CHEMICAL MODIFICATION OF STYRENE-BUTADIENE-STYRENE COPOLYMER BY GRAFTING OF N-CARBAMYL MALEAMIC ACID

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Abstract

A styrene-butadiene-styrene (SBS) block copolymer was functionalized using different amounts of N-carbamyl maleamic acid (NCMA) and benzoyl peroxide as initiator. The NCMA, which is a bifunctional monomer, was synthesized in our laboratories. The concentration of NCMA used in the functionalization of SBS ranged from 0.5 to 3%w/w based on the copolymer mass. Benzoyloxy radicals generated from the thermal decomposition of benzoyl peroxide initiated the grafting reaction. The concentration of the initiator was kept constant at 0.076% w/w.

FTIR spectroscopy was used to determine the amount of NCMA effectively grafted onto the SBS. The maximum amount of monomer grafted was about 0.3%w/w when the SBS was modified with 1%w/w of NCMA. The effect of grafting on the surface properties and the adhesion to polyurethane adhesive of the modified SBS were evaluated. Contact angle values were obtained using liquid droplets. When the concentration of the NCMA used in the grafting reaction was 1% w/w, the contact angles with water on original and modified SBS were 95° and 77°, respectively. Adhesion properties were evaluated by standard peel tests employing a commercial polyurethane adhesive. The modified SBS having the largest amount of NCMA displayed a T-peel strength value five times larger than the corresponding value measured with the original SBS.

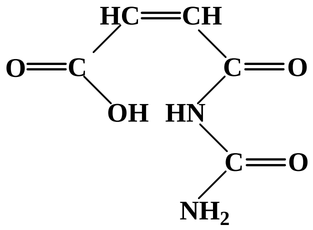
Keywords: Styrene-Butadiene-Styrene copolymers, Grafting, Contact angle, Peel strength.

1. INTRODUCTION

The incorporation of polar groups onto polymer chains by grafting monomers having C=C unsaturation constitutes a particularly effective method for modifying their properties [1]. Various types of monomers have been widely used for this purpose. Among them are maleic anhydride, acrylic and methacrylic acids and their ester derivatives, as well others containing hydroxide, nitrile or amide groups [2].

Styrene-butadiene-styrene (SBS) is a well-known thermoplastic copolymer having a blocky molecular structure. Its non-polar nature results in a material with low surface energy and poor adhesion properties. This is a disadvantage when this polymer is employed as sole material in the shoe industry, where it is necessary to bond it to other materials such as leather. In order to improve the quality of bonding of SBS to other materials, it is a usual practice to combine physical and chemical surface treatments. In a series of papers Martín-Martínez and co-workers. [3,4,5] have presented different surface modification methods, for improving the adhesive joint strength between synthetic vulcanized styrene-butadiene rubber and various adhesives. Jiang and Wilkie [6,7] studied graft copolymerization of methacrylic acid, acrylic acid and methyl acrylate onto styrene–butadiene block copolymers to make them polar in character. In a recent study Zhang and Chao [8] showed that maleic anhydride could be grafted onto SBS using benzoyl peroxide and 2,2’-azo-bis-isobutyronitrile as initiators. Sánchez Solís et, al. [9] studied the grafting of maleic anhydride onto SBS rubber initiated with peroxide to enhance the compatibility between SBS and poly(ethylene therephthalate) in order to improve the impact resistance of the blend. In a previous work [10] we showed that the grafting of maleic anhydride onto SBS improved the adhesive joint strength between SBS and polyurethane adhesive.

In this study, an SBS copolymer was functionalized with N-carbamyl maleamic acid (NCMA) with the aim to enhance its adhesion to polyurethane adhesive. This monomer, whose chemical structure is given in Scheme 1, has not been used for modifying SBS before. NCMA was chosen as the functionalizing agent because it contains two different functional groups, carboxylic (COOH) and amide ($CONH_2$), which offer a large number of bonding possibilities to polyurethane adhesive. In a previous work we grafted NCMA onto polyethylene using 2,5 dimethyl 2,5 diterbutyl peroxy hexane as initiator [11]. In the present work benzoyl peroxide was chosen as the initiator for the grafting reaction. According to the information available in the literature [6,8,12,13], the mechanism of reaction under the conditions adopted in this work should proceed by the formation of benzoyloxy radicals that remove allylic hydrogen from the polybutadiene blocks of the SBS. Then, the macroradicals generated in this reaction may be able to attack the NCMA, leading to its grafting onto the polymer chains. The results presented in this paper demonstrate successful grafting of NCMA onto SBS rubber and a significant improvement in the bonding of the modified material to polyurethane adhesive. The strength of the adhesion obtained with NCMA modified rubber was notably higher than that corresponding to unmodified SBS rubber.



Scheme 1. Molecular structure of NCMA.

