment (50 °C/24 h) of the chlorinated rubber was also carried out, the WBL was more effectively eliminated and the resulting adhesion was independent of the amount of chlorination agent applied to the rubber surface. Furthermore, this heat treatment favoured the elimination of WBL in the untreated rubber and also contributed to the removal of WBL produced by an excess of halogenation agent.

ii) WBL created by an excess of chlorination agent applied to the rubber surface. The excess of chlorination agent produced lack of adhesion in the rubber because there was significant damage of the rubber surface and a non-rubber surface layer was formed (mainly due to oxidized, chlorinating agent residues and cyanuric acid), which contributed to the formation of WBL. To avoid the creation of WBL, a postchlorination treatment of rubber with a solution of 25 wt% ethanol in water followed by a vacuum-drying process produced excellent results. The effectiveness of this treatment relied on combining an adequate degree of chlorination with no external surface deterioration of the rubber by the excess of chlorination agent.

KEY WORDS: weak boundary layer; styrene-butadiene rubber; surface treatments; solvent wiping; halogenation; mechanisms of adhesion; polyurethane adhesives.

1. INTRODUCTION

Several types of synthetic rubber need, in some applications, to be bonded to dissimilar substrates. Rubbers are most easily bonded to other materials during vulcanization, *i.e.* during crosslinking. In some instances, however, especially when complicated rubber shapes need to be bonded, it may be necessary to produce adhesive joints with rubbers after they have been vulcanized. Generally, formulations of synthetic rubbers contain several components to improve their properties and to adapt each formulation to a given use; but these components are able to produce poor adhesion. There are several sources of adhesion problems in rubber due to rubber components (antioxidants,

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mould-release agents), adhesive-rubber incompatibility, or poor durability (migration of antiadhesion substances to the interphase once the adhesive joint is made). Various surface treatments of rubber have been proposed to take care of most of these adhesion problems and to produce strong bonds, but sometimes even when the treatment used, appears to be adequate, a lack of adhesion appears. The creation of weak boundary layers (WBL) in rubber is one of the most difficult and common sources of poor adhesion in elastomers.

Bikerman[1] proposed the concept of WBL. He stated, based on several different arguments, that true interfacial failure rarely, if ever, occurs in the breaking of an adhesive joint by mechanical means. Failure is always cohesive: in one of the adherends, or in the adhesive, or in some (weak) boundary layer. His arguments were supported theoretically and experimentally. So-called weak boundary layers fall into the class of surface regions, intermediate to two materials in contact, that are now well-known and are referred to, more generally, as "interphases".

There are several sources of WBL in polymeric materials:[2-8]

i) Coating agents added to prevent the deterioration of the material, *e.g.* protective oils applied to metallic substrates.[2]

ii) Additives or components in the formulation of the material, which facilitate the manufacturing process, *e.g.* mould-release agents added in rubber manufacture.[7]

iii) Low-molecular weight compounds able to migrate from the surface of the substrate to the interphase, *e.g.* antioxidants in some rubber formulations.[7]

iv) Surface impurities (dust, air contaminants).

v) Air bubbles trapped in the interphase during the formation of the joint.

vi) Undesirable reactions between the adherend and the adhesive, or between the adherend and the surrounding atmosphere.

vii) Mechanical degradation of the substrate as a consequence of an inadequate or extended surface treatment, *e.g.* roughening of rubber.

viii) Surface layers forming on rubber.[8]

ix) Reorientation of polymer chains at the interphase.

In general, WBL are often found in a broad variety of surface-treated materials. In polyolefins, for instance, it has been shown[9] that a treatment with trichloroethylene vapour removes WBL and an improvement of adhesion is obtained; but if the etching treatment takes more than 10 s, there is a rapid decline in joint strength probably due to deterioration and weakening of the utmost surface layer of polyolefin. On the other hand, in adhesive joints of high surface energy materials,[10,11] there are several factors which may all produce a WBL on the surface and prevent a good joint strength from being attained. Some of these factors are: i) protective oils, greases, waxes used as coating agents to prevent corrosion processes; ii) atmospheric contaminants instantly adsorbed on the surface; iii) weak oxide layers.

A broad variety of strategies to avoid the formation of WBL has been suggested for plastics and metallic substrates.[9,12] Although some problems still exist, the use of a suitable surface treatment and adequate experimental conditions may, nevertheless, produce strong and durable adhesive joints. In elastomers, however, their complex composition and the variety of additives employed in their formulation makes it difficult to predict, and to avoid, the formation of WBL. There are excellent reviews[8,13,14] dealing with surface treatments of rubber to improve its adhesion to metals or polymers. It is well-known that the presence of zinc stearate and some antioxidant agents in a rubber formulation (*i.e.* microcrystalline paraffin wax)[3,7,15–19] might cause a lack of adhesion. In fact, these compounds create a WBL on the surface of the rubber and prevent any degree of interlocking with the adhesive. In order to eliminate these compounds a surface treatment of rubber should be used. Roughening[3,15,16] has been proposed as an effective physical surface treatment to withdraw zinc stearate from the rubber surface, but with the time there is a progressive migration of this compound from the bulk to the surface, producing a new WBL. Thus, an effective surface treatment should produce a permanent removal of WBL to assure a long service life of the adhesive joint.

Halogenation of rubber[3,7,15,16,18,20–22] has been suggested as the most powerful and effective surface treatment to produce strong adhesive joints and to avoid the formation of WBL. However, it has been previously shown[23] that, in some cases, the chlorination of rubber itself may produce WBL, especially when high concentrations of chlorinating agent are used. There are not many papers dealing with the origin, removal and prevention of WBL in rubber materials, so, in this study, several ways to prevent the formation of WBL in synthetic vulcanized styrene-butadiene rubber have been proposed.

2. EXPERIMENTAL

A vulcanized styrene-butadiene rubber, about 5 mm thick, was prepared using a moulding process (carried out at 150°C for 50 minutes) after open-mill mixing, using sulphur as the vulcanizing agent. The formulation, including silica (as a filler), zinc stearate and microcrystalline paraffin wax (among other components), is given in Table I. The oil and plasticizer content of this rubber is 12 wt% and its Shore A hardness is 77°. To prevent and/or eliminate WBL, several surface treatments were applied to this rubber:

TABLE I

Formulation of the synthetic vulcanized styrene-butadiene rubber

Component	Parts per hundred parts of rubber
SBR 1502	100.0
Silica	42.0
Sulphur	2.0
Cumarone-indene resin (85 °C)	5.0
Zinc oxide	1.5
Stearic acid	2.4
N-Cyclohexyl-2-benzothiazole sulphenamide	2.0
Phenolic antioxidant (mercaptobenzimidazole)	0.5
Dibenzothiazyl disulphide	2.5
Microcrystalline paraffin wax	0.8
Hexamethylene tetramine	1.0
Zinc stearate	5.4

i) *Solvent wiping.* The rubber surface was rubbed with a tissue paper impregnated with an organic solvent (2-butanone or ethyl acetate) and left for three hours to allow the solvent to evaporate. In some cases, one hour after the wiping of the rubber, a 25 wt% ethanol/water solution was also applied, leaving it to evaporate in open air or in vacuum (10^{-2} torr) for one hour.

ii) *Chlorination.* The rubber was wiped with a tissue paper impregnated with ethyl acetate and 30 min later the chlorination solution (0.5–9 wt% trichloroisocyanuric acid solutions in ethyl acetate) was applied using the same experimental procedure. The chlorination process was carried out for one hour and, generally, afterwards a post-chlorination treatment was carried out[20] with a 25 wt% ethanol/water solution, leaving it to evaporate in open air or in vacuum (10^{-2} torr) for one hour. In some cases, the chlorinated rubber was placed in an oven at 50°C for 24 to 168 h.

