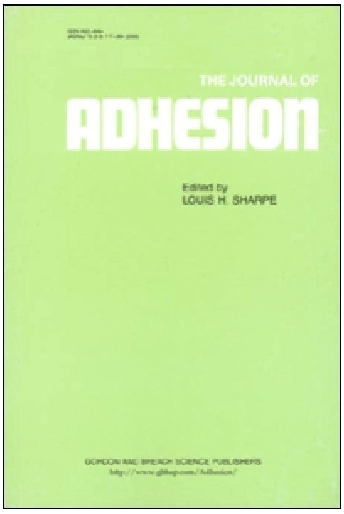

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TREATMENT OF THERMOPLASTIC RUBBER WITH CHLORINE BLEACH AS AN ALTERNATIVE HALOGENATION TREATMENT IN THE FOOTWEAR INDUSTRY

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Avoidance of solvents in bonding operations is a current demand in the footwear industry. Halogenation of rubber soles with solutions of trichloroisocyanuric acid (TCI) in different solvents has been successfully used to improve bonding to the leather uppers. In this study, the use of chlorine bleach as an alternative water surface treatment for a rubber has been tested.

A thermoplastic block styrene thermoplastic (TR) was treated with bleach to improve its adhesion to a water-based polyurethane dispersion adhesive (PUD). T-peel testing, scanning electron microscopy (SEM), contact angle measurements (ethanediol, 25°C), and infrared spectroscopy (ATR-IR) were used to analyze the modifications produced on the rubber surface. Adhesion values were obtained from T-peel testing of joints produced with similarly treated TR rubber test pieces. Different experimental variables were considered in this study, namely the immersion time (0.5–2 min) in bleach, the active chlorine content (43.9–55.6 g/l) in the bleach, the addition of a wetting agent (1-octyl-2-pyrrolidone) to

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the bleach, and the application of the surface treatment using an ultrasonic bath.

The treatment with bleach produced the chlorination of the hydrocarbon chains on the TR rubber surface and slightly changed the surface roughness. Chlorination of the TR rubber with bleach (free active chlorine = 55.6 g/l) was fast and needed only 30 sec immersion in the reagent mixture to produce high adhesion. Furthermore, the active chlorine content in the bleach was critical to assure an adequate T-peel strength value. The addition of 1-octyl-2-pyrrolidone to the bleach increased the wettability of the rubber surface, although it was necessary to carry out the surface treatment in the ultrasonic bath to obtain adequate adhesion to the PUD adhesive.

Keywords: Thermoplastic styrene-butadiene rubber; Water-based polyurethane adhesive; Bleach; Halogenation; Water-based surface treatment; Contact angle; ATR-IR spectroscopy; SEM; T-peel strength

INTRODUCTION

Thermoplastic rubber is a block copolymer of butadiene, a soft and elastic synthetic rubber, and styrene, a hard and brittle resin. These rubbers do not require vulcanization to provide dimensional stability. The butadiene-to-styrene ratio can be varied to produce rubber materials with different degrees of hardness and elasticity. The major fields of application of thermoplastic rubbers are footwear, adhesives manufacturing [1, 2], molded or extruded goods, and modifiers for asphalt and thermoplastic resins [3]. Due to the nonpolar nature of thermoplastics rubber, incompatibility with polyurethane adhesives is inherent, and a surface treatment must be carried out [4].

Halogenation with trichloroisocyanuric acid (TCI) solutions in ethyl acetate or MEK is the most common surface treatment used to improve the adhesion of rubber materials [5–8]. Surface treatment with TCI is effective as it increases both the degree of surface roughness and the surface energy, removes abhesive substances from the surface, and creates C–Cl and C–O moieties on the rubber surface [9, 10].

Previous studies [11] have shown that the nature of the rubber may affect the extent of the chemical modifications produced by surface treatment with solutions of trichloroisocyanuric acid. Furthermore, TCI is a strong oxidant and corrosive agent, and it must be applied to the rubber surface by means of organic solvents. The solvent carrier (generally organic solvents) makes this treatment hazardous to work with in shoe factories. Consequently, alternative and safer chemical surface treatments for rubbers must be used. In this study, the use of bleach as an alternative water-based chemical surface treatment to improve the adhesion of thermoplastic rubber materials used in the footwear industry is examined.

Bleach is an aqueous solution of sodium hypochlorite stabilized with sodium hydroxide. Previous studies [12] have shown that solutions of NaClO mixed with HCl produce chemical modifications on the rubber surface and an increase in wettability, which lead to improved peel strength. If HCl is not added, the treatment is not sufficiently successful.

In this study, the effect of the treatment of a thermoplastic rubber (TR) using chlorine bleach with or without the use of an ultrasonic bath was evaluated. Furthermore, a wetting agent (1-octyl-2-pyrrolidone) was added to the bleach in very low concentrations to decrease the surface tension of water to 26–28 dynes/cm. This is important to facilitate the wetting of the TR rubber by the bleach.

EXPERIMENTAL

Materials

A synthetic block styrene thermoplastic (TR) rubber was used in this study. The TR rubber was provided by INESCOP (Elda, Alicante, Spain). The formulation of the TR rubber is given in Table 1. Some properties of the TR rubber were obtained using standardized UNE Spanish procedures: Hardness = 60° Shore A; Density (20°C) = $0.97\,g.cm^{-3}$; Tensile strength = 4.7 MPa; Maximum elongation-at-break = 520%; Tear resistance = $10.1\,kN.m^{-1}$.

The adhesive joints were produced between treated TR rubber and canvas (provided by H. B. Fuller, St. Paul, Minnesota, USA). The

TABLE 1 Composition of Styrene-Butadiene-Styrene (TR) Rubber

Ingredient	Percentage (phr[a])
Rubber	100
Paraffin plasticizer	10
Polystyrene	20
Diesteramide	0.1
Antioxidant (Irganox 565)	0.2
Calcium carbonate	10
Carbon black	1.1

[a] Data are expressed in parts per hundred parts of rubber (phr).

adhesive used to produce the joints was a water-borne polyurethane dispersion (FI-4000BN) to which 5 wt% isocyanate crosslinker (FI-1000) was added; both materials were provided by H. B. Fuller (St. Paul, Minnesota, USA). 1-Octyl-2-pyrrolidone was supplied by Aldrich (purity higher than 98%).

Chlorination Procedure

The concentration of chlorine in the bleach ("free active chlorine") was obtained by adding an acidified potassium iodide solution. The resulting iodine was titrated with 0.1 N sodium thiosulfate solutions (starch was used as an indicator). Because chlorine is the reactant that produces the modifications on the rubber, the concentration of active reactant in the bleach was obtained as g Cl_2/l bleach.

The TR rubber was solvent wiped with isopropanol prior to application of the surface treatment. The treatment with bleach was carried out using three different procedures:

1. Immersion of the TR rubber in bleach (free active chlorine = 55.6 g/l) for different times (0.5–2 min), with or without ultrasonic treatment (25°C). Ultrasonic treatment was carried out in a Selecta Ultrasons ultrasonic bath (Selecta Ultrasons, Zug, Switzerland) operating at 200 watts.
2. A two-step process: (a) Immersion of the TR rubber in 0.5 wt% 1-octyl-2-pyrrolidone/water solution in an ultrasonic bath for different times (0.5–2 min); then (b) Immersion of the TR rubber in bleach (free active chlorine = 55.6 g/l) in the ultrasonic bath.
3. One step procedure: Immersion of the TR rubber in 0.5 wt% 1-octyl-2-pyrrolidone + bleach (free active chlorine = 55.6 g/l) mixture for different immersion times (0.5–2 min), with and without ultrasonic treatment.

After treatment the TR rubber was dried under infrared radiation at moderate temperature (lower than 60°C) for 30 min. During the study, deposition of NaOH crystals on the TR rubber surface was observed after drying and, therefore, cleaning was necessary to remove these crystals because they may cause adhesive coagulation due to the high pH on the rubber surface. Figure 1 shows the IR spectrum of bleach and the IR spectrum of the solid residues obtained on the treated TR rubber after drying. These spectra are compared with the IR spectrum of a high-purity solid NaOH. The three IR spectra show a strong band of 1420 cm^{-1}, which is due to

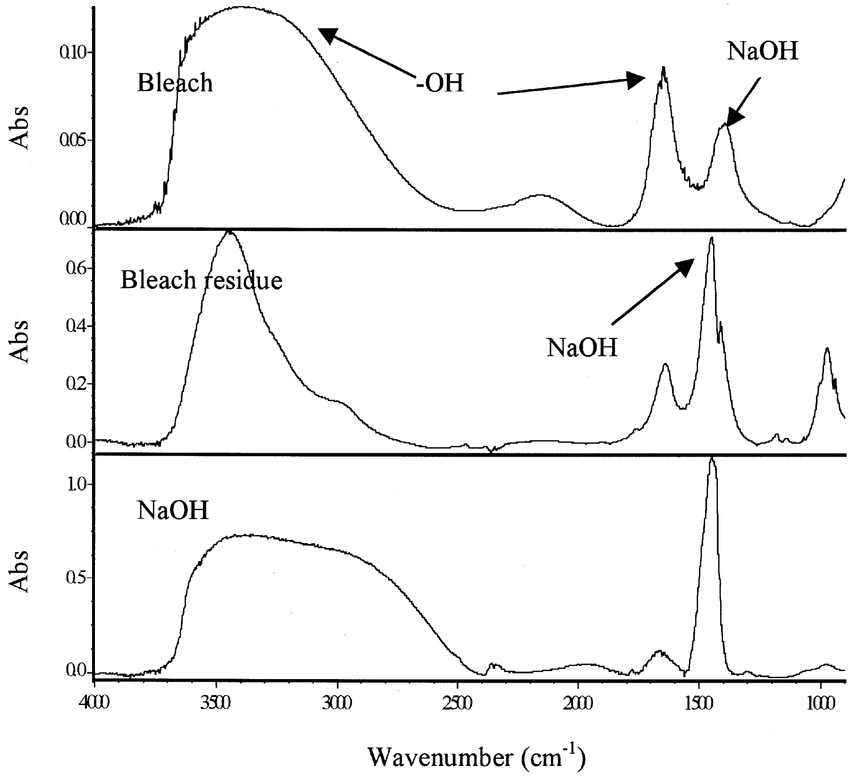


FIGURE 1 IR spectra of the chlorine bleach solution (obtained using a CaF_2 cell), the remaining residue obtained after bleach evaporation at 50°C/24 h under IR radiation (KBr pellet), and of solid NaOH (KBr pellet).

