Elimination of the reactivation process in the adhesion of chlorinated SBS rubber with polychloroprene adhesives

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Abstract. Chlorination treatment of a thermoplastic styrene-butadiene-styrene rubber (SBS) with a 3 wt% solution of trichloroisocyanuric acid (TCI) in methyl ethyl ketone (MEK) introduces chlorinated and oxidized moieties on the rubber surface which increase its surface energy and produces surface microroughness. Consequently adhesion properties, evaluated by T-peel strength measurements in chlorinated SBS/solvent based-polyurethane adhesive/leather joints, are enhanced. In this study, two solvent-based polychloroprene adhesives (PCP0 and PCP30R) have been considered as an alternative to the commonly used solvent-based polyurethane adhesive (PU). A thermoreactive phenolic resin was added to one of the polychloroprene adhesive formulations (PCP30R). This tackifier resin favors chlorination of the adhesive and reinforces the interface between the chlorinated adhesive and the chlorinated rubber surface. Besides, PCP30R adhesive does not need adhesive reactivation and considerable high T-peel strength value (5.7 ± 0.3 kN/m) was obtained. Elimination of the reactivation process implies a considerable improvement of the manufacturing process in the footwear industry.

Keywords: *rubber, SBS rubber, surface treatment, polychloroprene, polyurethane*

1. Introduction

Styrene-butadiene-styrene thermoplastic rubbers (SBS) are commonly used in the footwear industry as sole materials. Their non polar nature imparts poor adhesion properties to these rubbers, thus a surface treatment is required prior to adhesive joint formation [1, 2]. Halogenation with trichloroisocyanuric acid (TCI) solutions in organic solvents (ketones or esters) is the most widely used surface treatment for rubber soles in the footwear industry [3]. This treatment creates chlorinated and oxygenated species and imparts roughness to the rubber surface. Consequently, appropriate rubber-leather joints with a good performance are obtained when using a polyurethane adhesive [4, 5]. Once applied upon the treated rubber surface and the leather, the solvent of the polyurethane adhesive is allowed to evaporate for 1 hour. Then, the dry polyurethane adhesive film needs to be melted

under infrared irradiation (adhesive reactivation) in order to permit fluency of polyurethane chains, prior to the adhesive joint formation. This adhesive reactivation is a time consuming process and the temperature needs to be carefully controlled [6]. Polychloroprene adhesives do not need reactivation after solvent evaporation, as polychloroprene adhesive tack is maintained for a longer time (i. e. open time), compared to polyurethane adhesives. However, incompatibility between polychloroprene and the chlorinated species introduced on the rubber surface by the halogenating treatment is believed to be responsible for their often lack of adhesion, although this has not been demonstrated in the literature [6]. Thus, the aim of this study is to modify the formulation of the polychloroprene adhesive in order to achieve good adhesion properties with a chlorinated SBS rubber. The possible elimination of the reactivation process from the

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adhesive joint formation will be considered and the interactions produced between the polychloroprene and the chlorinated rubber will be analyzed.

2. Experimental

2.1. Materials

The thermoplastic styrene-butadiene-styrene (SBS) rubber used in this study was obtained from Kraton D-4270CS pellets, an oil-extended (45 phr non-staining paraffin oil) radial block SBS copolymer. The SBS rubber test samples (25 mm width, 150 mm length, 3 mm thick) were prepared by Synthelast, S.A. (Elche, Alicante, Spain) by injection molding in a heated mold (150°C) and contain 10 wt% calcium carbonate as filler and 0.3 wt% phenolic antioxidant.

The surface of the SBS rubber was treated with methyl ethyl ketone (MEK) solutions containing 3 wt% trichloroisocyanuric acid (TCI) (98 wt% purity, Merck): 3 wt% TCI/MEK. The solution was brushed on the SBS rubber surfaces and allowed to react at room temperature in air for one hour.