To determine the adhesion strength of surface-treated rubber,. a solvent-based ε-polycaprolactone polyurethane adhesive (*Pearlstick 45-40/15*) from Merquinsa S. A. (Barcelona, Spain) was used. This polyurethane had very high crystallization rate, medium thermoplasticity and short open time. The adhesive solution was prepared by mixing 15 wt% of the solid polymer with 2-butanone in a laboratory mixer, and stirring the mixture (400 rpm) for two hours at room temperature to obtain a homogeneous solution. Brookfield viscosity at 25°C was periodically monitored and a value of 1.3 Pa.s was obtained.

T-peel strength measurements were carried out on adhesive joints made with rubber strip test pieces (150 × 30 mm) which had been treated in the same way. The polyurethane adhesive solution was applied to the treated rubber with a brush and the samples were left to dry for 1 hour. The experimental procedure is described elsewhere.[3] An Adamel-L'Homargy DY-32 test machine (peel rate = 0.1 m/min) was used. The relative error in the measurements were always less than 10%.

The effects of the treatment on the rubber surface were monitored by several experimental techniques. Scanning Electron Microscopy (SEM) allowed the external surface modification of the samples to be analyzed (a JEOL SEM JSM 840 system was used). To follow the modifications of wettability in the surface-modified samples, advancing contact angles were measured with a Ramé-Hart 100 goniometer. Single drops (2 μl) of ethane diol (Merck, 99% minimum purity) were placed on the rubber surface and the measurements were taken 15 min after placing them. The chemical changes of the treated rubber were monitored by infra-red spectroscopy (Nicolet 205 FTIR spectrophotometer was used) using a multiple attenuated total reflectance technique (ATR); a KRS-5 (thallium bromo-iodide) crystal was used. More experimental details were previously given.[15]

3. RESULTS

The synthetic vulcanized styrene-butadiene rubber selected in this study contains zinc stearate and microcrystalline paraffin wax, two additives able to produce a lack of adhesion towards polyester urethane adhesives, due to the formation of WBL.[3,7,15,16] A surface roughening of the rubber causes partial removal of WBL, although once the treatment is carried out a progressive migration of zinc stearate occurs. Two kinds of treatments were applied to remove the WBL in the rubber: solvent wiping and chlorination.

Figure 1 shows the IR spectra of untreated, and ethyl acetate and 2-butanone wiped rubber in three spectral regions, and Figure 2 includes the corresponding SEM micrographs. Table II shows the contact angle (ethane diol, 25°C) and T-peel strength

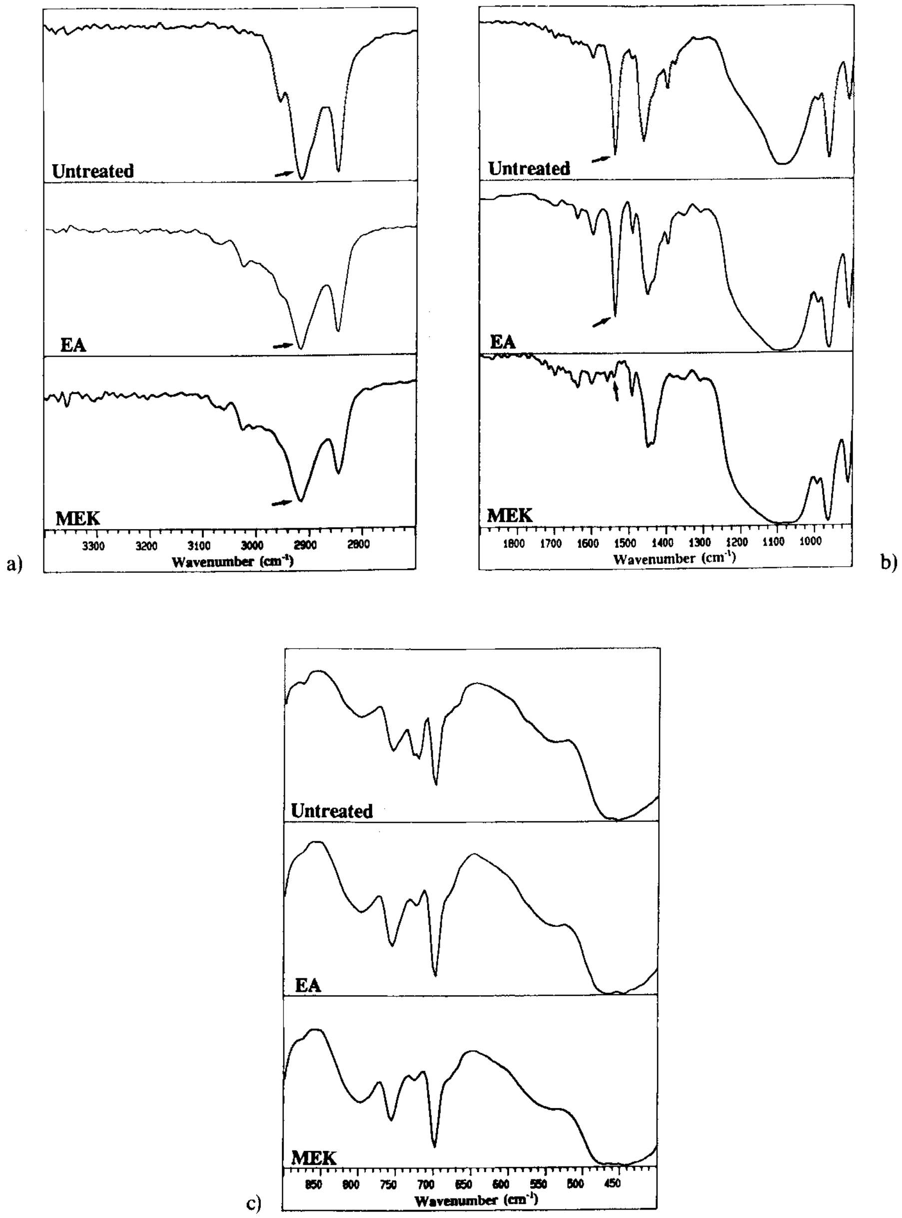


FIGURE 1 IR spectra of untreated, and ethyl acetate or 2-butanone wiped rubber surface.