2. Experimental

2.1. Materials

A radial block SBS copolymer (Finaprene 602) provided by Atofina Petrochemical (Belgium) was used. The polymer has a density of 0.96 g/cm^3 (ASTM D-297), and a styrene block content of 40%. The initiator employed to induce the grafting reaction was benzoyl peroxide (BPO) supplied by Sigma Chemical (St. Louis, MO, USA) and used without further purification. Maleic anhydride and urea were provided by Alfa Aesar (Ward Hill, MA, USA) and Anedra (Buenos Aires, Argentina), respectively; and they were used as received for the synthesis of NCMA.

A thermoplastic polyurethane adhesive (Desmocoll 540) supplied by Bayer (Germany) was employed to produce the adhesive joints for performing the adhesion tests. A solution of the adhesive was prepared by dissolving the polyurethane pellets in methyl ethyl ketone (MEK) to give a concentration of the polymer of 15% w/v.

2.2. Synthesis of N-carbamyl maleamic acid

The NCMA was synthesized from maleic anhydride and urea by thermal reaction following the procedure proposed by Paglialunga [14]. In brief, a mixture of maleic anhydride and urea was heated at 80°C under reflux for 30 minutes to induce chemical reaction. The NCMA was separated from the reaction mixture using hot ethanol. Then, the acid was purified by performing dissolution-precipitation sequences using ethanol as solvent. NCMA is a slightly yellow solid that melts at 155-156°C. It is barely soluble in water, but dissolves in hot ethanol and dimethylformamide (DMF).

2.3. Grafting Procedure

The reaction mixtures of SBS/NCMA/BPO were prepared on the basis of 100 g of SBS. The concentrations of NCMA employed were 0.5, 0.75, 1, 2 and 3% w/w, while the concentration of BPO was fixed at 0.076% w/w. The concentration of BPO was chosen considering previous works where we found that a concentration of about 3.15×10^{-4} moles of O-O peroxy groups per 100g of polymer produced the highest amount of maleic anhydride grafted onto SBS [10], and of NCMA grafted onto polyethylene [11].

Solutions of NCMA in DMF and of BPO in acetone were prepared to make the reaction mixture. The SBS and an aliquot of the solutions were put into contact in an amount sufficient to give the desired final concentrations of components after evaporation of the solvents (DMF and acetone). The grafting reactions were carried out using a Brabender Plastograph mixer equipped with a mixing chamber of 50 cm^3. The temperature of the mixer chamber was set to 145°C, the screw speed rotation was fixed at 40 rpm and the mixing time was seven minutes.

After the chemical reaction was completed, sheets of dimensions 150x150x1.5 mm were obtained by press molding the material between the plates of a hydraulic press at 130°C. Specimens were cut out from these sheets for performing contact angle measurements and peel tests as described below.

2.4. Characterisation of the grafted SBS

2.4.1. FTIR spectroscopy

To verify the grafting of NCMA onto the SBS by FTIR, it was necessary to remove all unreacted material and reaction by-products. For this purpose, about 1g of the grafted SBS was dissolved in 100 ml of toluene at room temperature and then precipitated in 800 ml of cold acetone. Then, the powdered precipitated sample was stirred in a solution of DMF for 2 hours at room temperature in order to extract the remaining by-products. Finally, the purified material was dried at room temperature under vacuum for 36 hours.

Attenuated total reflectance FTIR technique (ATR-IR) was employed to examine about 2 μm deep region from the surface of 0.5 mm thick sheets, which were obtained by compression moulding between steel plates using a hydraulic press at 130°C. A Nicolet FTIR 520 spectrometer was used for recording the ATR-IR spectra from 4000 to 400 cm^{-1} using a ZnSe crystal and an incidence angle of 33°. The same spectrometer was used for recording the FT-IR spectra of thin films of the original and the modified SBS samples using the transmittance mode. In order to avoid errors in the determination of the extent of grafting, the modified samples were purified to remove possible residues of unreacted NCMA as described above. The transmittance FT-IR spectra were also recorded from 4000 to 400 cm^{-1}. For the materials obtained using the lowest NCMA concentration, i.e., 0.5 and 0.75%w/w, it was not possible to ascertain the amount of monomer incorporated using the transmittance mode because the characteristic absorption bands of the NCMA groups were not noticeable in the spectrum.

2.4.2 Contact angle measurements

The differences in surface properties of grafted SBS with respect to ungrafted rubber were evaluated by measuring water contact angle. For this purpose the method based on the measurement of the dimensions of the water droplet resting on the surface of the material under study was employed [15,16,17]. The parameter measured was the contact diameter of a water drop of known volume resting on the surface of the grafted SBS. The contact angle was determined using the following equation [16,17]:

$$\frac{24\,V}{d^3} = \frac{\left(2 - 3\cos\theta + \cos^3\theta\right)}{\sin^3\theta} \qquad (1)$$

Here V and d are the volume and contact diameter of the drop, respectively, and θ the contact angle.