Adhesive strengths were evaluated from T-peel tests on joints produced between the surface chlorinated SBS rubber and roughened leather using two different polychloroprene adhesives. Both polychloroprene adhesives were formulated with the same base polymer (DENKA A-90) but PCP0 did not contain any resin and PCP30R was formulated with 30 phr (parts per hundred) of a thermoreactive phenolic resin (SP-154) provided by Shenectady Europe (SI Group, Béthune, France) [7]. Table 1 shows the formulations of the two polychloroprene adhesives. To prepare the PCP30R polychloroprene adhesive solution the resin and the metallic

oxides were previously stirred in a laboratory mixer at 1000 rpm (revolutions per minute) for 30 minutes. After that, the polychloroprene was added and the solution was stirred at 2000 rpm for 1 hour, and later on at 2500 rpm for 3 more hours. To prepare the polychloroprene adhesive solution with no resin in its formulation (PCP0) all the ingredients were simultaneously mixed and stirred at 2000 rpm for 1 hour and at 2500 rpm for 2 hours.

The results obtained with polychloroprene adhesives were compared with those obtained with a solvent-based polyurethane adhesive (PU). To prepare the solvent-based polyurethane adhesive solution polyurethane pellets (Desmocoll 540 provided by Bayer, Leverkusen, Germany) were added to MEK and stirred at 2000 rpm for 2 hours to obtain the adhesive solution.

Calf leather used in the adhesive joints was supplied by INESCOP (Elda, Alicante, Spain) (Tensile strength = 13 MPa; Elongation-at-break = 60%; ash content at 950°C less than 5 wt%).

2.2. Experimental techniques

2.2.1. Fourier transform infrared (FTIR) spectroscopy

The chemical modifications produced on the SBS rubber by treatment with 3 wt% TCI/MEK in about 3 µm depth were assessed by ATR-IR spectroscopy. A Bruker Tensor 27 FTIR spectrometer (Bruker Optik, Ettlingen, Germany) was used and a KRS-5 (thallium bromoiodide) crystal was employed. The angle of incidence of the IR beam was 45°, and 200 scans were collected and averaged with a resolution of 4 cm⁻¹.

2.2.2. X-Ray photoelectron spectroscopy (XPS)

XPS was used to determine the chemical composition on the outermost (5–10 nm) treated SBS surface. A VG Scientific Microtech Multilab spectrometer (VG Microtech, Hastings, E Sussex, UK) with a Mg Kα X-ray source (1253.6 eV) operating at 25 keV and 300 W, and a 45° take-off angle was used. Prior to analysis, the samples were placed in a vacuum chamber until a pressure lower than 1·10⁻⁶ Pa was obtained. The analysis was performed on 5 mm×2 mm pieces of SBS rubber at a residual pressure lower than 1·10⁻⁶ Pa. For each sample, a survey scan encompassing the region 0–1200 eV was first obtained. Multiplex scanning

Table 1. Formulation of polychloroprene adhesives PCP0 and PCP30R

Component [phr]	PCP0	PCP30R
PCP	100	100
MgO	–	4
ZnO	–	5
Antioxidant	2	2
Phenolic resin (SP154)	–	30
Solvents	333	431
H ₂ O	–	2

PCP: DENKA A-90
ZnO: ZINKOXYD AKTIV (Rubber Chemicals)
MgO: ANSCOR Q (Britmag)
Antioxidant: IRGANOX 1010 (Ciba)
Solvents: 45:20:35 (Hexane:toluene:acetone)

of all observed photopeaks in the survey scan were carried out in a 20 eV range. Binding energies of all photopeaks were referenced to the C 1s photopeak position for C–C and C–H (hydrocarbons) species at 285.0 eV. 1.8 eV was used as FWHM (Full Width at Half Maximum) for the C 1s photopeak. Atomic concentration calculations were carried out using a VGX900-W system.

2.2.3. Contact angle measurements

A Ramé Hart 100 goniometer (Ramé-Hart, Inc., Mountain Lakes, NJ, USA) was used to obtain the contact angle values on the treated SBS rubber surface. Prior to contact angle measurements, the treated SBS rubber surfaces were wiped with ethanol to remove organic contaminants and the solid by-product residues due to the chlorination treatment [8]. The treated SBS rubber pieces were placed into the thermostated chamber of the goniometer, which had previously been saturated with the vapour of the test liquid at 25°C for at least 10 minutes before placing 4 µl drops on the treated SBS rubber surface. The contact angles were measured 15 minutes after placing the drops. The test liquids used were bidistilled-deionized water and methane diiodide. The experimental error was ± 2 degrees. Surface energy was evaluated from contact angle measurements using the Owens and Wendt approximation [9].