NaOH. The IR spectrum of the residues on the TR rubber surface shows the presence of NaOH, which may be deposited during treatment on the TR rubber surface. Therefore, after treatment with bleach, the TR rubber surface was cleaned with isopropanol to remove NaOH solid residue.

Experimental Techniques

Contact Angle Measurements

The surface-treated TR rubber was placed into the thermostated chamber of a *Ramé Hart 100* goniometer (Ramé Hart, Mountain Lakes, NJ, USA). The chamber was previously saturated with ethanediol vapour at 25°C for at least 10 min before placing a drop of ethanediol on the TR rubber surface. The contact angles on the surface-treated TR rubber (1 h after treatment was carried out) were measured 15 min after placing 4 μl ethanediol drops on the surface. The experimental error was ±2 degrees.

Attenuated Total Multiple Reflection-Fourier Transform Infrared Spectroscopy (ATR-IR Spectroscopy)

The ATR-IR spectra of treated TR rubber were carried out to determine the chemical modifications produced on the surface by halogenation. Because the halogenation treatment is not restricted to the most external surface but penetrates into the rubber surface, ATR-IR spectroscopy is useful to obtain information about the effects of the surface treatment. The ATR-IR spectra of the treated samples were obtained using a *Nicolet FTIR 205* spectrometer (Nicolet, Isenberg, Germany). To avoid deep penetration of the IR radiation into the sample, the attenuated total multiple reflection method was employed (ATR-IR spectroscopy), using a germanium crystal (which gives a better resolution with polymers containing carbon black) and 45° as the angle of incidence of the IR beam; ATR-IR spectroscopy allows analysis of about 2 μm in depth of the treated TR rubber surface. Two hundred scans were recorded and averaged at a resolution of 4 cm^{-1}.

SEM

Scanning Electron Microscopy (SEM) allowed the external surface modifications on the TR rubber surfaces produced by the treatment to be analyzed (a *JEOL SEM JSM 840* system—Jeol, Tokyo, Japan—was used). The samples were secured on copper mounts by means of a silver paste and were gold-coated before the SEM micrographs were obtained.

Apparent Surface pH Measurements

The pH on the surface-treated rubber was measured at different times after placing 50 μl drops of deionized and bidistilled water on the TR rubber surface. A flat pH probe was used. For an acceptable water-based chemical treatment for rubber to be joined by means of PUD, the pH must be between 5 and 9.

T-Peel Strength Measurements

T-peel strength measurements were obtained between adhesive joints produced by joining test strip specimens (150 mm × 30 mm) of treated TR rubber and canvas. The polyurethane adhesive dispersion and the crosslinker were mixed in a ratio of 95:5 (weight) for 2 min, using a laboratory mixer (500 rpm). The polyurethane adhesive solution (PUD) was applied with a brush on the canvas surface and with a metering rod (5.2 mils = 132 μm) on the treated rubber surface. Two coatings of adhesive were applied on the canvas surface: first, a thin coating was applied using a brush and allowed to dry for 15–20 min; then a second coating was applied. After allowing it to dry at room temperature for 30–45 min, the PUD adhesive film was reactivated at 60–70°C using infrared radiation, to facilitate the interlocking of the two polyurethane coatings applied on the surfaces of the TR rubber and canvas. Immediately after reactivation, the two coatings were placed in contact under a pressure of 40–50 psi (0.2–0.3 MPa) for 10 sec to achieve a suitable joint. The peel values obtained were the average of five replicates. The adhesive joints were kept at 25°C and 50% relative humidity for 24 h before undergoing the T-peel test. The T-peel strength was measured using an *Instron 4411* test instrument (Instron, Canton, MA, USA) (peeling rate = 0.1 m/min).

RESULTS AND DISCUSSION

This section is divided in three parts: (1) The characterization of the surface modifications of TR rubber produced by immersion in bleach for different times (with or without ultrasonic treatment) is studied; (2) The influence of the addition of 0.5 wt% 1-octyl-2-pyrrolidone (a wetting agent) to the bleach on the surface modifications and adhesion of TR rubber is analyzed, and, the way to produce the treatment is also considered; and (3) The concentration of free active chlorine in the bleach used to modify the surface properties of TR rubber is also studied.

Treatment of TR Rubber with Bleach (Free Active Chlorine = 55.6 g/l) with or without Ultrasonic Treatment

The treatment of TR rubber was carried out by immersion in bleach (free active chlorine = 55.6 g/l) with or without ultrasonic treatment for 0.5 and 2 min. The wettability of the treated TR rubber surfaces was characterized by contact angle measurements. Table 2 shows the contact angle values obtained after placing drops of ethanediol on the treated TR rubber surfaces. The untreated TR rubber shows a relatively high contact angle (63–66 degrees) due to the poor wettability of this nonpolar rubber. In fact, the peel strength of the TR rubber/PUD

TABLE 2 Contact Angle Values (Ethanediol, 25°C) on TR Rubber Surfaces Treated with Bleach (Free Active Chlorine = 55.6 g/l) with or Without the Ultrasonic Treatment

t_i (min)	Ultrasonic treatment (degrees)	No ultrasonic treatment (degrees)
0	63	66
0.5	49	42
2	50	38

t_i, influence of the immersion time.

adhesive/canvas joint (Table 3) is very small (0.8–1.2 kN/m). Treatment with bleach (free active chlorine = 55.6 g/l) produces a decrease in contact angle values on the TR rubber surface. The increase in the immersion time (2 min versus 0.5 min) does not produce a significant change in contact angle value, indicating that a short immersion time in bleach (free active chlorine = 55.6 g/l) is sufficient to modify the surface properties of TR rubber. Somewhat better performance is obtained if the treatment of TR rubber is conducted without ultrasonic treatment (Table 3).

The increase in wettability of the TR rubber treated with bleach could be ascribed to chemical modifications, which were assessed using ATR-IR spectroscopy. The ATR-IR spectrum of the as-received TR rubber (Figure 2) shows bands due to =CH stretching at 3100 cm^{-1}, C–H stretching at 2920 and 2850 cm^{-1}, $-CH_2$ scissoring at 1452 cm^{-1}, $-CH_2$ twist at 1380 cm^{-1}, and *trans* 1,4–C=C stretching at 968 cm^{-1}. Furthermore, styrene absorption bands appear at 696 and 749 cm^{-1} (C–H out-of-plane deformation of vinyl group), 1601 cm^{-1} (aromatic C–C stretching), and 3034 cm^{-1} (aromatic C–H stretching). A very small amount of O–H stretching at approximately 3400 cm^{-1} is also noted.

TABLE 3 T-peel Strength Values (kN/m) of Bleach (Free Active Chlorine = 55.6 g/l) Treated TR Rubber/Polyurethane Adhesive/Canvas Joints

t_i (min)	Ultrasonic treatment (kN/m)	No ultrasonic treatment (kN/m)
0	1.2 (A)	0.8 (A)
0.5	10.7 (M)	11.7 (M)
2	10.5 (M)	12.3 (M)

t_i, influence of the immersion time; A, adhesion failure; M, cohesive failure in the TR rubber.

