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A study on the grafting of N-Carbamyl Maleamic acid onto a Styrene-Butadiene-Styrene Copolymer

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Abstract

A Styrene-butadiene-styrene block copolymer (SBS) was functionalized with N-carbamyl maleamic acid (NCMA) using two peroxide initiators with the aim of grafting polar groups onto the molecular chains of the polymer. The influence of the concentration of benzoyl peroxide (BPO) and 2,5-dimethyl, 2,5-diterbutylperoxy-hexane (DBPH) was studied. The concentration of peroxy groups ranged between 0,75 and 6×10^{-4} mol% while the concentration of NCMA was constant at 1 wt%. The reaction temperature was chosen according to the type of peroxide employed, being 140°C for BPO and 190°C for DBPH. FTIR spectra confirmed that NCMA was grafted onto the SBS macromolecules. It was found that the highest grafting level was achieved at a concentration of peroxy groups of about 3×10^{-4} mol%.

Contact angle measurements were used to characterize the surface of the SBS and modified polymers. The contact angle of water drops decreased with the amount of NCMA grafted from 95°, the one corresponding to the SBS, to about 73°. T-peel strength of polymer/polyurethane adhesive/polymer joints made with the modified polymers was larger than those prepared with the original SBS. The peel strength of SBS modified with 1.5 and 3×10^{-4} mol% of peroxy groups from BPO were five times larger than that of the original SBS. The materials modified using BPO showed peel strengths higher than the ones obtained with DBPH.

Keywords: Styrene-Butadiene-Styrene copolymer, grafting, contact angle, peel strength

1-Introduction

Block copolymers of Styrene-Butadiene-Styrene (SBS) constitute an important class of thermoplastics elastomers widely used in the rubber-industry due to their ability to combine both elastic and thermoplastic properties. The rather non-polar nature of these copolymers leads to materials with low surface energy and poor adhesion properties. This causes problems in some applications, especially in those where SBS compounds must be glued to other materials.

Several methods are used to promote adhesion and to improve peel and tack properties on these copolymers. The incorporation of polar moieties is one of the methods most frequently employed. This can be done by applying different approaches, for instance, Steinkamp and Grail added maleic anhydride onto several polymers, including SBS, without using chemical initiators.¹ Martín Martínez and co-workers used different surface treatments to modify the chemical characteristics of SBS surfaces.²⁻⁶ In one study, they exposed SBS surfaces to the combined action of ozone and UV radiation. They observed the generation of C=O and COO⁻ moieties on the rubber surface that induce some hydrophilicity on the polymer.² In other studies, the surface of raw and vulcanized SBS copolymers was treated with trichloroisocyanuric acid solutions.³⁻⁵ It was also shown that, under certain experimental conditions, the chlorination produced a noticeable increase in the peel strength of SB surfaces. This was attributed to the formation of C-Cl and C-O linkages, and heterogeneities on the surfaces as well, which favour the mechanical interlocking between the adhesive used and the rubber surface. In addition, three thermoplastic SBS having different styrene content were treated with sulphuric acid with the aim of improving the peel strength of polymer/polyurethane joints.⁶

Other well-known methods used for incorporate functional groups onto macromolecules are based on grafting reaction where partake a polymer, a polar monomer, and a free radical initiator.⁷ In particular, the grafting of diverse monomers onto styrene-butadiene copolymers initiated with radicals has been extensively studied. The improving in the inherent properties depends mainly on the amount of monomer incorporated, but it may also depends on the way that it is grafted to the backbone, for instance as an isolate unit or in block. This, in turn, is affected by a combination of factors such as type and concentration of monomer and initiator, reaction media, reaction time, temperature, among others.⁷ Fischer and Hellmann grafted methyl methacrylate and cyclohexyl methacrylate onto polybutadiene blocks of SB copolymers using benzoyl peroxide (BPO) as initiator.⁸ The modified copolymers were used to compatibilize blends of polystyrene and polyvinylchloride. Jiang et al. studied the grafting reaction of methyl methacrylate onto SBS in solution using either BPO or azo-bis-isobutyronitrile (AIBN) as initiators.⁹ The amount of graft depends upon the time and temperature of the reaction, the concentrations of all the reactant species, the type of initiator and the type of solvent if the reaction is performed in solution. Zhang et al. studied the grafting reaction mechanism of maleic anhydride (MA) onto SBS in presence of BPO or AIBN as initiators.¹⁰ Lee and co-workers used BPO as initiator for grafting N-isopropylacrylamide on SBS to enhance the water absorptivity and thermosensitivity of the polymer.¹¹ They found that the amount of monomer grafted depends on the concentration of species and on the temperature and reaction time. Applying reactive processing in the molten state Cordella and co-workers modified a SBS copolymer with glycidyl methacrylate using dicumyl peroxide as initiator. They studied the effect of concentration of monomer, initiator and reaction time on grafting.¹² In a previous work MA was grafted onto a SBS by the reactive processing method. The effect of the concentration of MA and of the