2.2.4. Scanning electron microscopy (SEM)

The morphological modifications produced on the treated SBS rubber surface were analyzed by SEM. An environmental scanning electron microscope HITACHI S-3000N (Hitachi Ltd, Tokyo, Japan) was used. The electron beam energy was 20 kV. The samples were gold coated to obtain sufficient contrast in the micrographs.

An EDX (Energy dispersive X-ray) analyzer coupled to the SEM instrument was used to monitor the chemical composition of the solid residues on the treated SBS rubber surfaces produced as a consequence of the chlorination treatment. For EDX analysis, the samples were not gold-coated.

2.2.5. Dynamical Mechanical Thermal Analysis (DMTA)

The mechanical and viscoelastic properties of the adhesives were assessed by dynamical-mechanical-

thermal analysis using a Rheometric Scientific DMTA MK III equipment (Rheometric Scientific, Piscataway, New Jersey, NJ). The measurements were obtained in two points bending mode, using a frequency of 1 Hz and a strain amplitude between peaks of 32 µm. The temperature range was varied from -80°C to 80°C by using a heating rate of $5^{\circ}\text{C}/\text{min}$. Rectangular test sample pieces of $(1.0\text{--}2.0\text{ mm}) \times (10.0\text{--}20.0\text{ mm}) \times (60.0\text{--}70.0\text{ mm})$ were used in the measurements.

2.2.6. Differential Scanning Calorimetry (DSC)

Thermal properties of the adhesives were determined by Differential Scanning Calorimetry in a TA Instruments DSC Q100 V 6.2 equipment (TA Instruments, Barcelona, Spain). Samples of 10–20 mg were analyzed. The sample was introduced in an aluminium hermetic sample holder. Two heating runs were performed. The samples were initially heated from -80°C to 80°C at a heating rate of $10^{\circ}\text{C}/\text{min}$, then they were suddenly cooled down to -80°C , and after that, a second heating run (under the same experimental conditions) was carried out. The glass transition temperature (T_g) values were determined from the DSC curves obtained in the second heating run. This procedure was used to remove the thermal history of the sample.

2.2.7. T-peel tests

Adhesive joints between test pieces of chlorinated SBS rubber ($150\text{ mm} \times 25\text{ mm} \times 7\text{ mm}$) and roughened leather ($150\text{ mm} \times 30\text{ mm} \times 3\text{ mm}$) were produced using a solvent-based polyurethane adhesive (PU) and two polychloroprene adhesives (PCP0 and PCP30R). Before bonding, the leather surface was roughened in a Superlema (Superlema S.A., Zaragoza, Spain) roughening machine operating at 2800 rpm. A P100 aluminium oxide abrasive cloth was used and about 0.5 mm of leather were removed. Then, two consecutive adhesive coatings (the second coating was applied 10 minutes after applying the first one) were applied with a brush on the roughened leather surface. On the other hand, one hour after chlorination, the adhesive solution was applied by brushing on the treated SBS rubber surface. The adhesive was allowed to dry for 45 min at room temperature. In some cases, the dried solid adhesive film was melted at 80°C under infrared radiation (reactivation process) and imme-

diately placed into contact under a pressure of 0.8 MPa for 10 seconds to achieve a suitable joint. To determine the adhesive strength values of the treated SBS rubber/polyurethane adhesive/roughened leather joints, an Instron 4411 (Instron Ltd., Buckinghamshire, United Kingdom) was used at a peel rate of 0.1 m/min. The adhesive joints were tested 72 hours after bond formation.