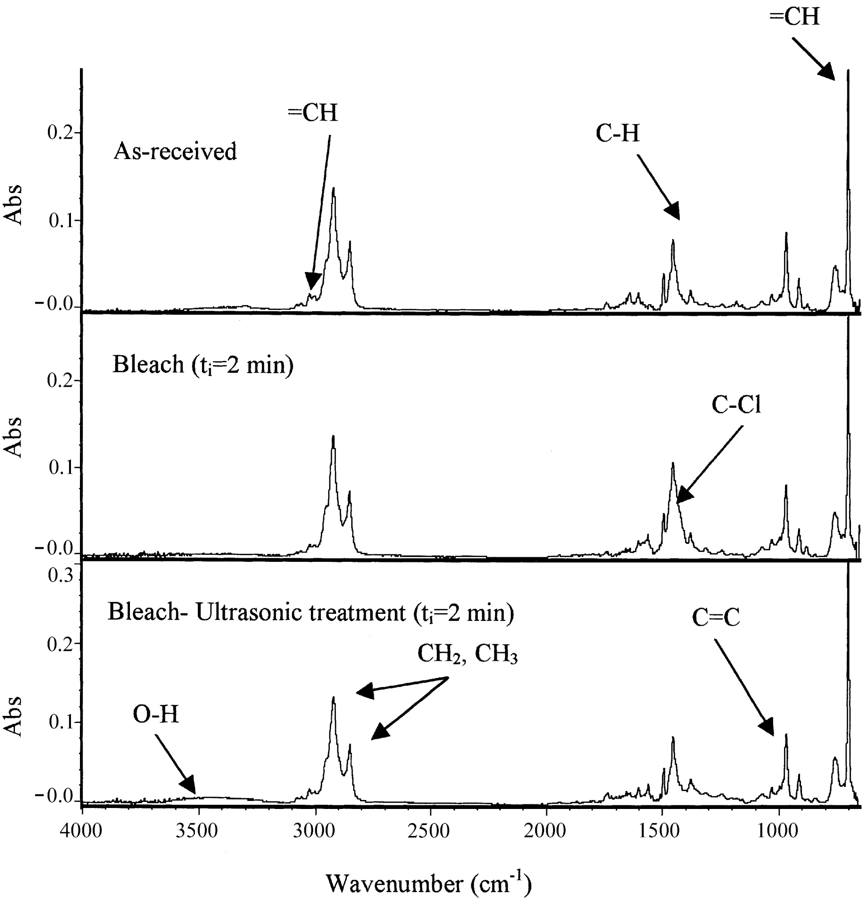
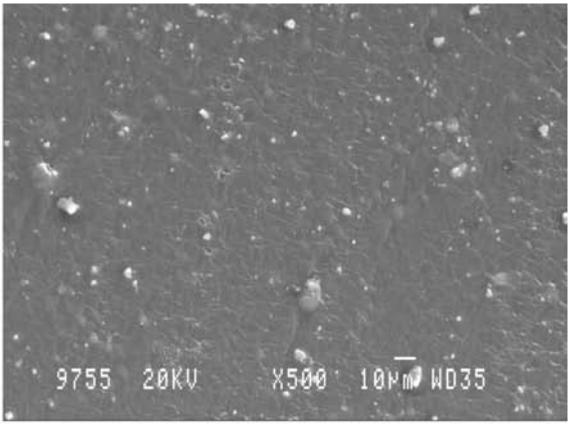


FIGURE 2 ATR-IR spectra of the TR rubber as received and treated with bleach (free active chlorine = 55.6 g/l) for 2 min with or without ultrasonic treatment.

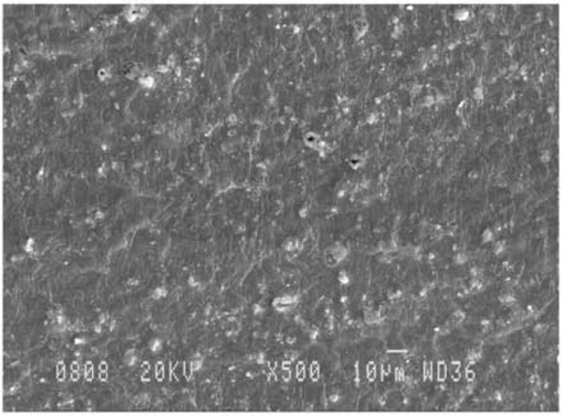
The ATR-IR spectra of the TR rubber treated with bleach for 2 min (Figure 2) show a decrease in the relative intensity (with respect to C–H bands) of the C=C bands due to butadiene (968 cm^{-1}), resulting from chlorination of C=C bonds. These changes on the treated TR rubber surfaces are somewhat more significant when the treatment was produced without ultrasonication. The increase of the immersion time in the solution does not produce marked changes in the ATR-IR spectra of the treated TR rubber.

The surface treatment with bleach (free active chlorine = 55.6 g/l) with or without ultrasonication does not markedly affect the mor-

As-received



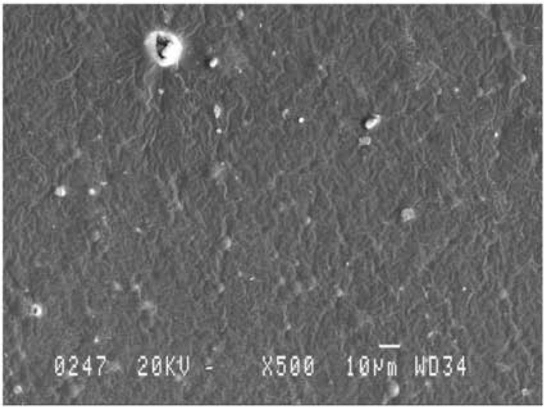
Bleach (t_i=2min)



Bleach-

Ultrasonic treatment

(t_i=2min)



phology of the TR rubber surface (Figure 3). The surface roughness created by the surface treatment ($t_i = 2$ min) was slightly more marked when the treatment was applied without ultrasonication. Increasing immersion time in bleach does not change the surface roughness of the TR rubber. On the other hand, the SEM micrographs of TR rubber treated with bleach without ultrasonic treatment show white rounded particles on the surface. Surface analysis by EDX (Energy Dispersive X-Ray Analysis) showed that these particles contain sodium, chlorine, and oxygen. Because NaClO is not a stable solid, the particles on the TR rubber surface may correspond to NaOH and/or NaCl. Furthermore, the pH on the TR rubber surface was about 10, which may cause adhesive coagulation.

The treatment with bleach produced a noticeable increase in T-peel strength values (Table 3) of treated TR rubber/PUD adhesive/canvas joints. Cohesive failure in the TR rubber was always obtained independently of the immersion time in the bleach solution and regardless of whether the treatment was carried out with or without ultrasonic treatment.

Therefore, only a 0.5 min treatment with bleach either with or without ultrasonication increases the wettability of TR rubber due to chlorination of the hydrocarbon chains. The treatment also produces some microroughness on the surface, mainly when the treatment is carried out without ultrasonication. The resulting apparent surface pH values of the TR rubber are acceptable for an aqueous PUD adhesive, although a solvent wiping with isopropanol after bleach treatment was necessary to avoid any adhesive coagulation. Excellent T-peel strength values are always obtained.

Treatment of TR Rubber with 1-octyl-2-pyrrolidone + Bleach (Free Active Chlorine = 55.6 g/l) Mixture

The treatment of TR rubber with 1-octyl-2-pyrrolidone (NOP) + bleach (free active chlorine = 55.6 g/l) mixture was carried out using two different procedures:

1. A two-step process consisting of (1) ultrasonic treatment of TR rubber in 0.5 wt% NOP aqueous solution, followed by (2) additional

◄

FIGURE 3 SEM micrographs of the TR rubber as received and treated with bleach (free active chlorine = 55.6 g/l) for 2 min with or without ultrasonic treatment.

ultrasonic treatment of this TR rubber in bleach (free active chlorine = 55.6 g/l).

2. A one-step process: Immersion of TR rubber in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture with or without ultrasonic treatment.

Treatment of TR Rubber with 0.5 wt% NOP Aqueous Solution Followed by Immersion in Bleach (Free Active Chlorine = 55.6 g/l) (Two-Step Process)

The influence of the immersion time ($t_i = 0.5$ and 2 min) for ultrasonic treatment of TR rubber in 0.5 wt% NOP followed by immersion in bleach (free active chlorine = 55.6 g/l) was evaluated. After treatment with NOP and bleach (free active chlorine = 55.6 g/l), the TR rubber was solvent wiped with isopropanol and dried under infrared radiation (30 min at 50°C on the surface) to avoid the adhesive coagulation.

The two-step process produces a decrease in contact angle values of TR rubber (Table 4) (63 degrees for the as-received TR rubber and 48–58 degrees for treated TR rubber), which are somewhat similar to the values obtained when the treatment was performed without NOP (Table 2). The increase in the immersion time in bleach or in NOP does not produce significant changes in the wettability of the TR rubber surface.

The IR spectrum of the NOP (Figure 4) shows C–H stretching bands at 2939 and 2860 cm^{-1}, C=O stretching at 1700 cm^{-1}, and C–N absorption at 1500 cm^{-1} and 1288 cm^{-1}. Figure 5 shows the ATR-IR spectra of the TR rubber surface after immersion for different times in 0.5 wt% NOP solution followed by immersion for 2 min in bleach (free active chlorine = 55.6 g/l). The surface treatment produces some

TABLE 4 Contact Angle Values (Ethanediol, 25°C) on Treated TR Rubber Surface with 0.5 wt% NOP + Bleach (Free Active Chlorine = 55.6 g/l) (Ultrasonic Treatment)

t_i in NOP (min) t_i in bleach (min)	0.5 θ (degrees)	2 θ (degrees)
0.5	49	49
2	48	58

t_i, influence of the immersion time in both solutions.