peroxide initiator, 2,5-dimethyl-2,5 di(tertbutylperoxy) hexane (DBPH), was analysed.¹³ The maximum grafting level was reached when 2 wt% of MA and 0.05 wt% of DBPH were employed. In other study N-carbamyl maleamic acid (NCMA) was grafted onto a SBS using various concentrations of the acid while keeping constant the concentration of BPO.¹⁴ In this case the maximum amount of monomer grafted was observed at a concentration of 1 wt% of NCMA. The grafting with both functionalising agents resulted in a noticeable enhancement of the adhesive strength of rubber/ polyurethane adhesive/ rubber joints.^{13,14}

In this work we extend our previous studies on the modification of SBS copolymers by examining the grafting reaction with NCMA in the presence of different concentrations of either BPO or DBPH to enhance the wettability and adhesive properties of the SBS. The peroxide concentration was chosen to give concentrations of peroxy groups ranging between 0,75 and 6×10^{-4} mol% based on the mass of polymer. The concentration of NCMA was kept constant at 1 wt% because, in our previous study, the largest amount of NCMA grafted onto the SBS was achieved using that concentration.¹⁴ There exist a large volume of information in the literature on the use of BPO as initiator of grafting reactions in polybutadiene and polybutadiene block copolymers. However, to our knowledge, there are not published articles reporting the use of DBPH as initiator of grafting reactions on SBS copolymers.

The present work demonstrates the successful grafting of polar moieties onto SBS when the reaction is initiated either with BPO or DBPH by applying a reactive processing method. As consequence, the peel strength of adhesive joints formed with the modified materials is significantly enhanced.

2. Experimental

2.1. Materials

A commercial block SBS copolymer, Finaprene 602, provided by Atofina Petrochemical (Belgium) was used. According to the manufacturer, the copolymer has a styrene content of 40 %. Benzoyl Peroxide (BPO) was supplied by Sigma Chemical and 2,5-dimethyl-2,5 di(tertbutylperoxy hexane (DBPH) was kindly provided by Akzo-Nobel Química S.A. from Argentina. Both peroxides were used as received without performing any further purification. Solutions of 0.25 wt% BPO in acetone and 0.52 wt% DBPH in n-hexane were prepared for handling the initiator.

Maleic anhydride, from Alfa Aesar (Ward Hill, MA, USA) and urea, from Anedra (Argentina), were employed as received to synthesize the NCMA following the method proposed by Paglialunga et al..¹⁵ In brief, a mixture of maleic anhydride and urea was heated to 80 °C under reflux for 30 min to induce the chemical reaction. Then, the NCMA was isolated from the reactive mixture using hot ethanol. After that, the acid was purified performing sequences of dissolution-precipitation 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). The scheme 1 shows the molecular structure of NCMA.

2.2 Grafting Procedure

Reactive mixtures of SBS/NCMA/peroxide were prepared on the basis of 100 g of SBS. A solution of NCMA in DMF was added to 36 g of SBS in an amount to give a concentration of NCMA of 1 wt% after evaporation of DMF. Then, an aliquot of a solution

of initiator, either BPO in acetone or DBPH in hexane, was added to the mixture in such proportion to give the desired concentration of peroxy groups after the evaporation of the solvents. Thus, the concentration of peroxy groups in the polymer was 0.75, 1.5, 3 or 6 $\times 10^{-4}$ mol%.