The surface of the SBS rubber sheets obtained by compression moulding was washed with DMF and isopropyl alcohol to remove the ungrafted residual NCMA and by-products. Specimens of size about 20 x 20 mm were cut out from the sheets where six bi-distilled 1μl water drops were placed on different locations of the specimen surface using a syringe. The specimens were maintained at 25ºC in an environmental chamber saturated with water vapor for 15 min before measuring the contact diameter of the drops to ensure equilibrium conditions. The contact diameters of the drops were measured using a Carl Zeiss Phomi III Pol microscope equipped with a JVC TV camera. The contact diameter of each drop was measured along several directions. Then, an average contact diameter was calculated for each drop that ranged from1.5 to 1.8 μm. The average contact diameter was used for calculating the water contact angle using equation (1) using volume of the drop of 1 μl. Each of the contact angles reported is an average of six measurements obtained as described before.

2.4.3. Peel Tests

Standards T peel tests were performed on specimens of the original and grafted SBS [18]. In preliminary peel tests, it was found that the applied force produced a large plastic deformation in the zone of specimens that was not part of the adhesive joint. In order to prevent this type of deformation a piece of cotton yarn fabric was bonded to the back of each of the SBS specimens prior to test. To do so, rectangular sheets of both the original and the modified SBS copolymer were laid on a clean piece of fabric, which was placed on the plate of a hydraulic press. Then, a slight pressure was applied on the layered assembly at 130°C to squeeze the polymer into the cloth yarn. This procedure allows a firm welding of the polymer to the fabric.

Rectangular specimens 20x100x1 mm in size were then cut from the sheets backed with the fabric. The fabric-free surfaces of the specimens were cleaned as described in the previous section. Then, about 0.8 ml solution of polyurethane adhesive was applied to each rubber surface. An open time of 30 minutes was allowed in order to facilitate evaporation of the solvent and to ensure a uniform wetting of the polymer surface. Then, the solidified film of the adhesive was melted and kept at about 100°C for 30 seconds. Immediately after that, the two polymer specimens were bonded under a compression pressure of 0.8 MPa, which was kept for 11 seconds. The adhesive joints were maintained at room temperature, about 23°C, for a period of 15 minutes. Finally, the peel tests were carried out using an Instron 1120 tester machine at a peel rate of 100 mm/min. The peel strength value reported here is the average of five measurements.

3. Results and discussion

Infrared spectroscopy is a valuable tool for the identification of grafted NCMA on

SBS polymer since it exhibits characteristic absorption bands corresponding to carbonyl, amide and amine groups which can be distinguished from those of the rubber. **Figure 1** displays the FTIR spectrum of pure NCMA that was recorded from a cast film on a KBr window. The two strong absorption bands centered at about 1650 -1690 cm^{-1} and 1710 cm^{-1} are assigned to the vibration of amide and acidic carbonyl groups (ν-C=O), respectively. In addition, absorption bands at 3200 and 3400 cm^{-1} corresponding to the vibration of the O-H group of the acid and the N-H stretching of the amide group, respectively, are also observed.

Figures 2a and 2b display different regions of the ATR-IR spectra of the original SBS, the SBS treated with BPO, and the SBS samples modified using different concentrations of NCMA as indicated beside each spectrum. These ATR-IR spectra were chosen as examples to illustrate the changes in the molecular structure of the SBS occurring after grafting. To allow a clear distinction of the differences between the spectra, they have been slightly shifted along the absorbance axis. According to Figures 2a and 2b, there are no differences in the characteristic bands between the ATR-IR spectra of the original SBS and that modified with BPO; therefore, the SBS polymer modified with BPO shows no evidence of the incorporation of new chemical groups. Carbonyl and hydroxyl groups in the 1700-1750 cm^{-1} and 3000 cm^{-1} ranges, respectively, do not seem to appear in detectable concentrations [19]. The presence of absorption bands corresponding to the NCMA in the purified grafted polymers confirms the grafting of the acid onto the SBS polymer. In the region from 1630 to 1780 cm^{-1} (Figure 2a), two bands centered at 1734 and 1660 cm^{-1} are clearly observed in the ATR-IR spectra of the grafted polymer samples that can be ascribed to the carbonyl group of carboxylic acid and the amide groups, respectively. Furthermore, the bands at 3400 and 3190 cm^{-1} in Figure 2b are attributed to the N-H stretching of the amide group of NCMA chemically grafted onto SBS chains [19].