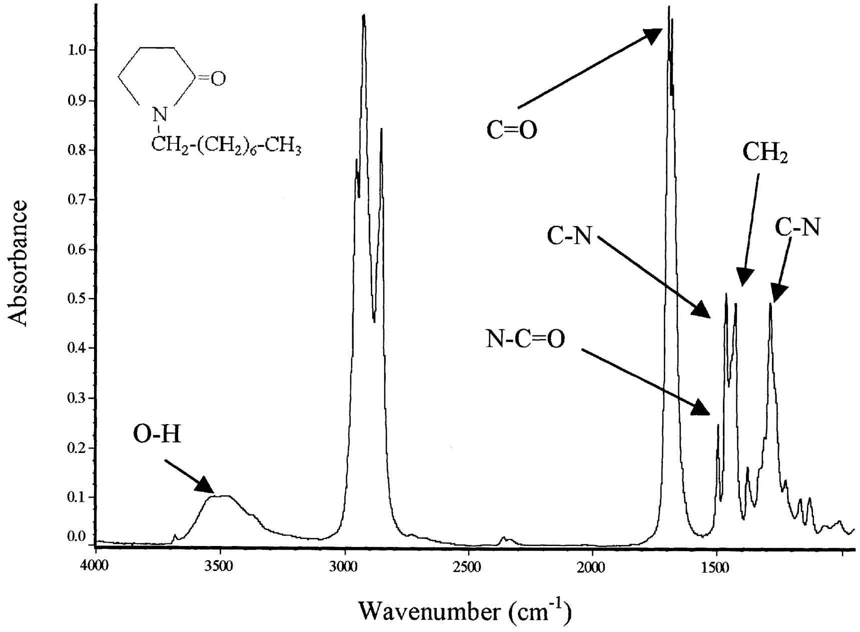


FIGURE 4 IR spectrum of NOP.

degree of chlorination of the hydrocarbon chains (bands at 1237, 1387, and 1420 cm^{-1}) (Figure 5) and some degree of oxidation of the rubber surface (C=O stretching absorption at 1630 cm^{-1}). Additionally, an enhanced amount of hydroxyl content was also noted after ultrasonic treatment in NOP (broad band centered at 3400 cm^{-1}), which can be ascribed to residual NOP remaining on the TR rubber surface.

The SEM micrographs of the TR rubber surface immersed for different times in 0.5 wt% NOP and followed by immersion for 2 min in bleach (Figure 6), show the swelling of the TR rubber and the presence of several round white particles on the surface which may correspond to NaOH (assessed by EDX). The increase in the immersion time in NOP aqueous solution favours the deposition of NaOH white particles.

The treatment with 0.5 wt% NOP followed by immersion in bleach (free active chlorine = 55.6 g/l) with ultrasonic treatment produces an increase in the TR rubber's apparent surface pH (Figure 7) (this is similar to the pH increase produced when the treatment was performed only with bleach). The pH slightly decreases by increasing the time between the placement of the water drop on the TR rubber surface and pH measurement, but neither the immersion time in NOP

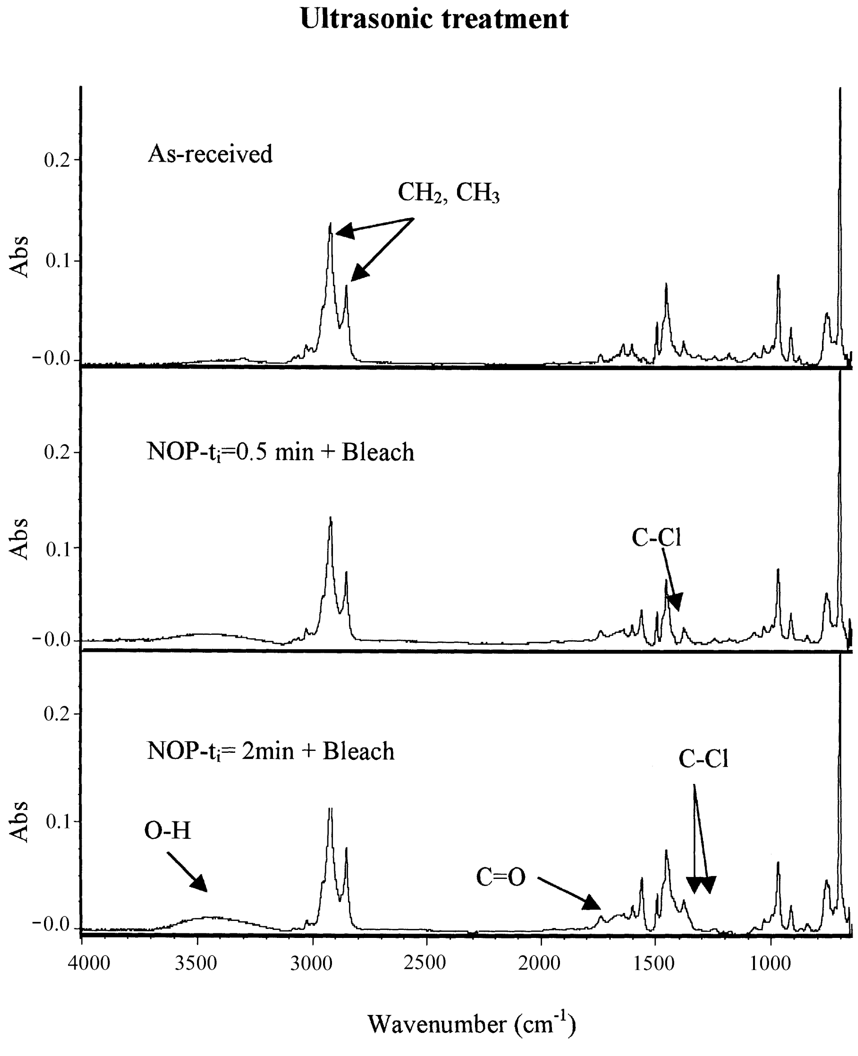
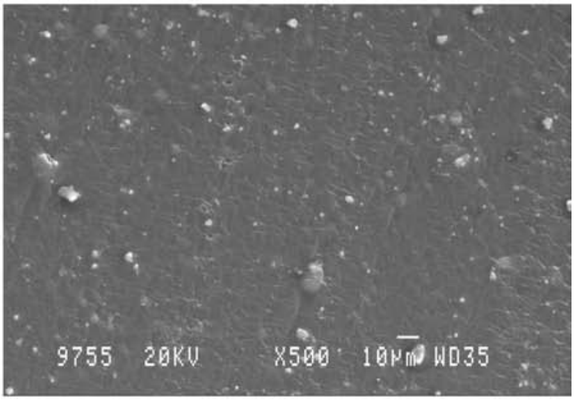


FIGURE 5 ATR-IR spectra of the TR rubber as received and treated by immersion in 0.5 wt% NOP aqueous solution followed by immersion in bleach (free active chlorine = 55.6 g/l) (ultrasonic treatment). Influence of the immersion time (t_i) in 0.5 wt% NOP aqueous solution. Immersion time (t_i) in bleach = 2 min.

FIGURE 6 SEM micrographs of the TR rubber as received and treated by immersion in 0.5 wt% NOP aqueous solution followed by immersion in bleach (free active chlorine = 55.6 g/l) (ultrasonic treatment). Influence of the immersion time (t_i) in 0.5 wt% NOP aqueous solution. Immersion time (t_i) in bleach = 0.5 min.

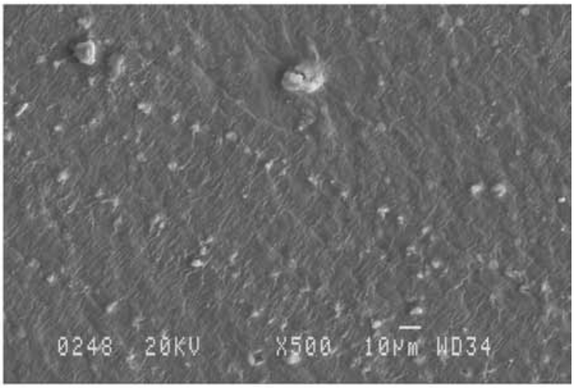
Ultrasonic treatment

As-received



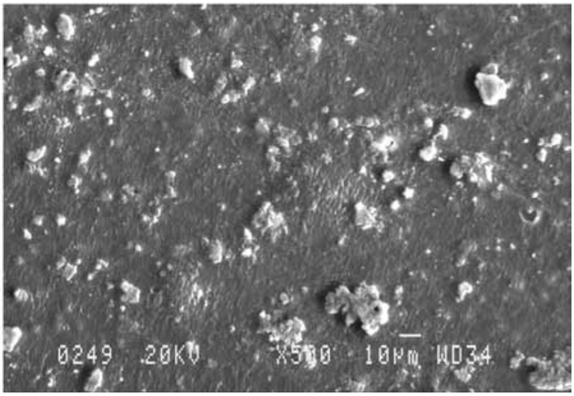
NOP (t_i=0.5 min)+

Bleach



NOP (t_i=2 min)+

Bleach



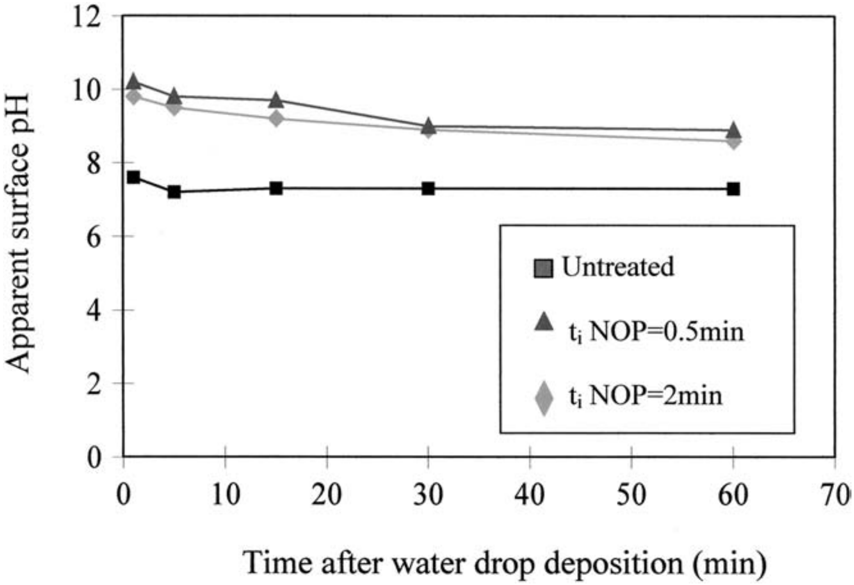


FIGURE 7 Apparent surface pH of the TR rubber as received and treated by immersion in 0.5 wt% NOP aqueous solution followed by immersion in bleach (free active chlorine = 55.6 g/l) (ultrasonic treatment). Influence of the immersion time (t_i) in 0.5 wt% NOP aqueous solution. Immersion time (t_i) in bleach = 0.5 min.

aqueous solution nor the immersion time in bleach noticeably decreases the apparent surface pH.