Depending on the initiator, different procedures were followed for grafting NCMA. The total reaction time and the reaction temperature were designed to assure complete reaction. When BPO was employed, the reactive mixture was intensively mixed in a Brabender Plastograph equipped with a mixing head of 50 cm³ of capacity. In this case, the grafting reaction was performed at 140 °C using a speed of blade rotation of 40 rpm. The reaction was allowed to proceed for 7 min. According to the information supplied by the manufacturer the half-life of BPO at 140 °C is approximately 30 s. Therefore, the time allowed for the grafting reaction was about 14 times the half-life of the peroxide to assure a complete decomposition of the initiator. After the reaction, the polymer was extracted from the mixing head and compression molded to sheets of 150x150x1.5 mm using a hydraulic press at 130 °C.

In the case of DBPH, the Brabender mixer was used to promote the mixing of the reactants, which was performed for 5 min at 130 °C using a speed of 40 rpm. Since the half-life of the initiator at 130 °C is about 1.5 hs, it is expected that a minimal quantity of DBPH decompose during this step. After the homogenization, the mixture was compression molded to sheets of 150x150x1.5 mm between the plates of a hydraulic press at 190 °C. Under this static condition, the reaction was allowed to proceed for 20 min to assure a complete decomposition of DBPH at 190 °C and, also, equivalent reaction time with respect to the used for the BPO.¹⁶ The modification reaction was not performed directly into the mixer at 190 °C because under this condition the DBPH generates a highly

crosslinked material. Thus, this material cannot be processed further in order to mould sheets for either measuring contact angle or peel strength.

2.3 Sample Purification

To verify the grafting of NCMA, it was necessary to eliminate all the unreacted chemicals and by-products of the reaction from the bulk of the modified polymers. Thus, when BPO was used as initiator, 1 g of material was dissolved in 100 ml of toluene at room temperature and then precipitated in 800 ml of cold acetone. The resultant powdered sample was stirred in a solution of DMF for 2 hs at room temperature. Finally, the material was dried at room temperature under vacuum for 36 hs.

Since a crosslinked material was generated when DBPH was used, the modified polymers were purified by Soxhlet extraction with DMF at 150°C during 48 hs. After this period of time, the materials were dried at room temperature under vacuum for 36 hs. The materials obtained after the purification process are identified in the paper as SBS-g-NCMA.

2.4. Characterization

2.4.1 FTIR spectroscopy

The evidence of grafting was determined by analysis of FT-IR spectra of the SBS and modified polymers. A Nicolet FTIR 520 spectrometer was used for recording transmission IR spectra on films of the materials in the range of 4000 – 400 cm^{-1} . The films with thickness of about 0.5 mm were prepared by compression molding using a hydraulic press set at 130 °C.

2.4.2. Contact Angle measurements

The contact angle of water droplets on the surface of the materials was obtained following the method of the drop dimensions.¹⁷⁻¹⁹ This procedure estimates the contact angle by measuring the contact diameter of a water droplet of known volume laying on the surface of the material. The following relationship is applied:

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

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

In order to obtain θ , the surface of the materials sheets obtained by compression moulding was washed with isopropyl alcohol to remove any residue arising from the moulding process. Then, specimens of about 20 x 20 mm were cut out from the sheets where six drops of 1 μ l of bi-distilled water were placed on different locations of the surface by means of a micro-syringe. To ensure equilibrium conditions the specimens were maintained for 15 min at 25 °C in an environmental chamber saturated with water vapor before measuring the contact diameter of the drops. The diameter measurements were done using a Carl Zeiss Phomi III Pol microscope equipped with a JVC TV camera. The contact diameter of each drop, which was viewed from the top, was determined by averaging several measurements performed along distinct directions. Then, an average diameter was calculated averaging the diameters of six drops, which typically ranged from 1.50 to 1.80 μ m. The average diameter was used to calculate the water contact angle by means of equation (1).