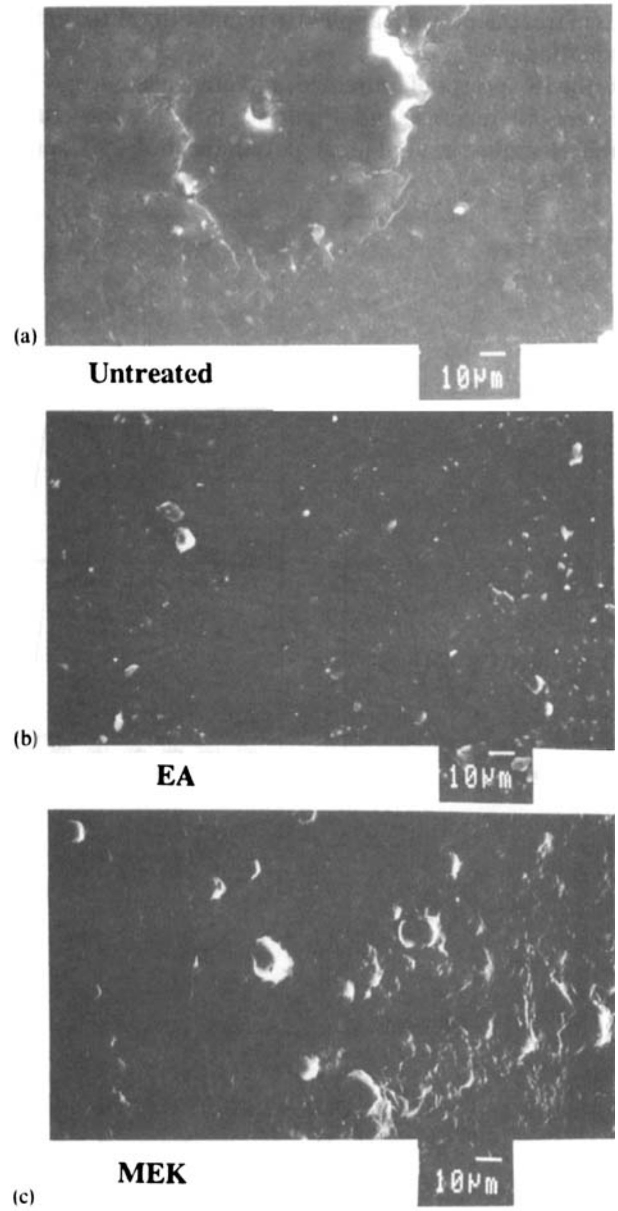


FIGURE 2 SEM micrographs of a) untreated; b) ethyl acetate wiped; c) 2-butanone wiped rubber surface.

obtained in the solvent-wiped rubbers. The IR spectrum of untreated rubber (Fig. 1) is dominated by broad Si-O bands near 450, 800 and 1100 cm^{-1}. Polymer bands occur near 700–760 cm^{-1} (C—H out of plane, styrene ring), 913, 968 and 998 cm^{-1} (C—H out of plane, vinyl and *trans* unsaturation in butadiene), 1452 cm^{-1} (CH_2 scissors, butadiene), and 2850–2920 cm^{-1} (CH_2 stretch, butadiene). Zinc stearate is identified

TABLE II

Contact angle (ethane diol, 25 °C) and T-peel strength of solvent-wiped rubber

Surface treatment	Contact angle (degrees)	T-peel strength (kN/m)
None	68	<1
EA[a]	72	1.4
EA + E[b]	64	1.0
EA + E[b] + vacuum	67	<1
MEK[c] + E	67	1.0

[a] EA = Ethyl acetate.

[b] E = 25 wt% ethanol/water solution.

[c] MEK = 2-butanone.

from the carboxylate band near 1540 cm^{-1}. Both stearate and paraffin wax contribute to CH_2 stretching (2850–2920 cm^{-1}) and scissoring (1452 cm^{-1}). The wiping of rubber with ethyl acetate (EA) (Fig. 1) does not eliminate noticeable amounts of zinc stearate or microcrystalline paraffin wax from the surface and no change of the surface topography is produced (Fig. 2). Furthermore, after surface treatment there is no variation of contact angle and only a slight increase of adhesion strength is produced. Therefore, the wiping of rubber with EA is not effective to eliminate WBL. On the other hand, there is a noticeable reduction of the amount of zinc stearate on the rubber surface wiped with 2-butanone (MEK) (Fig. 1) and a slight decrease of the concentration of paraffin wax is also produced. At the same time, a small degree of surface heterogeneity appears (Fig. 2) but the adhesion is not improved (Table II); an adhesion failure is produced. Thus, the partial elimination of the antiadhesioncompounds by wiping the rubber with MEK is not sufficient to increase its adhesion to polyurethane adhesives.

In order to improve the adhesion, a 25 wt% ethanol/water solution (E) was applied to the solvent-wiped rubber. According to Figure 3 and Table II, the addition of this solution (E) creates small cracks across the rubber surface which probably are responsible for the slight decrease in contact angle. T-peel strength does not increase, although noticeable changes are produced in the surface chemistry of the rubber. The IR spectra of EA + E treated-rubber (Fig. 4) shows how this treatment facilitates the removal of zinc stearate (more noticeably for a duration of the treatment of 6 hours) but there is no a great removal of paraffin wax (1452, 2850, 2920 cm^{-1}). On the other hand, secondary amides seem to be formed on the rubber surface (N—H bend, 1566 cm^{-1}; C=O, 1642 cm^{-1}; N—H stretching, 3296 cm^{-1}). The greatest effectiveness of this treatment is reached 6 h after the application of the 25 wt% ethanol/water solution.

A further modification of the previous treatment was the elimination of excess 25 wt% ethanol/water mixture in vacuum. The IR spectrum of the rubber dried in vacuum (Fig. 5) shows a more efficient removal of zinc stearate, although a high concentration of the paraffin wax still remains on the surface. Furthermore, the vacuum-dried rubber presents a more heterogeneous surface than the open-air dried rubber (Fig. 3), and some microcracks appear across the rubber surface. These surface modifications, however, do not contribute to increase the adhesion