Due to the improved wettability and the chemical modifications produced on the treated TR rubber, an increase in T-peel strength values of treated TR rubber/PUD adhesive/canvas joints is produced (Table 5). Furthermore, a short immersion time in NOP aqueous solution and in bleach (both with ultrasonic treatment) seems to be sufficient to produce high adhesion. The increase in the immersion time in bleach (after immersion in NOP aqueous solution) favours cohesive failure in the TR rubber.

Therefore, the improved adhesion of TR rubber after treatment with 0.5 wt% NOP aqueous solution followed by immersion in bleach (free active chlorine = 55.6 g/l) (both with ultrasonic treatment) can be ascribed to enhanced wettability and chemical modification of the TR rubber. Furthermore, a short immersion time in both NOP solution and bleach (free active chlorine = 55.6 g/l) is sufficient to produce high

TABLE 5 T-peel Strength Values (kN/m) of As-received and NOP + Bleach (Free Active Chlorine = 55.6 g/l) (Ultrasonic Treatment) Treated TR Rubber/Polyurethane Adhesive/Canvas Joints

t_i in NOP (min)	0.5	2
t_i in bleach (min)	T-peel strength (kN/m)	T-peel strength (kN/m)
0.5	9.9 (50%A; 50%M)	10.4 (M)
2	10.6 (M)	11 (M)

t_i, influence of the immersion time; A, adhesion failure; M, cohesive failure in the TR rubber.

adhesion of the TR rubber (cohesive failure in the TR rubber is obtained).

Treatment of TR Rubber with 0.5 wt% NOP + Bleach (Free Active Chlorine = 55.6 g/l) Mixture (One-Step Process)

The effectiveness of the immersion of the TR rubber in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture was tested. By using this procedure, the treatment time of TR rubber can be reduced. Two immersion times (0.5 and 2 min) in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture with or without ultrasonic treatment were evaluated. The effectiveness of these treatments was compared with immersion of the TR rubber without ultrasonication in a solution of 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) (prepared by mixing for 2 min in the ultrasonic bath).

The treatment with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture produces an important increase in the TR rubber's wettability (Table 6), independent of whether the treatment is carried out with or without ultrasonic treatment. The increase in immersion time in the NOP + bleach mixture does not affect the contact angle values. However, the immersion of the TR rubber (without ultrasonic treatment) in the NOP + bleach mixture prepared in the ultrasonic bath only produces a slight decrease in contact angle values (62 degrees). In fact, the contact angle on the TR surface treated with only 0.5 wt% NOP after mixing in the ultrasonic bath is higher than for the other control TR surfaces (Table 6) likely due to the deposition of NOP on the surface (Figures 8a and 8b).

The ATR-IR spectra (Figure 8a) of the TR rubber immersed for 2 min in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture, or immersed in the 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture prepared in the ultrasonic bath, show

TABLE 6 Contact Angle Values (Ethanediol, 25°C) on As-received and Treated TR Rubber with 0.5 wt% NOP + Bleach (Free Active Chlorine = 55.6 g/l) Mixture (with or without Ultrasonic Treatment)

t_i (min)	Ultrasonic treatment (degrees)	Immersion in a solution mixed in the ultrasonic bath (degrees)	No ultrasonic treatment (degrees)
0	63	77	66
0.5	42	—	45
2	46	62	44

t_i, influence of the immersion time in the mixture.

evidence of chlorination of the hydrocarbon chains (new bands at 1423 and 883 cm^{-1} appear, whereas bands at 2920, 2843, 909, and 966 cm^{-1} disappear) (Figure 8b). A higher degree of surface modification is obtained when the immersion is carried out with ultrasonic treatment. However, the ATR-IR spectrum of the TR rubber immersed in the NOP + bleach (free active chlorine = 55.6 g/l) solution treated without ultrasonic treatment shows some amount of NOP (C–N stretching at 1645 cm^{-1}, C=O stretching at 1742 cm^{-1}, and C–H stretching at 2848 and 2920 cm^{-1}) and also evidence of chlorination (Figure 8b).

The SEM micrographs of the TR rubber immersed in NOP + bleach (free active chlorine = 55.6 g/l) mixture (Figure 9) show noticeable surface heterogeneity and round holes when no ultrasonication is performed. The treatment with the 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) solution with ultrasonication produces a relatively homogeneous, rough surface. Because of the immiscibility between the NOP and bleach, deposition of NOP on the TR rubber surface may be favoured. The deposition of NOP favours the local degradation of the TR rubber by creating holes. The effect is more marked when the 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture is not prepared in the ultrasonic bath.

Apparent surface pH values of about 9.5 were obtained on the TR rubber surfaces with or without ultrasonication; furthermore, a slight decrease in these pH values was noticed as the residence time of the water on the TR rubber surface was increased prior to pH measurement (*i.e.*, a pH = 8.5 was measured 1 h after placing the water drop on the treated TR rubber surface).

A noticeable increase in T-peel strength values of treated TR rubber/PUD adhesive/canvas joints (Table 7) (10–11 kN/m) and a cohesive failure in the TR rubber is obtained if the treatment is carried out in the ultrasonic bath by immersion for either 0.5 or 2 min. Lower

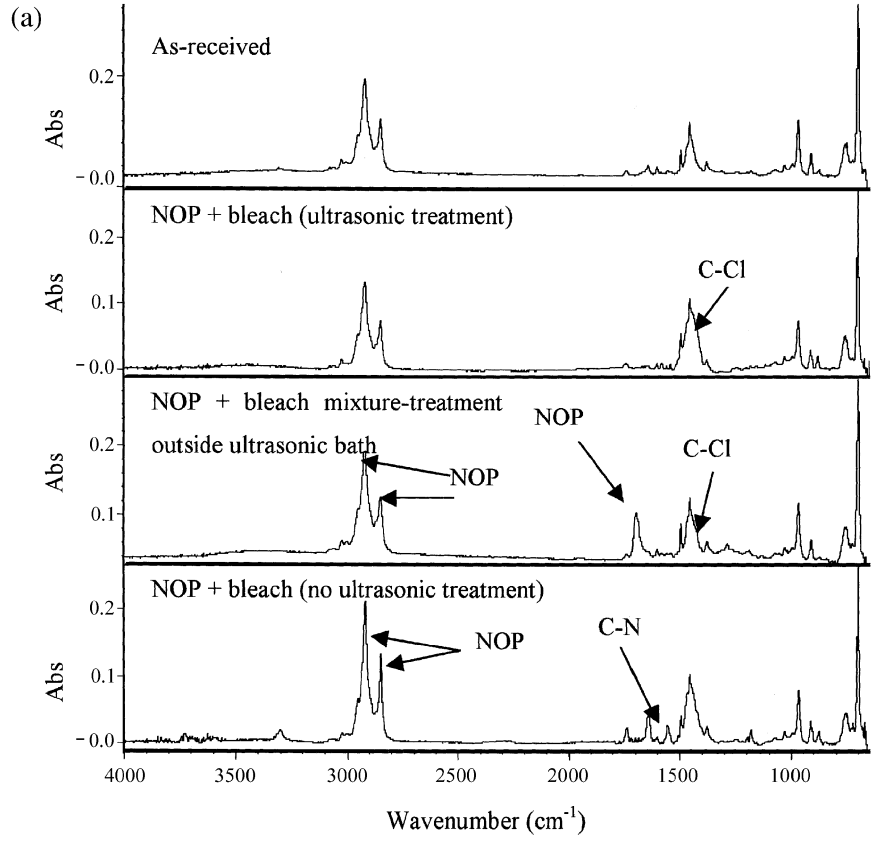


FIGURE 8 (a) ATR-IR spectra of the TR rubber as received and treated with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture with or without ultrasonic treatment, and by immersion in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) solution mixed in the ultrasonic bath. Immersion time (t_i) in the solution = 2 min. (b) Difference ATR-IR spectra of treated TR rubber with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture with or without ultrasonic treatment, and by immersion in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) solution mixed in the ultrasonic bath (with respect to the ATR-IR spectrum of the as-received TR rubber). Immersion time (t_i) in the solution = 2 min. (*Continued*)

adhesion is obtained when the immersion in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture is conducted without ultrasonic treatment, more markedly when the 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture is prepared outside the ultrasonic