2.4.3 Peel Tests

Standards T-peel tests were performed on adhesive joints formed by polymer/polyurethane adhesive/polymer specimens where the polymer could be either the original or the modified SBS.²⁰ In preliminary peel tests, it was observed that the force applied to detach the joint produced large plastic deformation on the zone of the specimens that was not part of the adhesive joint. In order to prevent from this type of deformation a piece of cotton yarn fabric was bonded to the back of the polymers sheets before cutting them to obtain the specimens for making the adhesive joint. Thus, a rectangular sheet of the material was laid on a clean piece of fabric, which was previously placed on the plate of the hydraulic press. Then, a slight pressure was applied on the layered assembly at 130 °C to squeeze slightly the polymer into the cloth yarn. This procedure allows a firm welding of the polymer to the fabric. Rectangular specimens of 20 x 100 mm in size were then cut off from the sheets backed with the fabric and their fabric-free surfaces cleaned with DMF and isopropyl alcohol.

A solution of adhesive was prepared by dissolving 0.5 g of the polyurethane in 100 ml of ethyl methyl ketone. Then, about 0.8 ml of the solution was placed on the specimen's surface. An open time of 30 min was allowed in order to facilitate the evaporation of the solvent providing a uniform wetting of the rubber surface. The adhesive layer deposited on the surface was melted and kept at about 100 °C for 30 s. Then, two adhesive-coated specimens were bonded under a pressure compression of 0.8 MPa for 15 s. These joints were maintained at room temperature, about 23 °C, for a period of 15 min before undergoing the T-peel test. The peel strength of the polymer/adhesive/polymer joints was determined using an Instron 1120 tester machine at a peeling rate of 0.1 m/min. Figure 1

shows a picture of a joint during a typical T peel test. Five replicates were tested and the strength values were averaged to obtain the adhesive strength for each material.

3. Results and discussion

IR spectroscopy is a method widely used for the identification of functional group in polymers. Figure 2 displays two region of the FTIR spectra recorded in transmission mode of the pure SBS and a physical mixture of SBS and NCMA. These spectra were used as a reference to locate the main absorption bands of chemical groups associated to the components of the reaction. The physical mixture was prepared by melt mixing the SBS and NCMA.

The spectrum of the SBS shows absorption bands typically associated to chemical groups belonging to butadiene and styrene. For example the band centered at 1950 cm^{-1} is assigned to an overtone of aromatic ring of styrene block, and the bands located in the region between 1670 at 1620 cm^{-1} are associated to stretching vibrations of the $\text{C}=\text{C}$ bonds of the polybutadiene block. The spectrum of the physical mixture shows the characteristics bands associated to the chemical groups of NCMA that can be discernible from the ones of SBS. For instance, there are three overlapping absorption bands centered at about 1680 , 1700 and 1720 cm^{-1} that can be associated to the vibration of amide and acidic carbonyl groups. In addition, two other characteristic bands appear at 3430 and 3400 cm^{-1} corresponding to the stretching of the N-H bonds of amide and OH bonds of acidic groups, respectively.²¹ All these bands are not present in the spectra of the SBS. The recognition of these bands in the spectra of the modified polymers was useful to verify the grafting of the NCMA, and their intensities allowed establishing an index indicative of the grafting efficiency.

3.1 Modification of SBS using BPO as initiator

Figure 3 shows two regions of the FTIR spectra of the SBS, the SBS-g-NCMA and the modified SBS (unpurified) obtained using 3×10^{-4} mol% of peroxy groups from BPO. These spectra were chosen as an example to illustrate the changes in the chemical composition of the SBS after their modification. The spectrum of the unpurified sample shows relatively intense overlapping absorption bands in the region between 1730 and 1660 cm^{-1} that can be assigned to the vibration of amide and acidic carbonyl groups. The bands associated to the stretching of NH are also observable at about 3420 cm^{-1} .

The presence of these absorption bands corresponding to the NCMA is also verified in the purified grafted polymers, SBS-g-NCMA. This confirms the grafting of the acid onto the SBS polymer. In this case, the bands centered at 1720, 1700 and 1690 cm^{-1} appear overlapped in the FT-IR spectra of the grafted polymer samples and the bands attributed to the N-H stretching of the amide group of NCMA are also observable at 3420 cm^{-1} approximately. As part of the non-grafted acid was removed during the cleaning process, all these peaks have relatively lower intensity than in the case of unpurified material.