The extent of grafting of NCMA, expressed as weight percent of grafting, was determined by analyzing the transmittance FTIR spectra of the modified polymers. The ATR-IR technique is not adequate for this purpose because there is no straight and simple relationship between the intensity of the absorption bands and the concentration of chemical species. The analysis was done by comparing the intensity of the absorption band at 3400 cm^{-1} with that at 1950 cm^{-1}, which is associated with an overtone of aromatic ring. The 3400 cm^{-1} /1950 cm^{-1} intensity ratio (A_{NH} /A_0) can be considered as a measure of the extent of grafting of the NCMA onto SBS polymer. The extent of grafting was converted into the amount of NCMA incorporated, expressed as weight percent, by using a calibration curve obtained from analysis of FTIR spectra of physical mixtures of SBS and NCMA. The mixtures were prepared by swelling a given amount of SBS in a solution of NCMA in DMF in an amount sufficient to give the desired concentrations of NCMA in the polymer after evaporation of DMF. The concentration of NCMA in the physical mixture varied from 0.05 to 1%w/w. Thin films of the mixtures were prepared by compression molding at 145°C and, then used to obtain the transmittance FTIR spectra. The spectra of the physical mixtures display absorption bands associated with the NCMA groups as well as those characteristics of the SBS polymer. The amount of NCMA grafted onto the SBS was deduced from the relationship between the A_{NH}/A_0 ratio and the NCMA concentration presented in **Figure 3**. The solid line in **Figure 3** represents the best linear fit to the measured values**.** **Table 1** compares the amount of NCMA added to the polymer during the grafting procedure with that effectively grafted as determined from the transmittance FTIR analysis. The best graft yield was obtained by adding

1%w/w NCMA to the reaction mixture that produced a material with about 0.3%w/w of NCMA effectively grafted onto the polymer. The bands associated with the NCMA were not detected in the transmittance FTIR spectra of the samples modified with acid concentrations lower than 1%w/w. Thus, for those samples it was not possible to determine the amount of grafted monomer. There is a reduction in the amount of NCMA grafted onto the polymer when concentrations higher than 1%w/w were employed. Therefore, the amount of NCMA that can be chemically grafted onto the polymer chains is limited. It is often found [10,20,21,22,23] that the dependence of graft yield on the monomer concentration either reaches a limiting value or passes through a maximum, as it is observed in the case studied here. For instance, Huang et. al. [20] noted the same trend in the graft yield with the monomer concentration when grafting long-chain unsaturated carboxylic acid onto polypropylene. They postulated that there might be insolubility of the monomer in the molten polymer during the grafting process. In addition, they also considered that when increasing the monomer concentration, the possibility of primary radicals reacting with the polymer chains is reduced. Shi et. al. [21] and Rätzsch et. al. [22] also found a maximum in the amount of maleic anhydride grafted onto polypropylene when the concentration of the monomer was increased.

When low concentrations of NCMA, such as 0.5 and 0.75 % w/w, were used the quantity of NCMA effectively attached onto SBS was undetectable by transmission FTIR measurements. However, distinctive peaks characteristic of the NCMA grafting were distinguished in the ATR-IR spectra as shown above. A plausible explanation for this is that the grafted groups may preferably concentrate on the surface of the SBS specimens [10].

Both water contact angle and peel strength values depend on the changes in the surface energy of the SBS rubber after grafting. As these parameters may also be affected by the roughness of the surface, we compared the topography of the original and modified SBS surfaces by scanning electron microscopy (SEM). In all cases the surfaces were smooth, without noticeable differences between the topographical details of the original SBS and that grafted with NCMA. Then the variations observed in the contact angle measurements and in the peel tests should be attributable to the NCMA grafting. The contact angles reported in **Table 2** show a high water contact angle for the original SBS polymer, indicating a poor wettability and a relatively low surface energy. Following grafting with concentrations of NCMA up to 1% w/w, a decrease in the water contact angle from 95 to 77 degrees is obtained. This indicates improved wettability and an increase in the polymer surface energy due to the presence of polar chemical moieties on the surface. The water contact angle followed a trend with the concentration of NCMA that was in accordance with the amount of monomer effectively incorporated into the polymer. That is, the contact angle passes through a minimum value at about the same concentration that the amount of NCMA effectively incorporated onto the polymer reaches a maximum value.

The modification in surface chemistry and wettability in the grafted SBS rubber also affects the peel strength values of SBS / polyurethane adhesive joints. The peel strength values obtained 15 minutes after joint formation are also reported in **Table 2.** The results show that the adhesion strength produced with the ungrafted SBS rubber is relatively low (530 N/m). The improvement in adhesion properties by NCMA grafting of SBS is significant. As the concentration of NCMA is raised to 1%w/w, the peel strength increases about five times the value measured for the joint produced with the original SBS. This is a significant improvement compared with our previous work, where maleic anhydride was used as the grafting agent for modifying SBS [10]. In that case, the peel strength barely reached a maximum of 1.8 times the value measured for original SBS/polyurethane adhesive joint tested 72 hours after its formation. The relative increment in the peel strength values of the joints produced with the SBS modified with NCMA is similar to that observed when a SBS polymer was surface treated by halogenation [24].