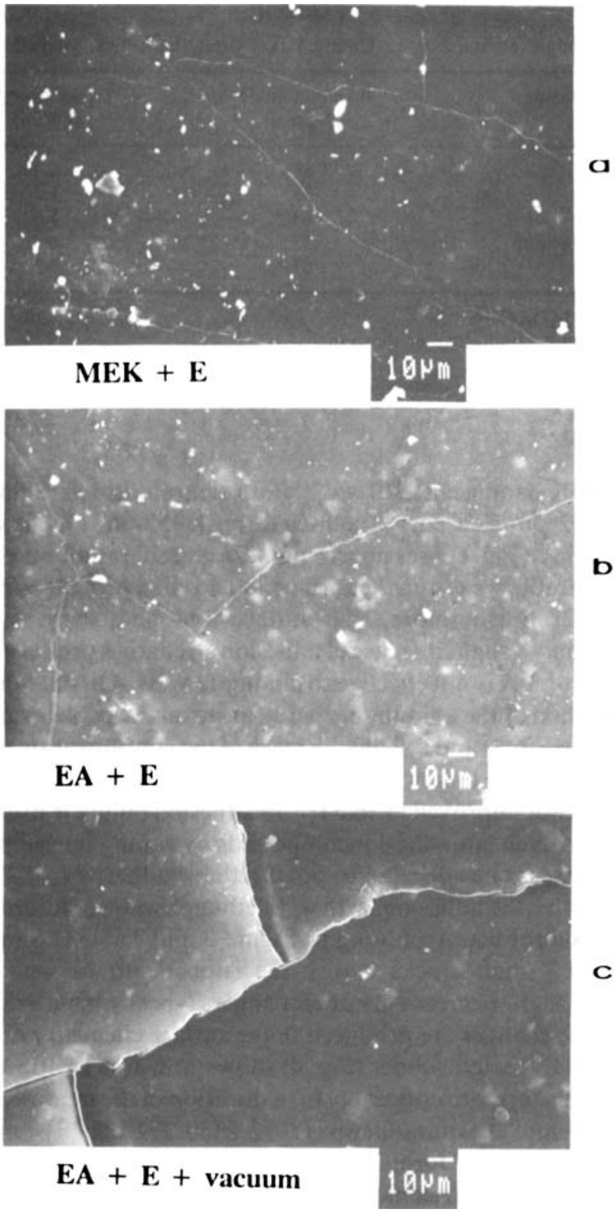


FIGURE 3 SEM micrographs of solvent-wiped rubber treated with a 25 wt% ethanol/water mixture (E): a) 2-butanone + E; b) ethyl acetate + E + dried in open air; c) ethyl acetate + E + dried in vacuum.

of rubber (Table II), probably because the microcrystalline paraffin wax is not eliminated.

Therefore, although the wiping of rubber with MEK or EA + E, and drying for 6 hours in open air or for 1 hour in vacuum, facilitates the removal of zinc stearate and

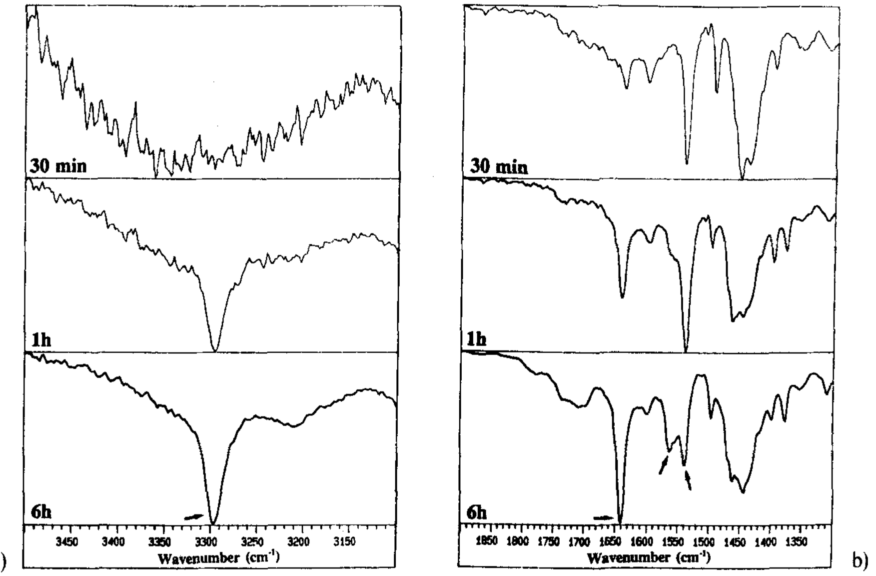


FIGURE 4 IR spectra of ethyl acetate wiped rubber treated with a 25 wt% ethanol/water mixture. Influence of the duration of the treatment.

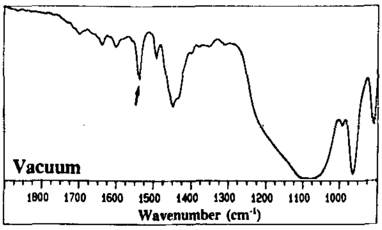


FIGURE 5 IR spectrum of ethyl acetate + 25 wt% ethanol/water mixture treated rubber surface dried in vacuum.

creates a certain degree of surface heterogeneity on the surface of the rubber, there is no improvement in T-peel strength, probably because the paraffin wax contributes to the creation of WBL. Thus, a more effective, stronger chemical treatment seemed to be necessary to obtain a noticeable increase of adhesion and chlorination was selected. Although several halogenation agents for rubber have been proposed,[18–21] the trichloro isocyanuric acid (TCI) (1,3,5-trichloro-1,3,5-triazine-2,4,6-trione) is the most common and useful.[3,7,15,16,20,22] It has been extensively demonstrated[3,7,15,16] that the chlorination of styrene-butadiene rubber with TCI produces a noticeable improvement in T-peel strength of joints between rubber and polyurethane, due to the creation of surface roughness and microcracks, an increase of the polar component of the surface free energy, the removal of antiadhesion substances and the creation of polar groups on the rubber surface. Oxidized carboxylic species are the main cause of the strong adhesion between the chlorinated rubber surface and the polyurethane adhesives.[24] On the other hand, chlorination is a fast reaction and is produced with a small concentration of chlorinating agent.[24]

WBL on the rubber surface may be removed by chlorination. The highest effectiveness of the treatment is reached by increasing the length of the treatment and/or the concentration of the chlorinating agent. This subject has been extensively analyzed in a recent paper,[24] so only the IR spectra will be shown here. Figure 6 includes the IR spectra of the rubber wiped with EA and chlorinated with 2 wt% TCI/EA (ethyl acetate solutions containing 2 wt% TCI). The length of the treatment studied was between 1 and 6 h (a 25 wt% ethanol/water solution was applied to the rubber surface 1 and 6 h after the chlorination). Rubber treated with EA + E shows strong evidence of paraffin wax (1452 cm^{-1} band, relatively intense 2850–2920 cm^{-1} bands). The chlorination of the rubber removes zinc stearate and paraffin wax; the longer the length of the treatment, the greater the amount removed from the rubber surface. In addition, oxidation (carboxylic functionalities -1720 cm^{-1}) and chlorination (chlorinated hydrocarbon chains -534, 1237, 1420 cm^{-1}) are produced by reaction between TCI and the rubber. Finally, most of the bands ascribed to oxidation and chlorination processes occur in the IR spectrum of cyanuric acid (more clearly evidenced by bands at 3000–3250 cm^{-1}), an expected product of the reaction left on the surface. T-peel strength increases from < 1 kN/m (rubber wiped with EA + 25 wt% ethanol/water) to 7.7 kN/m (rubber chlorinated with 2 wt% TCI/EA for 1 hour). This value is independent of the length of the chlorination treatment,[25] so it seems that there is no migration of antiadhesion compounds to the rubber surface after the application of the treatment, under the experimental conditions used in this study. Increasing the length of chlorination to 6 h produces a further increase of T-peel strength (8.4 kN/m), probably due to the additional contributions of surface roughness and microcracks and to the most effective removal of zinc stearate from the rubber surface.