3.2 Effect of initiator concentration on the grafting level

In order to evaluate the effect of the BPO concentration on the grafting level we analyzed the FTIR spectra of all the modified materials. The study of the carbonyl region of the FTIR spectra of the SBS and SBS-g-NCMA allowed a clear distinction of the differences between both. The carbonyl absorption bands corresponding to the NCMA varied with the peroxide concentration. The polymers obtained using 1.5×10^{-4} and 3×10^{-4} mol% of peroxy displayed the largest intensity of those bands.

A relationship between the intensity of the bands associated to the NCMA and groups characteristic of the SBS was used to estimate qualitatively the amount of NCMA incorporated. We have also defined an index (explained below in the text) that was used as indicative of the grafting efficiency. In this analysis, no distinction was made whether NCMA was incorporated as single units or as oligomeric sequences. The relationships between the absorption of the C=O vibration band of the grafted NCMA at approximately 1720 cm^{-1} , ($A_{\text{C=O}}$), and the reference band at 1950 cm^{-1} (A_0), which is attributed to aromatic overtones of the SBS were calculated and are reported in the second column of Table 1. The index of the grafting efficiency, expressed as percentage, was obtained from the relationship between $A_{\text{C=O}}/A_0$ of the SBS-g-NCMA and that corresponding to the same ratio $A_{\text{C=O}}/A_0$ obtained from the unpurified materials, which took a fairly constant value of 3.4 since the same amount of NCMA was added for grafting to all the samples. Roughly the same results would be obtained if other carbonyl bands were taken into account for performing the calculations. The third column of Table 1 shows the values of the efficiency index for the materials.

The value of $A_{\text{C=O}}/A_0$ increases with the concentration of BPO reaching a maximum value at the concentration of $3 \times 10^{-4}\text{ mol\%}$, and so does the efficiency index. When the concentration of peroxide is increased further, these values diminish meaning that the process becomes less efficient for incorporating NCMA onto the polymer backbone. The effect of peroxide initiator concentration on the grafting process qualitative agrees with that observed by other authors when studying the grafting of different polar monomers to SBS and other kind of polymers. For instance, Lee and co-workers used BPO as initiator for grafting N-isopropylacrilamide on SBS in a solution of toluene.¹¹ They found that the amount of monomer grafted reached a maximum when the concentration of initiator was $3 \times 10^{-2}\text{ mol\%}$. The observed decrease in the amount of grafted monomer beyond some

critical peroxide concentration was suggested to be likely due to enhancement of recombination of primary radicals and termination reaction of growing grafted chains. Cordella et al. carried out grafting reactions of glycidil methacrylate onto SBS using dicumyl peroxide (DCP) as initiator.¹² These authors found that the amount of monomer grafted to the polymer reaches a maximum value at a concentration of peroxide of 3.7×10^{-4} mol%. They considered that the use of concentrations of peroxide higher than the corresponding to the maximum favours macroradicals formation that could participate in combination reactions leading to crosslinking.

One aspect that lately drew special attention is the mechanism for what the grafting reaction is initiated when using radical initiators. There exist agreement in the literature in that grafting of monomer into butadiene-co-styrene copolymers initiated by radical occurs mainly in the polybutadiene block.²²⁻²⁴ When BPO is employed as initiator, two slightly different mechanisms are considered for the initiation step. One of them considers that the primary radical generated by the thermal decomposition of BPO either abstracts allylic hydrogen atoms or adds to the C=C double bond of polymeric chain.^{10,22,23} The other mechanism postulates that the abstraction of allylic hydrogen is the sole initiation step for grafting proceeds onto polybutadiene-based polymers.^{7,24,25} With the aim of establishing the plausible site of grafting in the system under study here we analysed further the FTIR spectra of the modified SBS using various concentrations of BPO. On this respect, we followed the variation of the C=C stretching band at 1634 cm^{-1} , and the olefinic C-H out of plane at 910 cm^{-1} , as a function of peroxide concentration. The relationship between the absorbance of these bands with that of the styrene ring overtone at 1950 cm^{-1} , that was used as internal reference, was calculated. The results are also presented in Table 1. They indicate that the concentration of double bonds does not seem to change noticeably with the peroxide concentration. This gives support to the