NCMA concentrations higher than 1%w/w do not produce such a high improvement in peel strength, which is in agreement with the dependence of both contact angle and amount of NCMA grafted with the concentration of NCMA used for modifying the SBS.

All adhesive joints exhibited an interfacial failure (adhesion failure), i.e., the joint failed at the interface between the adhesive and the SBS polymer surface. We analyzed the surface of the modified SBS by ATR-FTIR once the adhesive layer was removed using MEK. We intended to identify the presence of new chemical groups that could be formed after a plausible reaction between the polyurethane and NCMA groups of modified SBS. The results gave no evidence of occurrence of such reaction. Therefore, the observed increments in the peel strength of the joints compared to that formed with the original SBS are probably attributable to physical interactions (i.e. hydrogen bond) between the adhesive and modified polymer.

4. Concluding Remarks

In this study, an interesting and simple procedure to increase the adhesion of SBS rubber to polyurethane adhesive is proposed. The particular feature of this process is the use of a novel bifunctional monomer such as NCMA as the grafting agent. ATR-IR and transmittance FTIR spectroscopies demonstrate that NCMA was successfully grafted onto the SBS polymeric chains.

The optimal concentration of NCMA, which ensures not only the maximun graft yield but also the optimum surface properties, is found to be about 1%w/w. The T-peel strength value of SBS/polyurethane adhesive joints reaches the highest value when 1%w/w of NCMA is added for modifying the SBS. The peel strength measured for adhesive joints made with grafted SBS is about five times larger than the value obtained for the original SBS. NCMA is a better adhesion promoter for SBS rubber than maleic anhydride. Additional studies considering the effects of other experimental variables, such as the type and concentration of initiator, on the extent of grafting on SBS polymer are underway.

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FIGURE CAPTIONS

Figure 1. FTIR spectra of pure NCMA in the region between 3800 and 600 cm^{-1}

Figure 2a. ATR-IR spectra in the region between 2000 and 1500 cm^{-1} for the original SBS, the SBS modified with 0.076%w/w of BPO, and the SBS modified with the concentration of NCMA indicated beside each curve.

Figure 2b. ATR-IR spectra in the region between 3900 and 3100 cm^{-1} for the original SBS, the SBS modified with 0.076%w/w of BPO, and the SBS modified with the concentration of NCMA indicated beside each curve.

Figure 3. Absorbance ratio (A_{NH}/A_0) as a function of the concentration of NCMA in the physical mixture with SBS. The solid straight line represents the best linear fit to the experimental data that were used for determining the weight percentage of grafted NCMA. The equation and residual sum of squares of linear fit are, $y=0.23\ x$ and $8.3\ 10^{-4}$, respectively.