3. Results and discussion

3.1. Surface modifications introduced on the SBS rubber surface by the treatment with a 3 wt% TCI/MEK solution

The ATR-IR spectrum of the as-received SBS rubber (Figure 1) shows typical absorption bands from polybutadiene (C–H stretching at 2925 and 2850 cm^{-1} , $-\text{CH}_2$ scissoring at 1450 cm^{-1} , $-\text{CH}_2$ twisting at 1380 cm^{-1} and out of plane deformation of 1,4-trans C=C at 960 cm^{-1}) and from polystyrene (aromatic C–H stretching at 3010 cm^{-1} , aromatic C–C stretching at 1601 cm^{-1} , out of plane deformation of aromatic C–H at 910 and 700 cm^{-1}) units. There is also C–O–C bending absorption at 870 cm^{-1} of calcium carbonate in the rubber formulation. The treatment of the SBS rubber with a 3 wt% TCI/MEK solution introduces oxygenated (C=O stretching at 1700 cm^{-1} , C–H bending of $-\text{CH}_2\text{CO}$ at 1400 cm^{-1} and C–O stretching at 1065 cm^{-1}) and chlorinated (C–H bending of $-\text{CH}_2\text{Cl}$ at 1420 cm^{-1} and C–Cl stretching at 760 and 540 cm^{-1}) moieties on the rubber surface. Besides, a N–C=O stretching band appears at 1750 cm^{-1} (probably due to the TCI and/or isocyanuric acid crystals, reaction by-product between

Figure 1. ATR-IR spectra of the as-received SBS rubber surface and SBS rubber surface treated with 3 wt% TCI/MEK

Figure 2. SEM micrographs of (a) as-received SBS rubber surface and (b) SBS rubber surface treated with 3 wt% TCI/MEK

TCI and rubber, deposited on the treated rubber surface).

SEM micrograph of as-received SBS rubber shows calcium carbonate particles (filler in the SBS rubber formulation) (Figure 2). The nature of these calcium carbonate particles was assessed by EDX analysis. Besides, the treatment of the SBS rubber surface with TCI/MEK partially dissolves the rubber surface and creates microcracks [10]. On the other hand, chlorinated SBS rubber shows not only calcium carbonate but also chlorine containing crystals, from unreacted TCI on the rubber surface. Considering that these TCI crystals may act as a weak boundary layer preventing contact of rubber surface with the adhesive, chlorinated rubber surfaces were wiped with absolute ethanol (95 wt%) 1 hour after chlorination treatment to remove unreacted TCI from the rubber surface [11]. After ethanol wiping, XPS analysis and contact angle measurements on SBS rubber surface were assessed.

The XPS analysis of the as-received rubber and rubber treated with TCI/MEK shows that the treatment with this chlorinating system introduces oxygen and chlorine on the rubber surface (Table 2a). On the other hand, some nitrogen is detected on the treated rubber surfaces, probably due to TCI or isocyanuric acid crystals deposited on the treated rubber surface, which has been previously detected by ATR-IR spectroscopy (Figure 1). C1s curve fitting (Table 2b) reveals the creation of C–O, C=O and C–Cl polar moieties on the chlorinated SBS rubber surface and also the presence of N–C=O from unreacted TCI and/or isocyanuric acid on the treated rubber surface.

The introduction of the oxygenated and chlorinated species on the SBS rubber surface by the treatment with TCI/MEK produced a decrease of contact angle (evaluated with bidistilled-deionized water and methane diiodide) and an increase of the rubber surface energy from 41.2 to 51.2 mJ/m^2 , mainly

Table 2a. Elemental atomic percentages (XPS) obtained on the as-received SBS rubber surface and SBS rubber surfaces treated with TCI/MEK

	Atomic percentage		
	Binding energy [eV]	As-received [at %]	Treated with TCI/MEK [at %]
C1s	285.0	97.9	88.4
O1s	531.0	0.6	6.6
N1s	398.0	0.3	1.6
Si2p _{3/2}	99.0	0.6	–
Zn2p _{3/2}	1022.0	0.6	–
Cl2p _{3/2}	199.0	–	3.3
	O/C	0.01	0.07

Table 2b. Atomic percentages (XPS) of C1s curve fitting obtained on the as-received SBS rubber surface and SBS rubber surfaces treated with TCI/MEK

	Binding energy [eV]	As-received [at %]	3 wt% TCI/MEK [at %]
C–H,C–C	285.0	95.6	83.8
C–O, C–Cl	286.5	4.4 (C–O)	14.8 (C–O, C–Cl)
C=O, N–C=O	288.0	–	1.1
RCOO–	288.9	–	0.3