hypothesis that there is not an appreciable addition of primary radicals onto the C=C bonds of SBS. Additional evidence was obtained by analysing the spectrum of samples obtained by performing the reaction of SBS with BPO without adding NCMA. If the peroxy radicals were attached to the macromolecules, absorption bands of new chemical groups should be detected in the infrared spectrum. Figure 4 displays the FTIR spectra obtained for the SBS treated with 3×10^{-4} mol% of peroxy groups, which was selected as an example. In the spectrum corresponding to the unpurified sample bands at 1169 and 1202 cm^{-1} are identified that can be assigned to ν symmetric and asymmetric C-O-C bond associated to benzoyloxy radicals. These bands do not appear in the spectrum of the material purified, reinforcing the idea that the addition of benzoyloxy radicals to the SBS molecules does not occur in a noticeable manner.

From these results, we postulated that a tentative route for the grafting reaction of NCMA onto SBS may follow two main steps under the process condition used here. In the first place the thermal decomposition of the initiator produces benzoyloxy radicals. In a second step, the benzoyloxy radicals attack the polymer backbone abstracting an allylic H from the polybutadiene block. Then, the reactive macroradical formed could react with molecules of NCMA present in the reaction media leading to the grafting of the monomer onto the SBS macromolecules.

3.2 Modification of SBS using DBPH as initiator

The SBS was also grafted with NCMA using DBPH as initiator. FTIR spectra of the modified polymers were analyzed to obtain evidence of the grafting of the monomer. Figure 5 shows two regions of the spectra of SBS, unpurified SBS, and SBS-g-NCMA that was modified with 3×10^{-4} mol% of peroxi groups from DBPH. In the spectra of the

unpurified sample, there are bands that can be associated with NCMA in the region between 3200 and 3500 cm^{-1} , and between 1715 and 1745 cm^{-1} . However, when the material was washed to obtain the SBS-g-NCMA polymer some of them were not longer distinguished in the corresponding spectra. The spectra of the SBS-g-NCMA shows a band corresponding to the stretching of NH bonds that can be slightly distinguished in the region between 3450 and 3300 cm^{-1} . In addition, an absorption band centered at 1730 and 1715 cm^{-1} is clearly noted, which can be associated with carbonyl groups. These observations indicate that the NCMA suffered a chemical transformation. The comparison of the spectrum of the physical mixture, see Fig. 2, with the spectrum that corresponds to the SBS-g-NCMA in Figure 6 supports this observation. The changes in the chemical nature of NCMA are due to the effect of the temperature, 190 °C, chosen to carry out the reaction. Under this condition, inter or intra-molecular condensation reactions between the amine (NH_2) and carboxyl (COOH) groups may be induced. The literature contains references of intramolecular condensation of maleamic acid to form amides that is promoted at temperatures above 170 °C.²⁶ At higher temperatures, such as 190 °C, derivative maleimide and a complex polymer could also be formed.²⁶⁻²⁸ To verify these changes, pure NCMA was heated at 190 °C during 20 min under N_2 atmosphere. After this treatment, a mixture of a red solid (I) and a brown rubbery (II) substance were obtained as product of the reaction. Region of FTIR spectra of these compounds were compared to those of pure NCMA as shown in Figure 6. In the region of absorption of carbonyl groups, the NCMA displays absorption bands due to acid and amide carbonyl at 1715, 1700 and 1690 cm^{-1} , while the substances exhibit a more complex overlapping of different absorption bands covering the range from 1770 to 1500 cm^{-1} . Furthermore, in the region where appears bands of absorption associated to NH and OH, the substances I and II also display a complex spectra compare to the NCMA where there exist a set of

overlapped bands in the region between 3500 and 3000 cm^{-1} . From these observations, we may deduce that at least part of the NCMA decomposes either before or after being grafted to the SBS.

We have tried to quantify the amount of NCMA that is effectively incorporated into the SBS using DBPH analyzing the FT-IR results, albeit the chemical changes already described. The evolution of the relationship of the intensity of band at 1715 cm^{-1} , $A_{\text{C=O}}$, arising from the grafted species, to the reference one at 1950 cm^{-1} , A_0 , as a function of peroxide concentration is presented in Table 2. The value of the $A_{\text{C=O}}/A_0$ relationship increases with increasing the peroxide to reach a maximum at 3×10^{-4} mol% of peroxide groups, in coincidence with what was observed when using BPO.