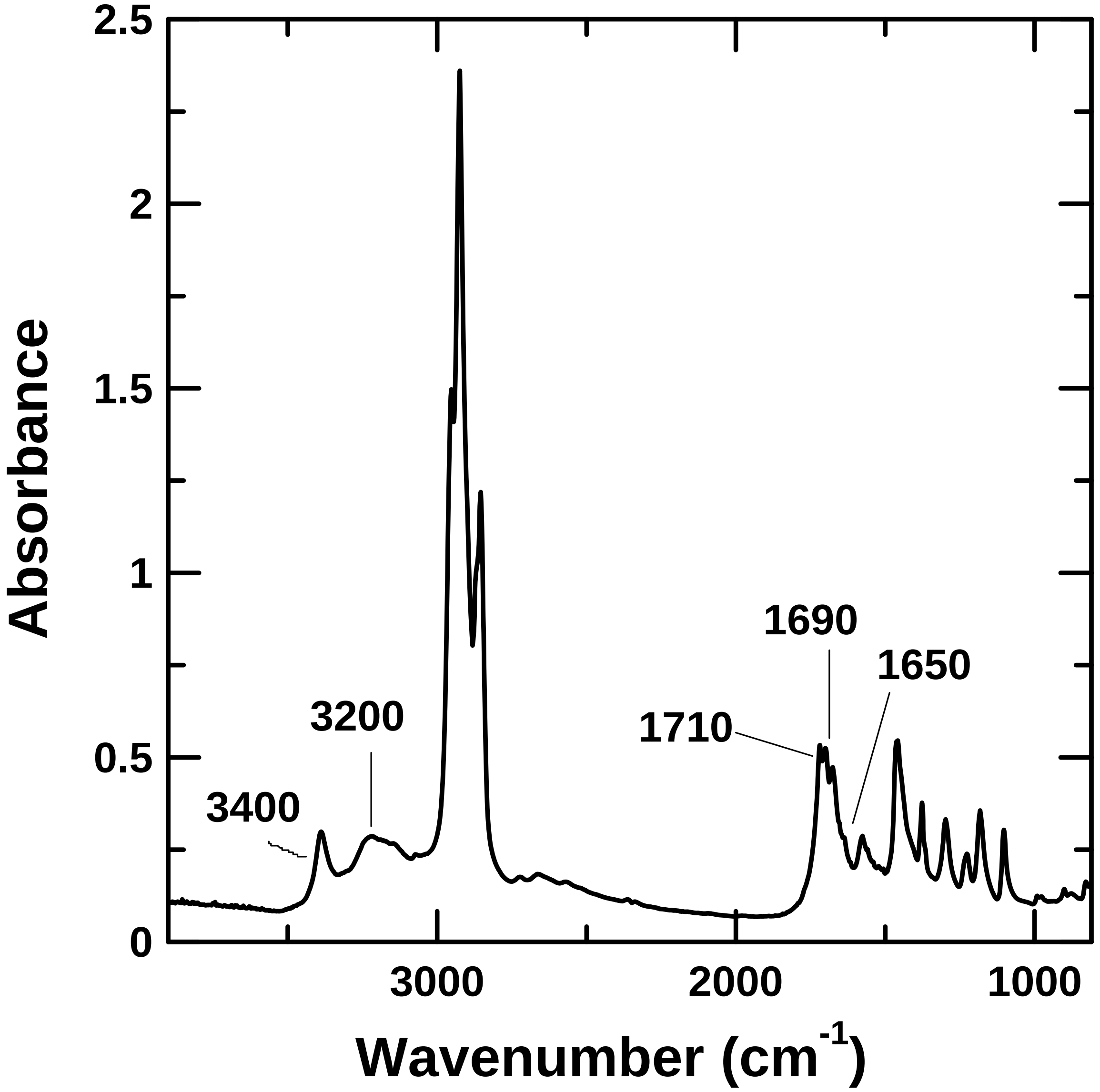

Figure 1

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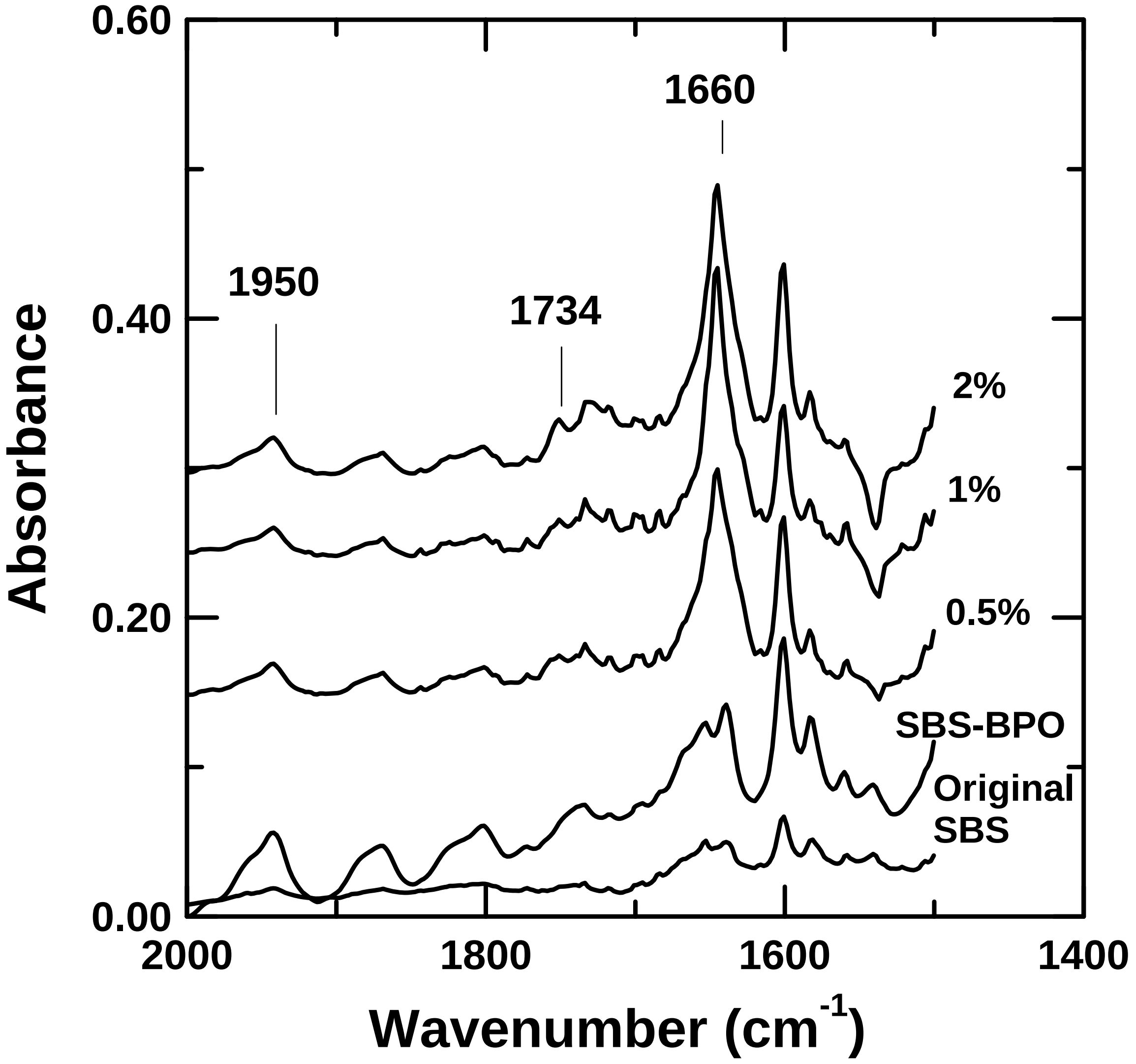