Table 3. Contact angle measurements (bidistilled-deionized water and methane diiodide), total (γ_s), polar (γ_s^p) and dispersive (γ_s^d) components of the surface energy of as-received SBS rubber and SBS rubber treated with TCI/MEK

Adhesive	θ_{H_2O} [°]	$\theta_{CH_2I_2}$ [°]	γ_s^d [mJ/m ²]	γ_s^p [mJ/m ²]	γ_s [mJ/m ²]
As-received	88±2	37±1	40.0	1.2	41.2
3 wt% TCI/MEK	62±1	51±1	40.5	10.7	51.2

due to the increase of its polar component (from 1.2 mJ/m² to 10.7 mJ/m²) (Table 3).

3.2. Adhesion properties of the chlorinated SBS rubber with polyurethane and polychloroprene adhesives

3.2.1. Characterization of the Polyurethane and Polychloroprene adhesives

Three different adhesives were considered in this study: a polyurethane adhesive (PU) with a % solid content of 17.2±0.1 and two polychloroprene adhesives: PCP0 (23.4±0.2% solid content) and PCP30R (26.3±0.3% solid content). Brookfield viscosities of these adhesives were 2865±60, 11710±90 and 4180±60 mPa·s, respectively.

Figure 3. DSC thermograms of PU, PCP0 and PCP30R adhesives

Thermal properties of the PU, PCP0 and PCP30R adhesives were characterized by DSC. In the thermograms (Figure 3) obtained from the second thermal run of polychloroprene adhesives a melting peak does not appear, indicating that the crystallization of the polychloroprene adhesives is slower than the polyurethane crystallization. Thus, the open time of polychloroprene adhesives (time when tack properties are maintained) is higher than that of the polyurethane adhesive. For this reason, the adhesive joints formation with polychloroprene adhesives may not require the adhesive heat reactivation. On the other hand, the T_g values obtained for the PU, PCP0 and PCP30R adhesives are similar.

Figure 4a shows the logarithm of the storage modulus ($\log E'$) obtained for the PU, PCP0 and PCP30R adhesives by DMTA analysis. It can be observed that the polyurethane adhesive is more elastic than the polychloroprene adhesives. On the other hand, the phenolic resin added to the polychloroprene adhesive increases its storage or elastic modulus. Thus, the addition of this phenolic resin to the adhesive formulation improves the rheological properties of the polychloroprene adhesive. The $\tan \delta$ curves (Figure 4b) obtained for the three adhesives (PU, P0 and P30R) display the same behaviour than the $\log E'$ curves.

On the other hand, the dry solid film of polyurethane adhesive shows the highest surface energy (47.2 mJ/m²) (Table 4), which is more similar to chlorinated rubber surface energy (51.2 mJ/m²) (Table 3). On the other hand, polychloroprene

Figure 4. (a) $\log E'$ (storage modulus) versus temperature and (b) $\tan \delta$ versus temperature for PU, PCP0 and PCP30R adhesives

adhesives present similar surface energy (38 mJ/m^2) (Table 4).

Chemistry of the adhesives was analyzed by ATR-IR spectroscopy (Figure 5). The ATR-IR spectrum of the polyurethane film shows typical bands due to N–H stretching at 3330 cm^{-1} , C–H stretching at 2955 and 2855 cm^{-1} , C=O stretching due to urethane at 1725 cm^{-1} , aromatic C–C stretching at 1600 cm^{-1} , N–CO stretching, N–H bending and C–N stretching due to urethane at 1530 cm^{-1} , C–H bending at 1460 cm^{-1} , C–N stretching and N–H bending at and 1260 cm^{-1} , C–O–C stretching at 970 , 1065 , 1165 and N–H out of plane deformation at 730 cm^{-1} . The ATR-IR spectra of PCP0 and

Table 4. Contact angle measurements (bidistilled-deionized water and methane diiodide), total (γ_s), polar (γ_s^p) and dispersive (γ_s^d) components of the surface energy of dry solid adhesive films (PU, PCP0 and PCP30R)

Adhesive	$\theta_{\text{H}_2\text{O}}$ [°]	$\theta_{\text{CH}_2\text{I}_2}$ [°]	γ_s^d [mJ/m ²]	γ_s^p [mJ/m ²]	γ_s [mJ/m ²]
PU	69±2	27±2	39.7	7.6	47.2
PCP0	72±2	51±1	27.5	10.2	37.7
PCP30R	84±2	43±2	35.4	2.9	38.2