Figure 7 includes the IR spectra of rubber chlorinated with 2 wt% and 5 wt% TCI/EA. The increase of the concentration of chlorinating agent produces a more noticeable removal of zinc stearate. There is evidence of loss of unsaturation (900–1000 cm^{-1}) for high amounts of chlorination agent, so the effects due to chlorination are more marked (increase of relative intensity of bands at 534, 1237, 1398, 1458 cm^{-1}). T-peel strength obtained is 7.7 kN/m, independent of the concentration of TCI, probably because the increase of the concentration of chlorinating agent produces a reaction in a thicker region of the rubber (from the outermost surface to the bulk rubber), which does not contribute to increase the amount of oxidized or chlorinated species in the external surface.[24] Nevertheless, the WBL is effectively removed and high adhesion is obtained.

Chlorination of rubber is generally carried out at room temperature and no studies dealing with the effects produced by the treatment temperature have been carried out. In this work, some interesting results were obtained when the chlorinated rubber was heated at 50 °C before applying the polyurethane adhesive. Although the duration of the heat treatment was monitored, no noticeable differences were found for periods longer than 24 h; then, all the experiments were carried out at 50 °C for 24 h. Figures 8 to 10 include the experimental results obtained. IR spectra

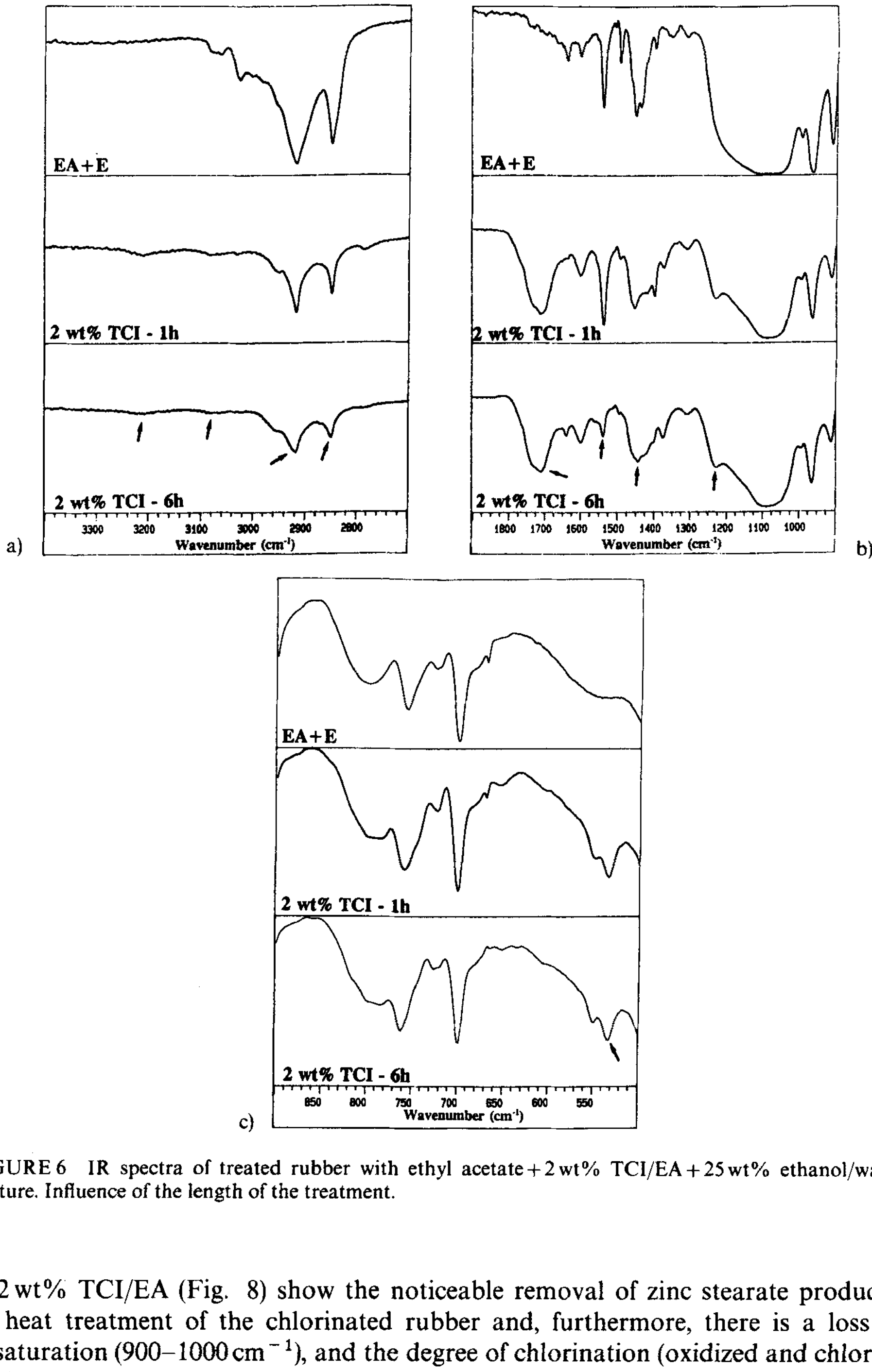


FIGURE 6 IR spectra of treated rubber with ethyl acetate + 2 wt% TCI/EA + 25 wt% ethanol/water mixture. Influence of the length of the treatment.

of 2 wt% TCI/EA (Fig. 8) show the noticeable removal of zinc stearate produced by heat treatment of the chlorinated rubber and, furthermore, there is a loss of unsaturation (900–1000 cm^{-1}), and the degree of chlorination (oxidized and chlorinated species) is also increased. The temperature treatment should favour the migration of antiadhesion compounds to the rubber surface, where they will be removed by

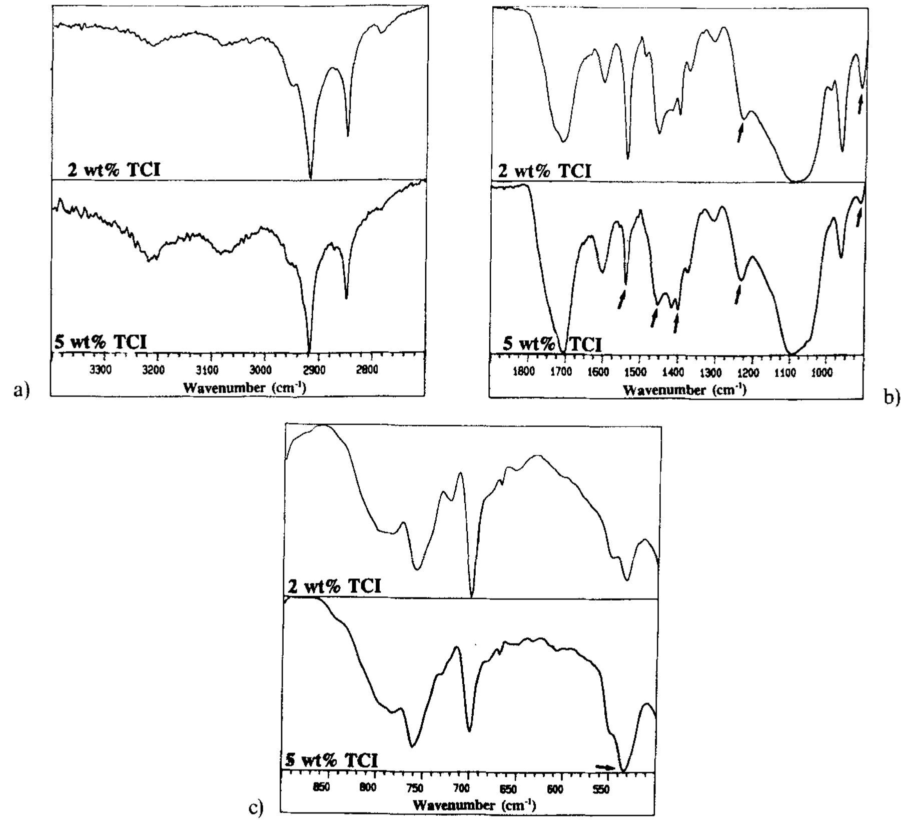


FIGURE 7 IR spectra of treated rubber with ethyl acetate + (2-5) wt% TCI/EA + 25 wt% ethanol/water mixture. Length of the treatment: 1 h.