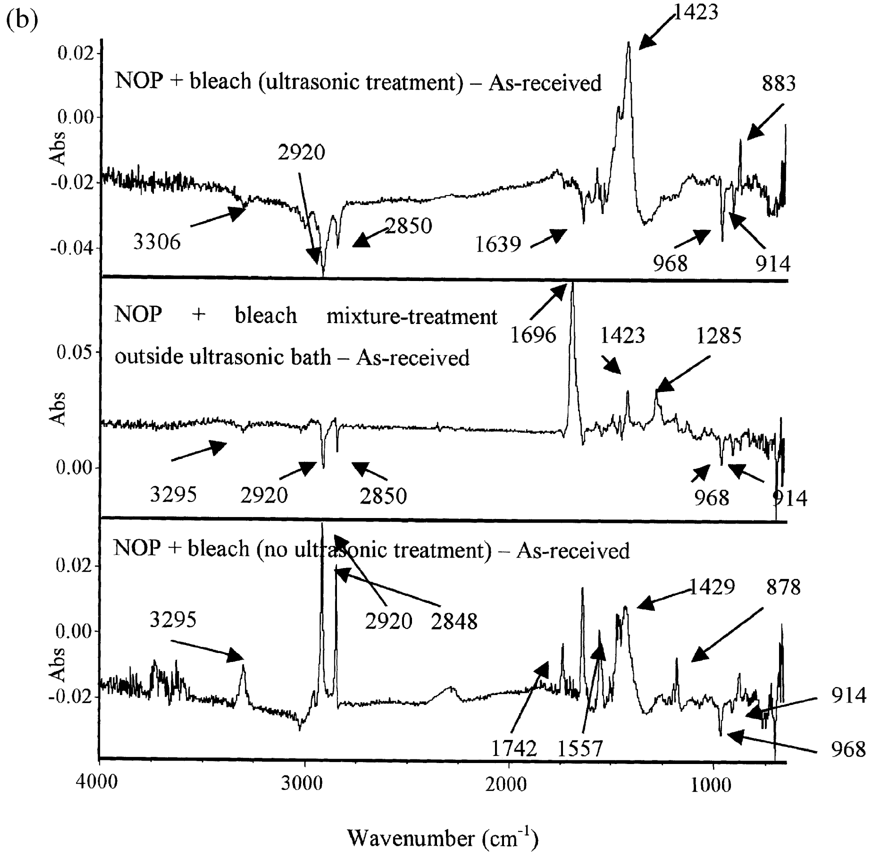


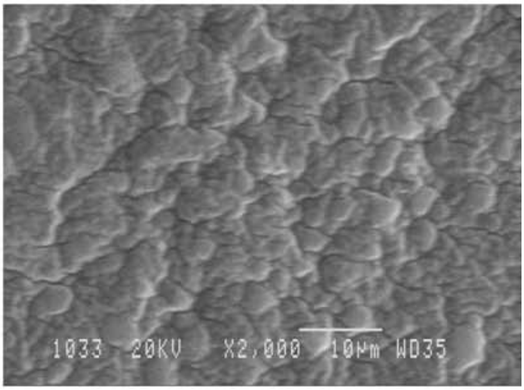
FIGURE 8 (Continued.)

bath. In those cases where the immersion in NOP + bleach (free active chlorine = 55.6 g/l) mixture is carried out outside the ultrasonic bath, the PUD adhesive does not wet the TR rubber surface, likely due to an excess of 1-octyl-2-pyrrolidone on the TR rubber surface, which should

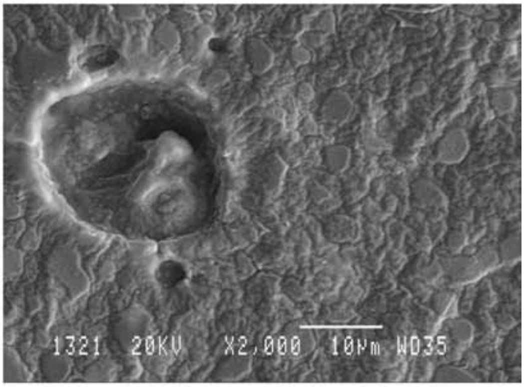
FIGURE 9 SEM micrographs of TR rubber treated with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture with or without the ultrasonic treatment, and by immersion in 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) solution mixed in the ultrasonic bath. Immersion time (t_i) in the solution = 2 min.

0.5 wt% NOP + Bleach solution

Ultrasonic treatment



Immersion in 0.5wt%
NOP + bleach solution
(mixed in the ultrasonic
bath)



No ultrasonic treatment

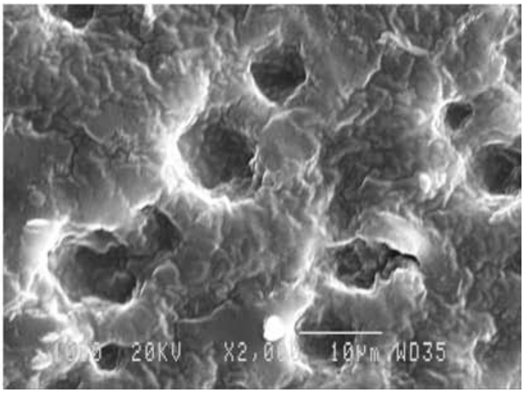


TABLE 7 T-peel Strength Values (kN/m) of As-received and 0.5 wt% NOP + Bleach (Free Active Chlorine = 55.6 g/l) Mixture (with or without Ultrasonic Treatment, and Immersion in a Solution Mixed in the Ultrasonic Bath) Treated TR Rubber/Polyurethane Adhesive/Canvas Joints

t_i(min)	Ultrasonic treatment (kN/m)	Immersion in a solution mixed in the ultrasonic bath (kN/m)	No Ultrasonic treatment (kN/m)
0	1.2 (A)	3.2 (A)	0.8 (A)
0.5	11.3 (M)	—	2.7 (A)
2	10.8 (M)	7.6 (75%A; 25%M)	5.0 (A)

t_i, influence of the immersion time in the 0.5 wt% NOP + bleach solution; A, adhesion failure; M, cohesive failure in the TR rubber.

be responsible for the decrease in adhesion. Therefore, segregation of the sparingly soluble NOP from the bleach mixture is likely responsible for the reduced adhesion. However, the control shows relatively higher peel strength (3.2 kN/m) likely due to mechanical interlocking between the PUD and the roughness on the TR rubber treated with 0.5 wt% NOP solution mixed in the ultrasonic bath.

The differences in peel strength values also determine the loci of failure of the joints. Table 7 shows the loci of failure of the joints obtained by visual inspection. When the immersion of the TR rubber is conducted without ultrasonic treatment, an adhesion locus of failure was obtained (one of the failed specimens corresponded to the rubber (R surface) and the other to the polyurethane (A surface)). In order to assess the loci of failure of the joints more precisely, ATR-IR spectroscopy was used. Figure 10 shows the ATR-IR spectra of the canvas and the polyurethane adhesive before the adhesive joint is produced. These ATR-IR spectra show different typical bands from those of the TR rubber surface, which could be used to assess the loci of failure in the joints. Thus, the ATR-IR spectrum of the PUD adhesive shows typical bands associated with the urethane groups at 3250 (N−H band), 1730 (NH−CO band) and 1595 (C−N band) cm^{-1}, whereas the ATR-IR spectrum of the TR rubber (Figure 2) shows the typical bands of styrene at 696 and 749 cm^{-1}, and butadiene at 968 cm^{-1}. The bands corresponding to the CH_2 and CH_3 groups are displaced about 15 cm^{-1} to lower wavenumber in the TR rubber with respect to the polyurethane. On the other hand, the ATR-IR spectrum of the canvas (Figure 10) shows bands associated with the hydroxyl groups at 3336 cm^{-1}, C=O stretching at 1652 cm^{-1}, $-CH_2$ deformation at 1427

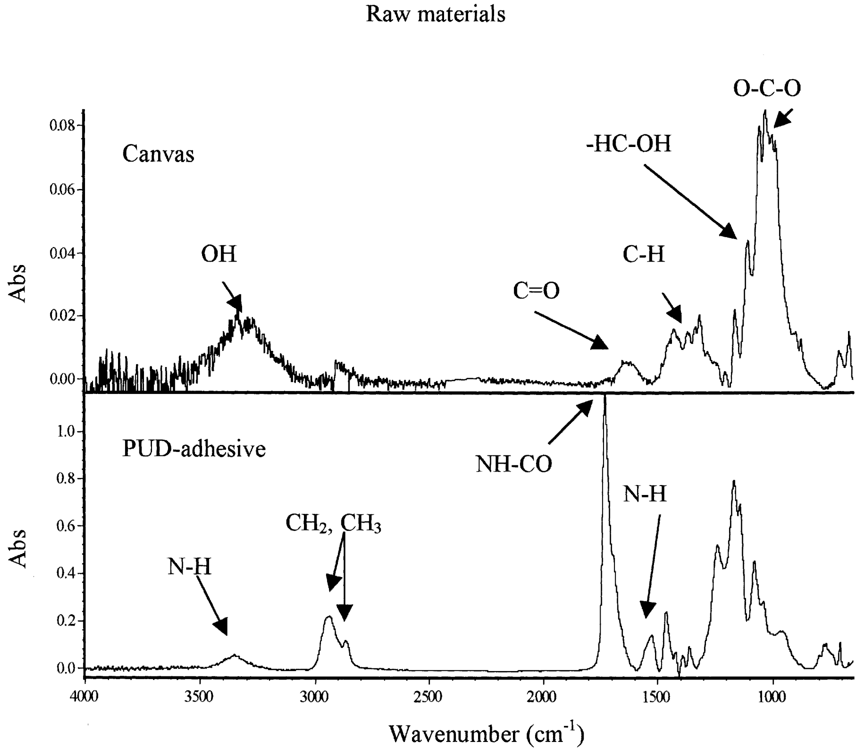


FIGURE 10 ATR-IR spectra of polyurethane adhesive and canvas.

and 1314 cm^{-1}, –HC–OH stretching at 1104 and 1161 cm^{-1}, and C–O–C stretching at 983 and 1029 cm^{-1}. All these bands are typical of cellulosic compounds.