Figure 5. ATR-IR spectra of the roughened leather, PU, PCP0 and PCP30R adhesives before joint formation

PCP30R polychloroprene adhesives show the following absorption bands: =C–H stretching of aromatic rings (3025 cm^{-1}), C–H stretching (2910 , 2860 cm^{-1}), C=C stretching (1650 cm^{-1}), C–H bending (1445 cm^{-1}), out of plane bending =C–H (820 , 780 , 675 cm^{-1}), C–Cl stretching (820 cm^{-1}). PCP30R polychloroprene adhesive also shows absorption from the thermoreactive phenolic: aromatic C–C stretching (1600 cm^{-1}), asymmetric C–H bending (1480 cm^{-1}), CO–H bending and symmetric C–H bending (1360 cm^{-1}), out of plane C–O stretching (1210 cm^{-1}), asymmetric C–O–C stretching (1070 cm^{-1}) and symmetric C–O–C stretching and aromatic C–H out of plane bending (875 cm^{-1}). On the other hand, the ATR-IR spectrum of the roughened leather used in the adhesive joints (Figure 5) shows several bands due to collagen (the main constituent of animal skin): N–H and C–N bands (N–H stretching at 3300 cm^{-1} , C–N stretching and N–H bending at 1540 cm^{-1} , C–N bending at 1240 cm^{-1}), methylene bands (C–H stretching at 2920 and 2845 cm^{-1} , C–H bending at 1450 cm^{-1}), and ester bands (C=O stretching at 1650 cm^{-1} , C–O stretching at 1030 cm^{-1}).

3.2.2. Elimination of the reactivation process in the adhesion of chlorinated SBS rubber with polychloroprene adhesive

Table 5 shows that the treatment of the SBS rubber with TCI/MEK improves the adhesion properties of the rubber to PU and PCP30R adhesives. However, the chlorinated SBS rubber exhibits poor adhesion properties to PCP0 adhesive. In all cases the dry adhesive film was melted at 80°C under infrared radiation (reactivation process) and immediately

Table 5. T-peel strength [kN/m] obtained for joints produced between as-received and TCI/MEK-treated SBS rubber and roughened leather using PU, PCP0 and PCP30R adhesives. Failure mode: A – adhesion failure; M – cohesive in the rubber failure (failure obtained by ATR-IR spectroscopy on both failed surfaces)

Adhesive	T-peel strength [kN/m] (Failure mode)	
	As received	TCI/MEK
PU	0.2±0.1 (A)	6.1±0.1 (M)
PCP0	0.7±0.1 (A)	0.4±0.1 (A)
PCP30R	0.2±0.1 (A)	6.9±0.1 (M)

Figure 6. ATR-IR spectra of the failed surfaces obtained after T-peel test of (a) as-received SBS rubber/PU adhesive/roughened leather joint; (b) as-received SBS rubber/PCP0 adhesive/roughened leather joint; (c) as-received SBS rubber/PCP30R adhesive/roughened leather joint

placed into contact under a pressure of 0.8 MPa for 10 seconds to achieve a suitable joint.

The T-peel strength values obtained for the adhesive joints prepared with chlorinated SBS rubber using PU and PCP30R adhesives were high and a cohesive in the chlorinated rubber failure (*M*) was obtained, while an adhesion failure (*A*) was obtained for joints produced with the as-received SBS rubber. The failure mode was assessed by ATR-IR spectroscopy comparing ATR-IR spectra of as-received rubber (Figure 1), leather and adhesives (Figure 5) to ATR-IR spectra of failed surfaces (Figures 6 and 7). Thus, Figure 6 shows that on the leather failed surfaces adhesive absorption is present while the rubber failed surfaces shows absorption from rubber. Thus, adhesion failure is produced with as-received rubber (Figure 8a) irrespective of the adhesive used (polyurethane or polychloroprene). On the other hand, Figures 7a and 7c show the absorption bands from chlorinated rubber (C–H bending of –CH₂Cl at 1420 cm^{–1} and C–Cl stretching at 760 and 540 cm^{–1}) on both failed surfaces, indicating that a cohesive in the chlorinated rubber failure is produced (Figure 8b) when using polyurethane adhesive or polychloroprene adhesive with a phenolic resin in its formulation (PCP30R).