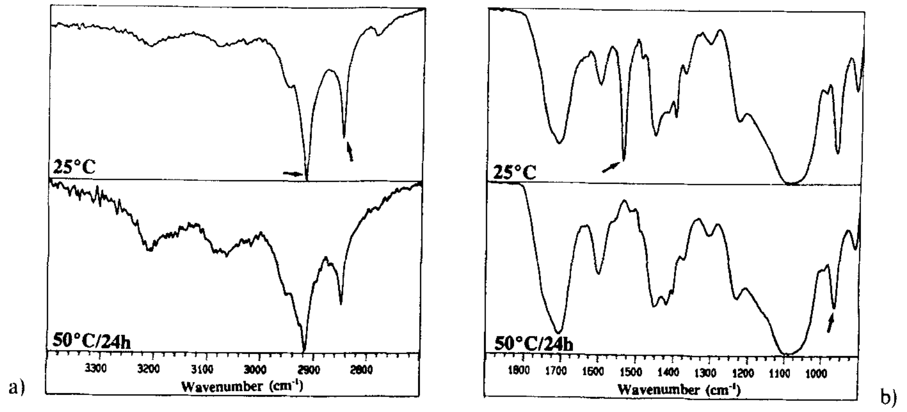
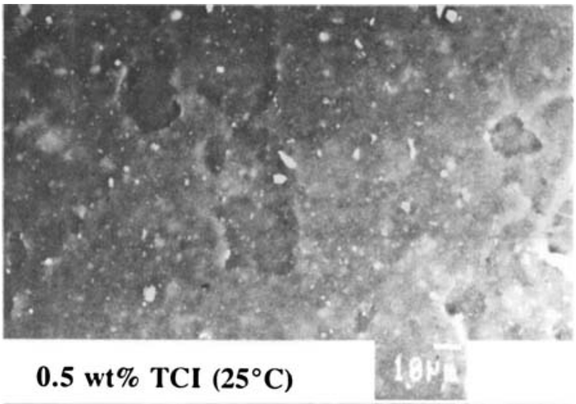
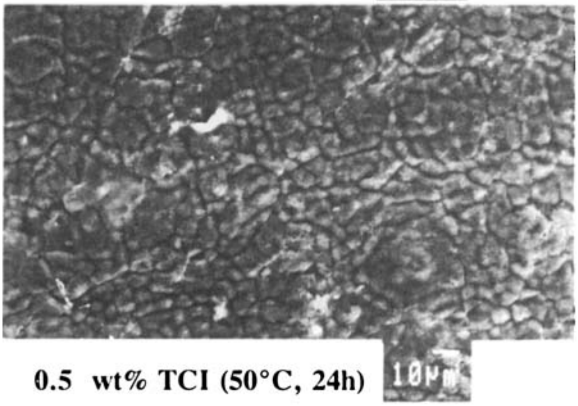


FIGURE 8 IR spectra of treated rubber with ethyl acetate + 2 wt% TCI/EA + 25 wt% ethanol/water mixture. Length of the treatment: 1 h. Influence of the temperature treatment.

the halogenating agent; thus, a more effective chlorination treatment will be produced. For this reason, there is a decrease of contact angle (ethane diol, 25 °C) from 42° to 37° when the chlorinated rubber is treated at 50 °C (the surface free energy is increased). In fact, SEM micrographs of chlorinated rubber treated with 0.5 and 2 wt% TCI/EA (Figs. 9a and 9b) show how the heat treatment favours the creation of not-very-deep but well-distributed microcracks which should contribute to increased mechanical adhesion of the rubber. T-peel strength of chlorinated rubber/polyurethane adhesive joints (Fig. 10) is always around 6 kN/m for the heat-treated chlorinated rubber, independent of the percentage of chlorination agent used. Therefore, in respect to the room temperature-chlorinated rubber, smaller T-peel strengths are obtained in the heat-treated one for amounts of TCI lower than 3 wt%, probably because a certain amount of chlorination agent is used to remove the antiadhesion compounds, giving a reduced global degree of chlorination in the rubber. For TCI percentages larger than 5 wt% there are, however, higher T-peel strengths for the heat-treated rubber. As will



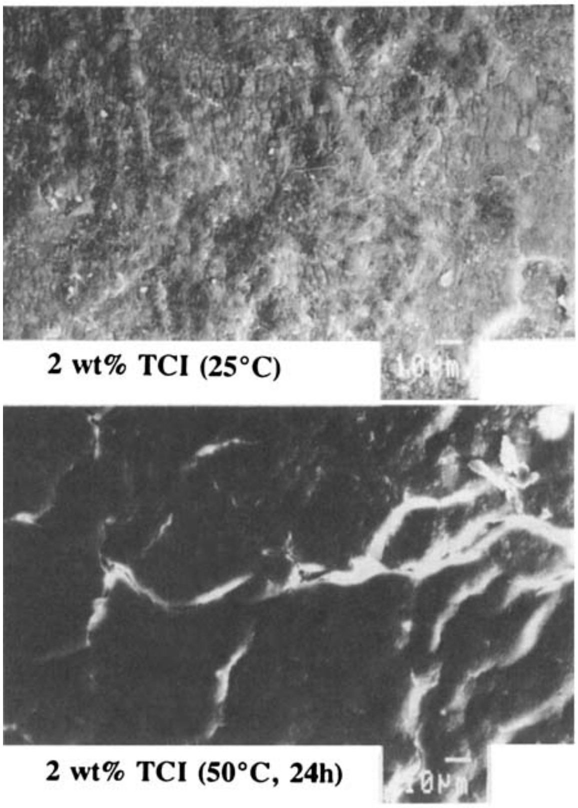
0.5 wt% TCI (25°C)



0.5 wt% TCI (50°C, 24h)

a

FIGURE 9 SEM micrographs of chlorinated rubber: a) 0.5 wt% TCI/EA; b) 2 wt% TCI/EA. Influence of the temperature treatment.



b

FIGURE 9 *(Continued)*

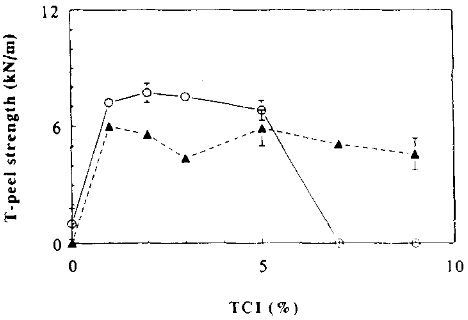


FIGURE 10 T-peel strength obtained for chlorinated rubber: (○) room temperature; (▲) heat-treated at 50 C/24 h.