Figure 11a shows the ATR-IR spectra of the failed surfaces corresponding to the isopropanol-wiped TR rubber/PUD adhesive/canvas joint peeled 24 h after bond formation. These ATR-IR spectra correspond to the ATR-IR spectrum of the TR rubber on one of the failed surfaces (R surface), and the ATR-IR spectrum of the other (A surface) exhibits bands corresponding to both the polyurethane adhesive and the TR rubber (968 cm^{-1}), indicating that the failure is mixed (*i.e.*, mainly adhesion failure but some TR rubber is found on the adhesive surface as a result of the peel test).

Figure 11b shows the ATR-IR spectra of the failed surface of 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) (without ultrasonic treatment) treated TR rubber/PUD adhesive/canvas joint. The ATR-IR spectrum of the failed A surface mainly shows the bands

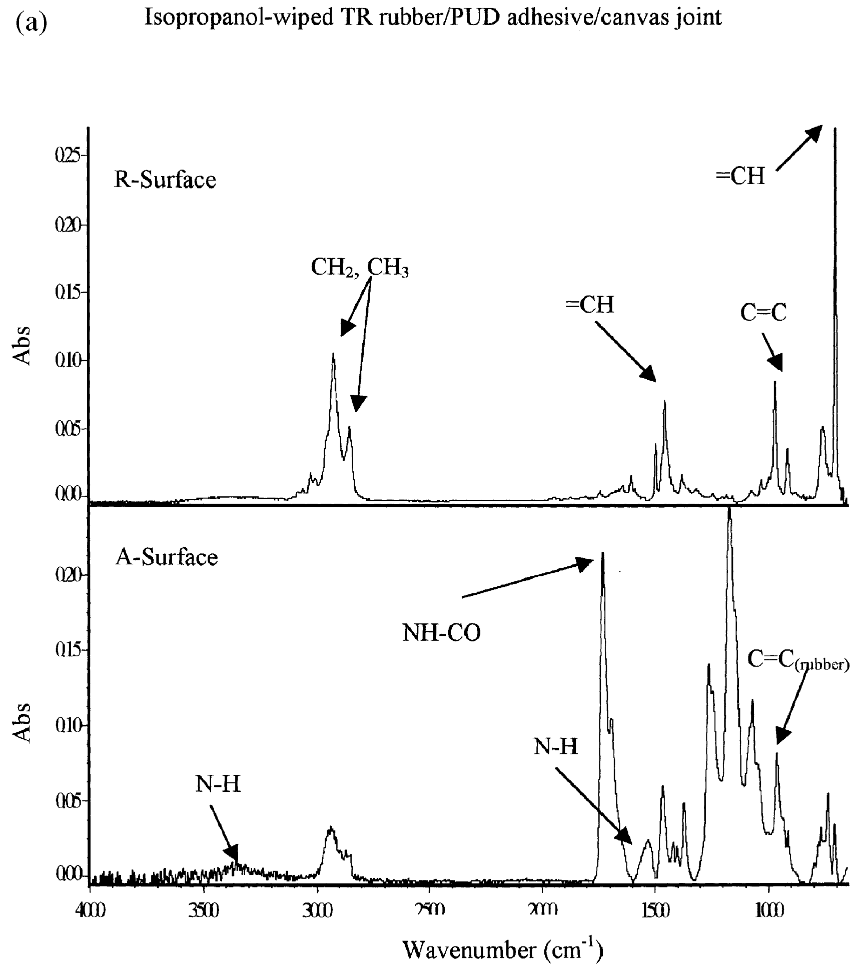
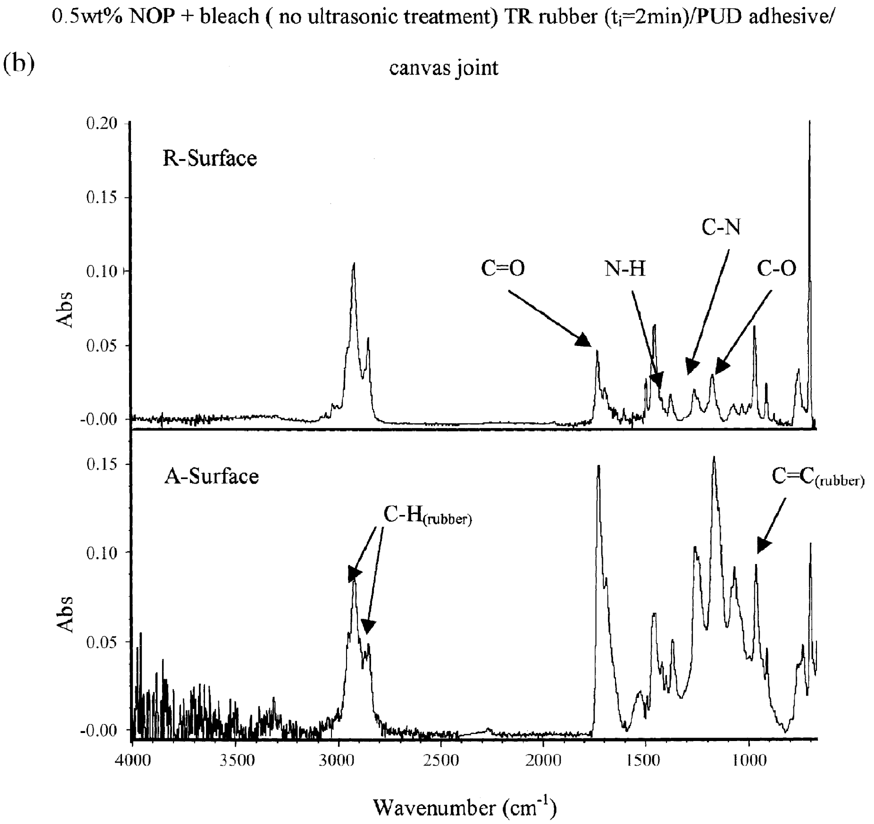


FIGURE 11 ATR-IR spectra of the failed surfaces of treated TR rubber/PUD adhesive/canvas joints (24 h after joint formation). Joints produced with: (a) Isopropanol-wiped TR rubber; (b) 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) (without ultrasonication) for $t_i = 2$ min.

corresponding to the PUD and a few bands due to the TR rubber (749, 968, 2850, and 2920 cm^{-1}). On the other hand, the ATR-IR spectrum of the failed R surface shows the bands due to the chlorinated TR rubber, to the PUD adhesive, and to the NOP at 1100–1200, 1265, 1690, and 1730 cm^{-1} (both the PUD adhesive and the NOP show



(b) 0.5wt% NOP + bleach (no ultrasonic treatment) TR rubber (t_i=2min)/PUD adhesive/ canvas joint

FIGURE 11 (Continued).

bands at similar wavenumber). These results are consistent with an adhesion failure with some cohesive failure in the PUD adhesive. The decrease in peel strength and the locus of the failure produced when the TR rubber is treated with the reagent mixture without ultrasonic treatment can likely be ascribed to a degradation of the PUD adhesive and the TR rubber by the remaining NOP on the treated TR rubber surface.

Consequently, the treatment with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture is more effective when it is applied with ultrasonic treatment, most likely because ultrasonication enhances the miscibility between the reagent components.

Active Chlorine Content in the Bleach

The active chlorine content of the bleach may determine the effectiveness of the surface treatment of TR rubber. In this section, the treatment of TR rubber with bleach containing different amounts of active chlorine was studied. Bleach containing 55.6 g/l active chlorine was mixed with deionized and bidistilled water in a 3:1 ratio (volume) to reduce the active chlorine content to 43.9 g/l. The treatment of the TR rubber by immersion for 2 min in the two bleach solutions was carried out using three different procedures:

1. Immersion in bleach without ultrasonic treatment.
2. Immersion in bleach with ultrasonic treatment.
3. Immersion in 0.5 wt% NOP + bleach mixture with ultrasonic treatment.

The reduction of the active chlorine in the bleach decreases the wettability of TR rubber (Table 8), independently of the procedure used to produce the treatment. Always, the contact angle values on the TR rubber treated with the bleach with high active chlorine (55.6 g/l) are low, especially when the treatment is carried out in absence of NOP and without ultrasonic treatment. On the other hand, the surface treatment of the TR rubber with bleach having 43.9 g/l active chlorine content shows a poor modification of the surface chemistry of the TR rubber (Figures 12a and 12b), *i.e.*, typical low-intensity band due to chlorination is found at 1418 cm^{-1} (Figure 12b). For all the procedures considered, the apparent pH on the TR rubber surface was about 8. On the other hand, Figure 13 shows that the decrease in the active chlorine content of the bleach produces less roughness. Finally, the T-peel strength values of treated TR rubber/PUD adhesive/canvas joints are lower when the treatment with 43.9 g/l active chlorine content bleach is carried out

TABLE 8 Equilibrium Contact Angle Values (Ethanediol, 25°C) on As-received and Bleach-treated TR Rubber, Influence of the Active Chlorine Content in the Bleach

Treatment	55.6 g/l (degrees)	43.9 g/l (degrees)
As received	77	77
Bleach $t_i = 2$ min (without ultrasonic treatment)	38	69
Bleach $t_i = 2$ min (ultrasonic treatment)	50	69
0.5 wt% NOP + bleach $t_i = 2$ min (ultrasonic treatment)	46	61

t_i, immersion time = 2 min.