Figure 2a

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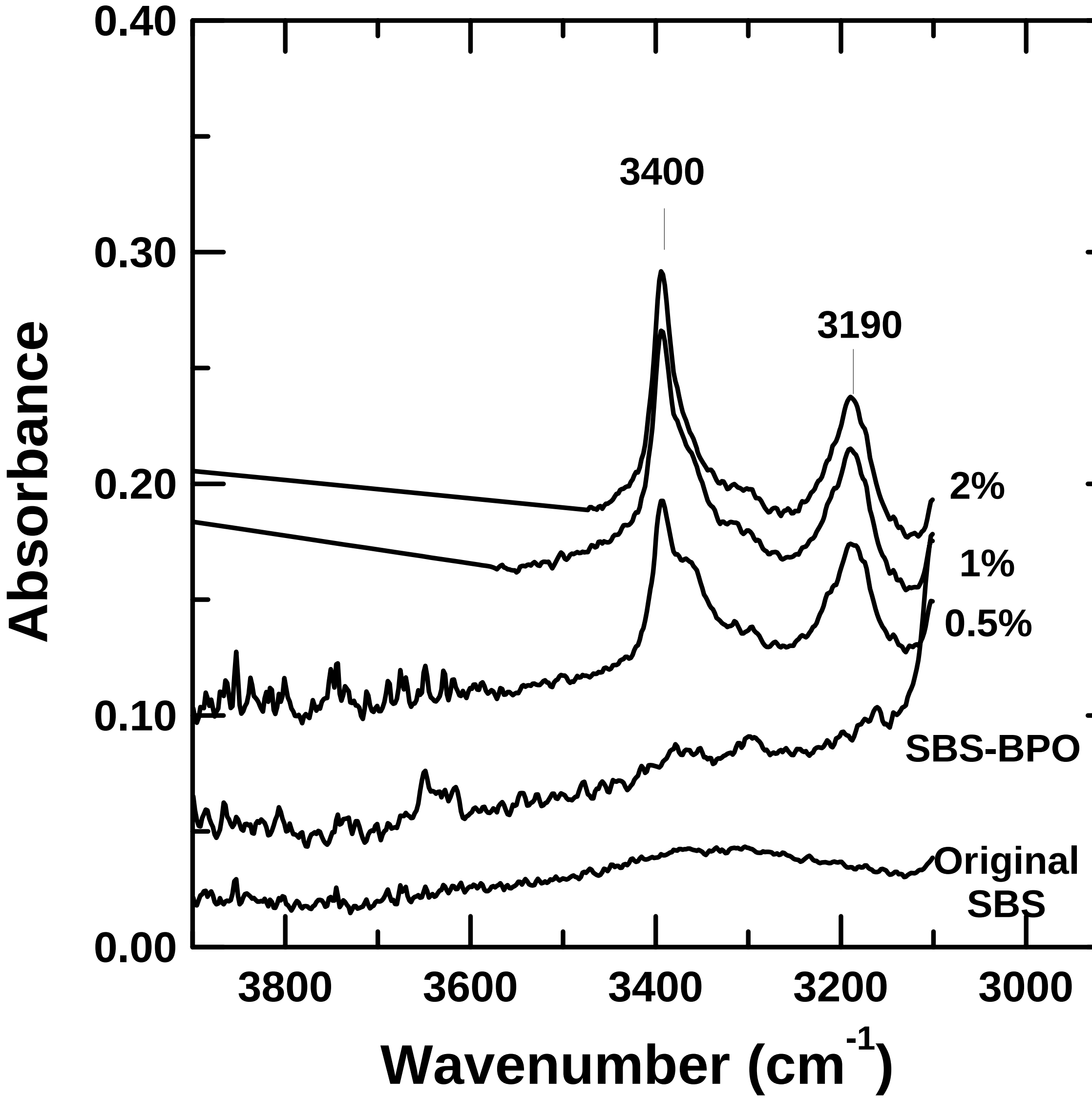