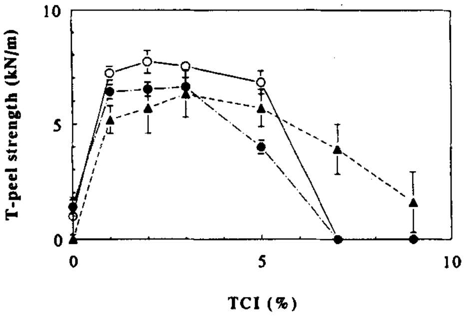


FIGURE 11 T-peel strength obtained for ethyl acetate wiped rubber: (○) chlorinated, (●) chlorinated + 25 wt% ethanol/water mixture and (▲) chlorinated + 25 wt% ethanol/water mixture + dried in vacuum.

be shown below, the use of higher amounts of chlorinating agent produces a WBL, as a consequence of the excess of TCI as well as cyanuric acid on the rubber surface, giving a noticeable decrease of T-peel strength (there is a lack of adhesion for 7 wt% TCI/EA). However, the heat treatment at 50 °C avoids the creation of such WBL on the chlorinated rubber. Hence, the heat treatment favours the migration of antiadhesion compounds in the untreated rubber, facilitating their elimination from the surface; when an excess of halogenation agent is used, the formation of WBL on the rubber surface is avoided.

As stated in the Introduction section of this paper, an inadequate or too aggressive surface treatment of a substrate may cause the formation of WBL. Figure 11 shows T-peel strength of chlorinated rubber/polyurethane adhesive joints as a function of the concentration of chlorinating agent in EA. The halogenation treatment was applied in a solvent wiping with ethyl acetate followed by chlorination with TCI/EA solutions. The evolution in T-peel strength of Figure 11 is consistent with previous papers:[3,15,16] there is a sudden increase of adhesion for a small amount of TCI, which does not vary by increasing the percentage of chlorinating agent, until a sudden decrease of T-peel strength is produced for TCI percentages larger than 7 wt%. This loss of adhesion produced with a high amount of chlorination agent has been attributed to the formation of a weak boundary layer on the surface. In fact, the SEM micrographs of the 7 wt% TCI/EA treated-rubber (Fig. 12a) show big cracks across the entire rubber surface and a great number of almost-spherical and weakly-attached small rubber particles. This damaged surface will act as a weak layer during the T-peel test and the joint failure mode will start from this. Nevertheless, the formation of this WBL can be avoided by applying a postchlorination treatment with a 25 wt% ethanol/water solution. The way in which the excess of ethanol/water solution is eliminated from the rubber surface determines the creation of the WBL. According to Figure 11, when the ethanol/water solution is removed in vacuum, reasonable adhesion levels are obtained for TCI percentages larger than 7 wt% and, consequently, a WBL on the rubber surface is not created.

Results included in Figures 12 to 14 may explain how the postchlorination + vacuum treatment prevents the formation of WBL, although the rubber is chlorinated with

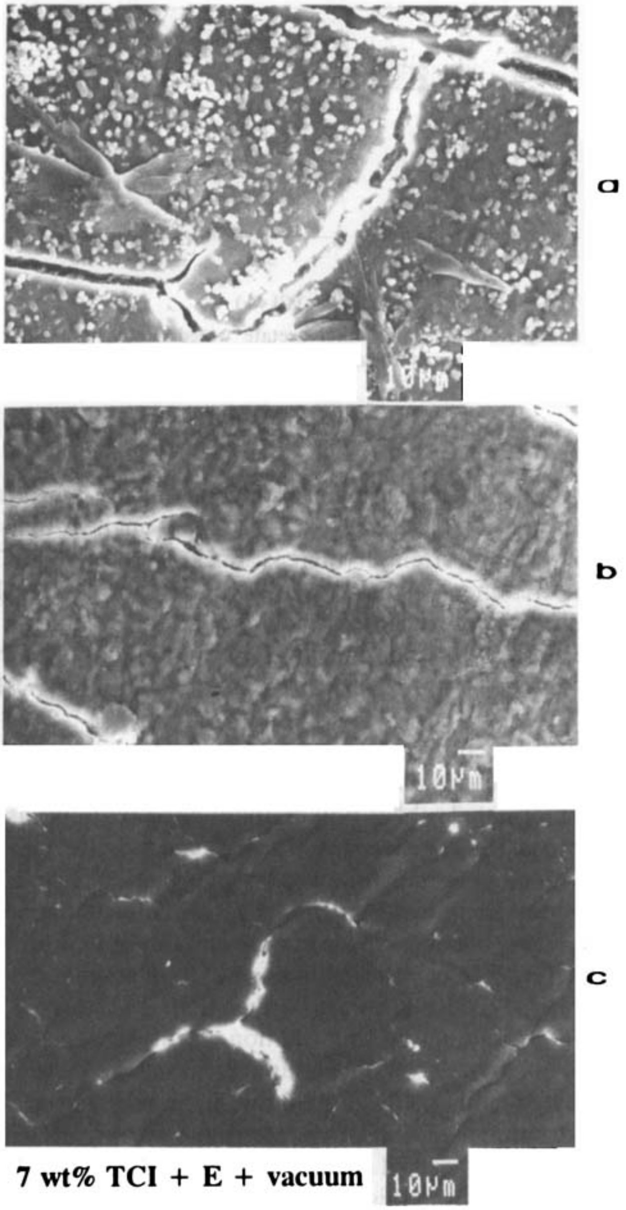


FIGURE 12 SEM micrographs of ethyl acetate wiped rubber: a) chlorinated with 7 wt% TCI/EA; b) chlorinated with 7 wt% TCI/EA + 25 wt% ethanol/water mixture (E); c) chlorinated with 7 wt% TCI/EA + 25 wt% ethanol/water mixture (E) + dried in vacuum.

noticeable amounts of halogenating agent. The IR spectrum of 7 wt% TCI chlorinated rubber without postchlorination treatment (Fig. 13) contains clear evidence of excess TCI (702, 798, 1157, 1369, 1720 cm^{-1}) as well as cyanuric acid. The absence of significant Si-O absorptions near 1100 cm^{-1} confirms the presence of a non-rubber