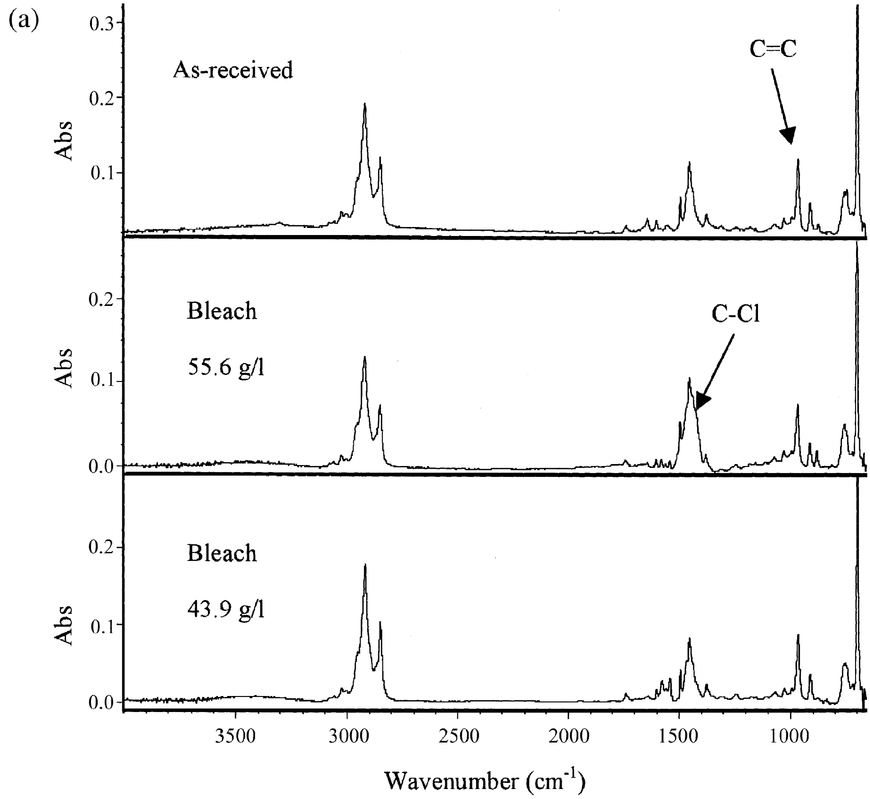


FIGURE 12 (a) ATR IR spectra of the TR rubber as received and treated with 0.5 wt% NOP + bleach (ultrasonic treatment). Influence of the active chlorine content in the bleach. Immersion time (t_i) in the solution = 2 min. (b) Difference ATR-IR spectra of treated TR rubber with 0.5 wt% NOP + bleach (ultrasonic treatment) (with respect to the ATR-IR spectrum of the as-received TR rubber).

(Table 9), and only when NOP is added to the reagent solution were somewhat higher adhesion values and a mixed failure (adhesion + cohesive failure in the TR rubber) obtained.

Therefore, the treatment with bleach having less active chlorine content (43.9 g/l) does not produce as significant modifications of the TR rubber surface, and the use of bleach with high active chlorine is mandatory to produce high adhesion of the TR rubber and to obtain a cohesive failure in the rubber.

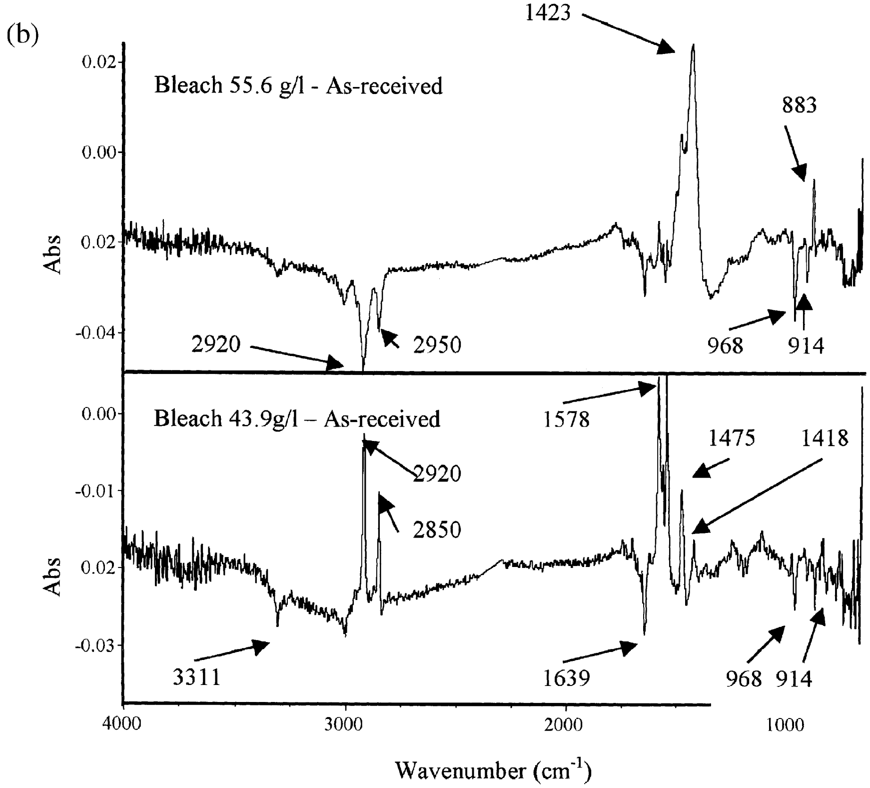


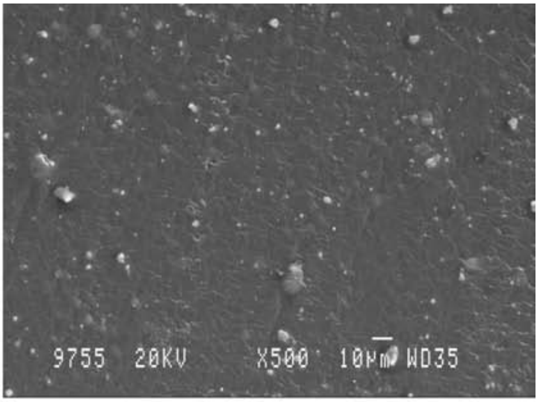
FIGURE 12 (Continued).

CONCLUSIONS

The treatment of TR rubber with bleach (free active chlorine = 55.6 g/l) produced an increase in wettability, which can be ascribed to the creation of C–Cl moieties in the hydrocarbon chains and to the creation of surface roughness. The treatment with bleach (free active chlorine = 55.6 g/l) produced a noticeable increase in T-peel strength values with cohesive failure in the rubber. The increase

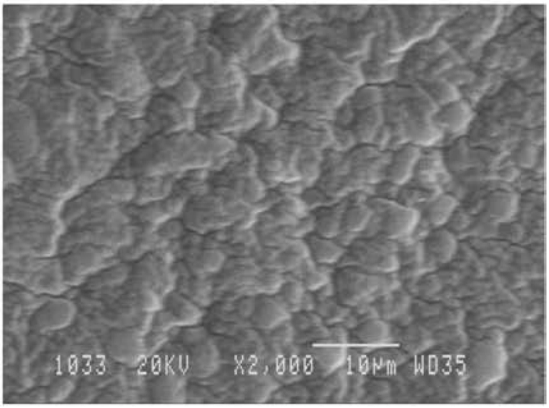
FIGURE 13 SEM micrographs of TR rubber as received and treated with 0.5 wt% NOP + bleach (ultrasonic treatment). Influence of the active chlorine content in the bleach. Immersion time (t_i) in the solution = 2 min.

As-received



Bleach

55.6 g/l



Bleach

43.9 g/l

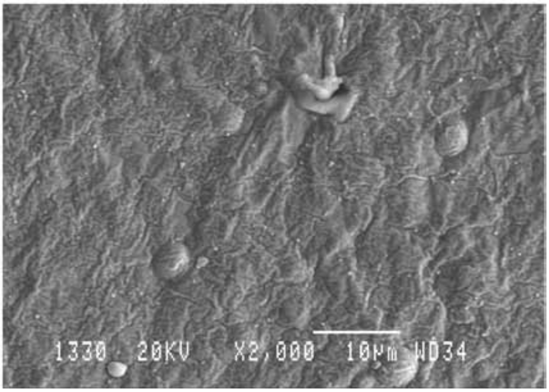


TABLE 9 T-peel Strength Values (kN/m) of As-received and Bleach-treated TR Rubber/Polyurethane Adhesive/Canvas Joints, Influence of the Active Chlorine Content in the Bleach

Treatment	55.6 g/l (kN/m)	43.9 g/l (kN/m)
As received	3.2 (A)	3.2 (A)
Bleach $t_i = 2$ min (no ultrasonic treatment)	12.3 (M)	3.3 (A)
Bleach $t_i = 2$ min (ultrasonic treatment)	10.5 (M)	3.5 (A)
0.5 wt% NOP + bleach $t_i = 2$ min (ultrasonic treatment)	10.8 (M)	7.4 (75% A; 25% M)

t_i, immersion time in bleach = 2 min: A, adhesion failure; M, cohesive failure in the rubber.

in the immersion time or the immersion of the TR rubber with or without ultrasonic treatment did not affect the adhesion.

On the other hand, the treatment with 0.5 wt% NOP + bleach (free active chlorine = 55.6 g/l) mixture produced high T-peel strength values in TR rubber joints, although the use of an ultrasonic bath to carry out the treatment was mandatory to enhance the miscibility of the reagent components and to avoid NOP deposition on the TR rubber surface; in this way, degradation of the rubber surface and/or the PUD adhesive after joint formation was prevented.

Finally, bleach having at least 55.6 g/l active chlorine content was critical to assure the effectiveness of the treatment and to produce a significant increase in adhesion of the TR rubber.

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