Figure 2b

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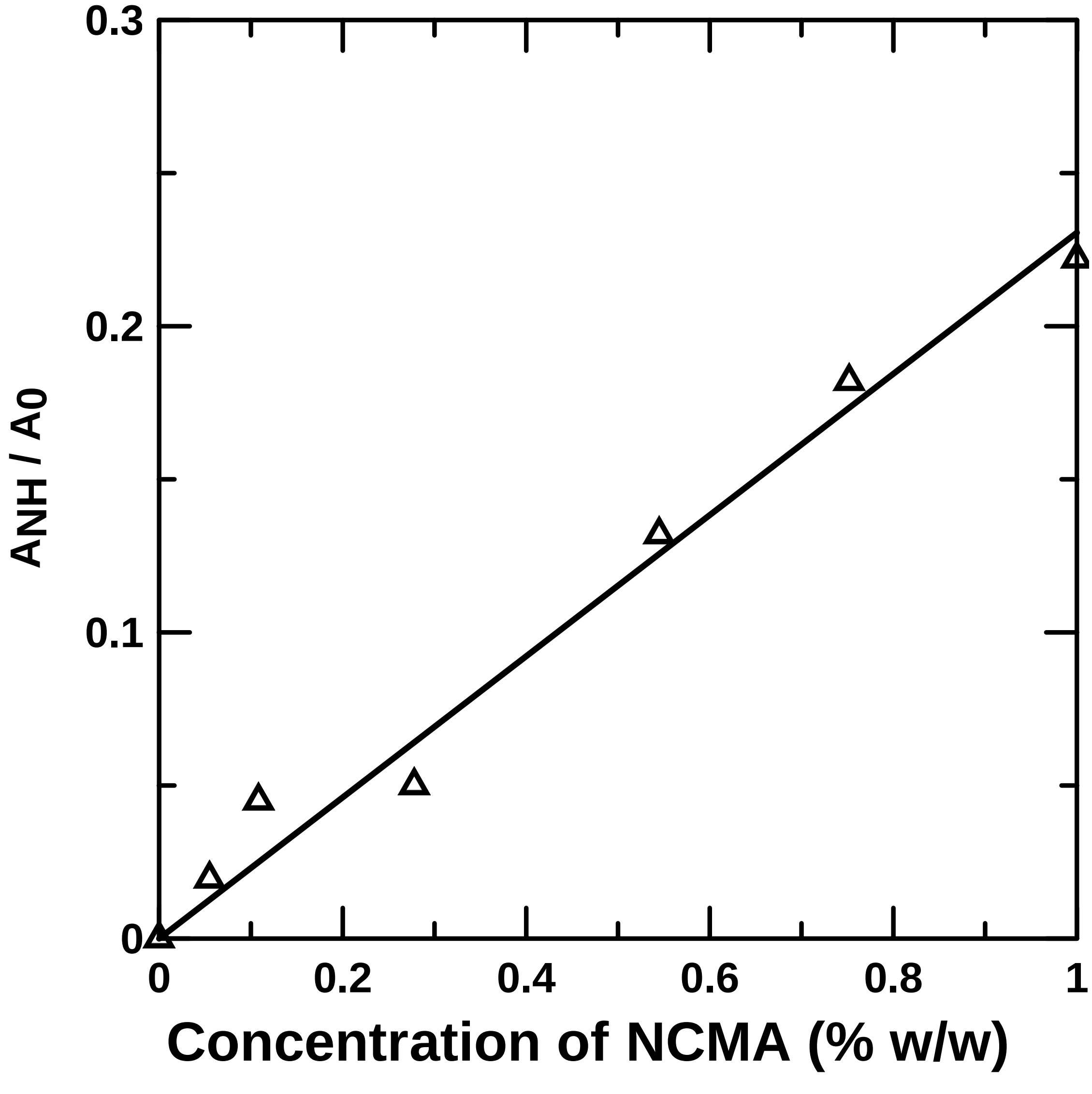

Figure 3

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Table 1- Amount of grafted NCMA, expressed as weight percent, obtained from

transmittance FTIR analysis as a function of the concentration of NCMA used in the modification.

Concentration of NCMA (%w/w)	**A_{NH}/A_0(*)**	**Grafted NCMA (%w/w)**
0.50	**Not detectable**	**-**
0.75	**Not detectable**	**-**
1.0	**0.08**	**0.35**
2.0	**0.07**	**0.29**
3.0	**0.04**	**0.16**

(*) A_{NH} corresponds to the absorbance of amide group at 3400 cm^{-1} of the NCMA, and A_0 is the absorbance of the reference band at 1950 cm^{-1}, which is assigned to overtones of styrenic ring.

Table 2. Water contact angle, θ, and T-peel strength values of SBS/polyurethane adhesive joints as a function of the concentration of NCMA used in the modification.

Concentration of NCMA (%w/w)	θ (Degrees)	T-Peel Strength (N/m)
0	95	530
0.5	87	740
0.75	89	1340
1.0	77	2570
2.0	79	2350
3.0	86	--