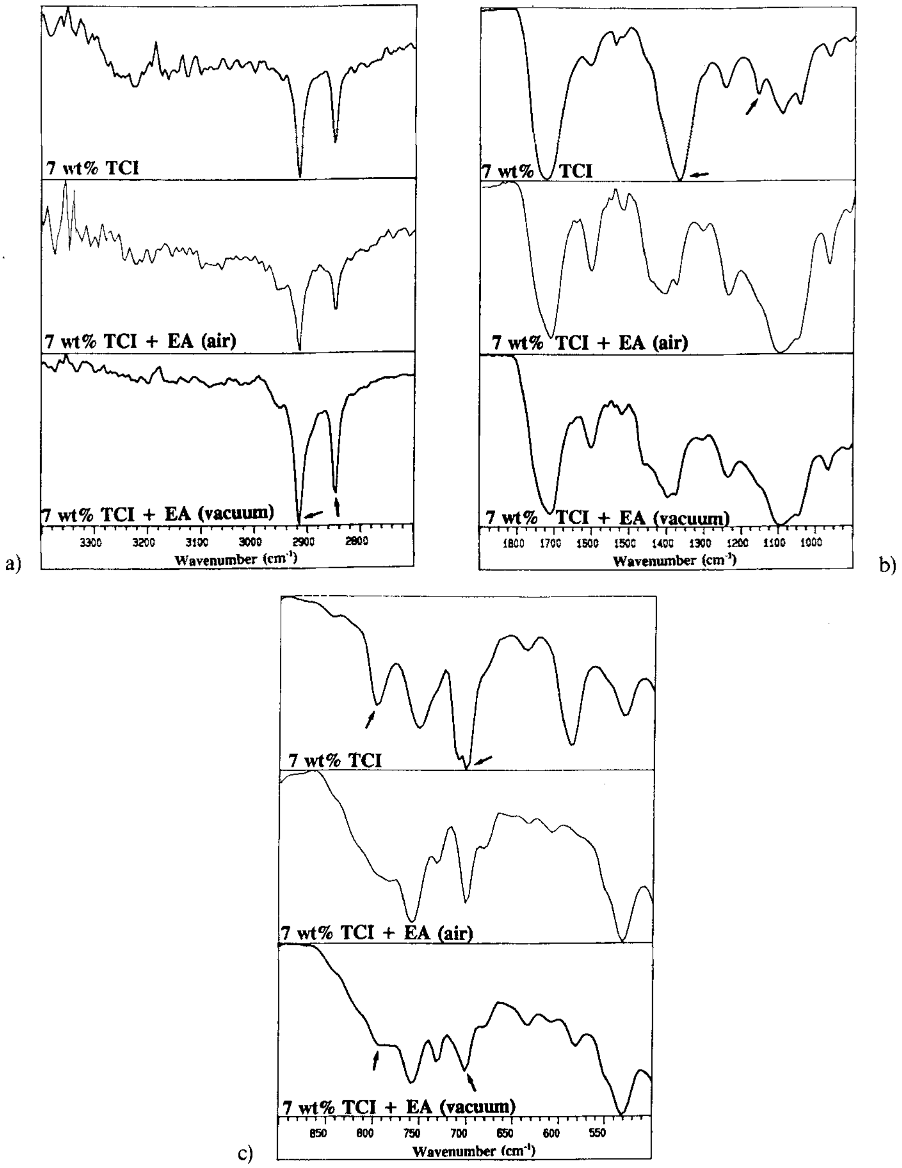


FIGURE 13 IR spectra of ethyl acetate wiped rubber chlorinated with 7 wt% TCI/EA. Influence of the drying procedure for removal of the postchlorination agent.

surface layer. According to the IR spectrum of Figure 13, the postchlorination treatment of 7 wt% TCI/EA treated rubber eliminates a greater amount of TCI as well as cyanuric acid from the rubber surface in respect to the simple chlorination. The surface of the postchlorinated rubber (Figs. 12b, c) presents a smaller amount of narrow microcracks and a lower degree of surface roughness than the rubber without

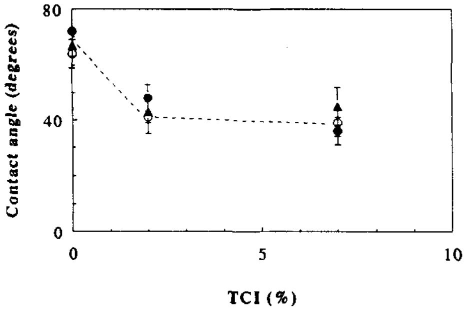


FIGURE 14 Contact angle (ethane diol, 25 °C) of ethyl acetate wiped rubber: (●) chlorinated with 7 wt% TCI/EA; (○) chlorinated with 7 wt% TCI/EA + 25 wt% ethanol/water mixture (E); (▲) chlorinated with 7 wt% TCI/EA + 25 wt% ethanol/water mixture (E) + dried in vacuum.

postchlorination treatment. The surface, however, is highly deteriorated and a WBL is formed. Contact angle (Fig. 14) does not vary when the postchlorination treatment is applied.

The removal in vacuum of the excess ethanol/water solution after the postchlorination treatment produced some changes in the rubber surface. The IR spectrum of chlorinated rubber dried in vacuum is very similar to the one dried in air (Fig. 13), but the amount of CH_2 groups remaining on the surface is higher. However, these variations are probably caused by a combination of poor optical contact and the non-linear transmission scale in IR spectra. Although the degree of chlorination is similar in vacuum-dried and air-dried postchlorinated rubber, the surface roughness and microcracks are greatly reduced under vacuum (Fig. 12). In this way, the WBL is not produced and good adhesion is obtained (Fig. 11). Again, no variations in the contact angle (Fig. 14) with respect to the chlorinated + 25 wt% ethanol/water treated rubber are produced.

4. CONCLUSIONS

In this paper two kinds of weak boundary layers (WBL) in synthetic vulcanized styrene-butadiene rubber have been described: i) WBL produced by the presence of compounds of the rubber formulation (zinc stearate, paraffin wax); ii) WBL created by an excess of chlorinating agent applied to the rubber surface. These two kinds of WBL have been analyzed and some experimental procedures have been proposed to eliminate or avoid their formation.

WBL produced by the presence of some rubber compounding ingredients can be effectively removed by chlorination with small amounts of TCI/EA solutions. Solvent wiping with 2-butanone, whether followed by washing with an ethanol/water solution or not, allows a significant removal of zinc stearate although the amount of paraffin wax is not greatly reduced, the latter compound being the probable cause of the poor adhesion of the rubber. A small concentration of chlorinating agent (0.5 – 5 wt%

TCI/EA) and/or a long chlorination treatment time increases the T-peel strength and effectively eliminates the zinc stearate from the rubber surface. When a heat treatment (50 °C/24 h) of the chlorinated rubber was carried out, the WBL was more effectively eliminated and the T-peel strength obtained was independent of the amount of chlorinating agent used. Furthermore, the heat treatment favours the elimination of WBL existing in the untreated rubber and avoids the formation of WBL when an excess of the halogenating agent is used.

An excess of chlorinating agent produces a lack of adhesion in the rubber due to an important degradation of the surface and the formation of a non-rubber surface layer of TCI as well as cyanuric acid, creating a WBL. To avoid the formation of this WBL, a postchlorination treatment of the rubber with a 25 wt% ethanol/water solution followed by drying in vacuum may be performed; this produces improved results. The proposed treatment was effective due to a good degree of chlorination of the rubber without a noticeable deterioration of the external surface by the chlorinating agent.

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