However, Figure 7b shows polychloroprene absorption on the leather failed surface and rubber absorption on the rubber failed surfaces. Consequently, when using a polychloroprene adhesive with no resin in its formulation (PCP0) in the joints between chlorinated SBS rubber and roughened leather, a low T-peel strength value was obtained (Table 5) and a mainly adhesion to rubber failure (*A*) mode (Figure 8a). Thus, the addition of the phenolic resin to the polychloroprene adhesive formulation is appropriate to obtain good adhesion performance with a polychloroprene adhesive.

As the reactivation process is time consuming and temperature must be carefully controlled, reactivation process was eliminated from the adhesive joints preparation (Figure 8c) when using the PCP30R polychloroprene adhesive. This is possible as open time (time when tack properties are maintained) for polychloroprene adhesive is longer than for polyurethane adhesive (Figure 3). Adhesive reactivation is not necessary with the PCP30R adhesive as a considerable high T-peel strength value (5.7±0.3 kN/m) was obtained in the joint

Figure 7. ATR-IR spectra of the failed surfaces obtained after T-peel test of (a) chlorinated SBS rubber/PU adhesive/roughened leather joint; (b) chlorinated SBS rubber/PCP0 adhesive/roughened leather joint; (c) chlorinated SBS rubber/PCP30R adhesive/roughened leather joint

between chlorinated SBS rubber and roughened leather using a not reactivated PCP30R adhesive, value that is just slightly lower than the T-peel strength value obtained for the reactivated PCP30R adhesive (6.9 kN/m) (Table 5). Previous studies dealing with the interface produced between polyurethane adhesive and chlorinated SBS rubber showed that chlorination of the polyurethane adhesive was produced by the unreacted TCI deposited on the treated SBS rubber. The creation of an interface with a distinctive chemistry resulted in the improvement of the adhesion prop-

Figure 8. (a) Adhesion failure mode; (b) cohesive in the chlorinated rubber failure mode; (c) Preparation of adhesive joints

Figure 9. ATR-IR spectra of PCP0 and PCP30R adhesive films before and after immersion in a 0.5 wt% TCI/MEK solution

erties of the treated SBS rubber towards polyurethane adhesive [12–15]. Therefore, possible chlorination of the polychloroprene adhesives was considered and both PCP0 and PCP30R solid adhesive films were immersed in the chlorinating solution.

ATR-IR spectra (Figure 9) were obtained for PCP0 and PCP30R adhesive films before and after immersing the adhesive films in a 0.5 wt% TCI/MEK solution during 10 s. It can be observed that the PCP0 adhesive film was not modified by immersion in a 0.5 wt% TCI/MEK solution. Only a weak absorption band due to C=O stretching can be observed. However, the PCP30R adhesive film reacts with TCI to create C=O moieties (C=O stretching at 1720 cm⁻¹) and O-CH-O moieties (C-H wag vibration at 1385 cm⁻¹).

Consequently, the improvement of the rheological properties of the polychloroprene adhesive produced by the addition of a thermoreactive phenolic resin (which imparts elasticity to the polychloroprene adhesive) together with the ability of chlorination of the polychloroprene adhesive by the TCI may be responsible for the good adhesion performance.

4. Conclusions

The surface treatment with a 3 wt% TCI/MEK increases the SBS rubber surface energy and introduces surface roughness improving the adhesion properties of the SBS rubber surface towards PU and PCP30R adhesives.

The rheological properties and the adhesion properties of the polychloroprene adhesive towards chlorinated SBS rubber improved by addition of a thermoreactive phenolic resin in its formulation. The presence of a thermoreactive phenolic resin in the polychloroprene adhesive formulation imparts elasticity and also favours the oxidation of the adhesive film by TCI, resulting in good adhesion properties.

It is possible to eliminate the reactivation process from the adhesive joint formation when using a polychloroprene adhesive with a thermoreactive phenolic resin in its formulation.

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