It is not possible to propose a grafting mechanism when using DBPH because the thermal decomposition of the initiator follows a more complex mechanism than the BPO and a large variety of radicals might be generated in the reaction media, which have different reactivities.²⁹ It is though that the predominant reactive radicals are alkoxy and methyl that have a propensity for abstracting hydrogen and adding to $\text{C}=\text{C}$, respectively.³⁰

3.3 Surface and adhesive properties of functionalized SBS

Changes in the chemical composition of the outermost surface layer of SBS modified with NCMA were evaluated by measuring the contact angle of water drops laid on the surface of the film used for the FTIR characterization. As this parameter may be affected by the quality of the surface, we compared the film topography of the original and modified SBS surfaces by scanning electron microscopy. We found that the surfaces of all the samples were smooth, without noticeable differences between the topographical

details of the original SBS and that grafted with NCMA. Even though, a deep surface analysis was not performed, for instance by measuring roughness, we consider that the contact angle is not significantly affected by the topography of the sample surface. Figure 7 compares the values of the contact angle of SBS and modified materials as a function of the concentration of peroxy groups. The lines in the figure were drawn for connecting the data values. It is clear from the plot that the set of data points for both peroxides follows the same decreasing trend. The water contact angle for the original SBS polymer is high, 95 °, indicating a poor wettability and a relatively low surface energy. Following grafting with NCMA, a decrease in the water contact angle from 95 ° to either 73 ° or 79 ° is obtained with the concentration of BPO and DBPH, respectively. This indicates improved wettability and an increase in the polymer surface energy due to the presence of polar chemical moieties on the surface. We did not observe noticeable differences in the values of contact angle for the materials obtained using both peroxides, except in the case of peroxy concentration of 1.5×10^{-4} %mol, where the values of contact angles were 73 ° and 81 ° when the grafting was promoted by BPO and DBPH, respectively.

The water contact angle followed a trend with the concentration of peroxide that was in accordance with the amount of NCMA 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 correlation of the contact angle and the relationship $A_{C=O}/A_0$ obtained from the SBS-g-NCMA employing both initiators was utilized to better illustrate the aforementioned tendency. Figure 8 shows the evolution of the contact angle as a function of $A_{C=O}/A_0$ revealing that there is a practically linear relation between both parameters. These results let us confirm that the grafting of polar groups on the SBS changes its highly non-polar nature, producing materials with less hydrophobic surfaces.

The change in the hydrophobic character of the surface of modified SBS affects the peel strength values of polymer/polyurethane/polymer adhesive joints. In Table 3, the values of peel strength of the joints are listed. All adhesive joints exhibited an interfacial failure (adhesion failure) assessed by visual inspection, i.e., the joint failed at the interface between the adhesive and the SBS polymer surface. The results show that the adhesion strength produced with the SBS is relatively low (530 N/m), which is in concordance with previous work¹⁴, and with the value reported by other authors when studying SBS joints.^{2,6} The improvement of adhesive properties of SBS due to the grafting of NCMA is very significant. The peel strength of materials obtained with both initiators showed higher values than the corresponding to the SBS. The peel strength seems to go through a maximum with the concentration of peroxy groups. The maximum is observed at 1.5×10^{-4} and 3×10^{-4} mol% for the material modified with BPO and DBPH, respectively, reaching peel strength five and two times higher than the SBS. The improvement in the peel strength is comparable with the observed by other authors after applying a surface modification method to change the chemical characteristics of a SBS having similar composition to the one used here.⁶ The use of concentrations of peroxide higher than the corresponding to the maximum in peel strength does not produce an improvement in this property. This is in agreement with the observed dependence of both, contact angle and the effective amount of NCMA grafted to SBS, with the concentration of peroxy groups used.

Both initiators lead to similar values of peel strength when they were used at the lowest concentration of peroxy groups. While, at concentrations higher than 0.75×10^{-4} mol% the polymer obtained using BPO displays peel strength about two-times higher than those obtained using DBPH. This difference could be associated to the different polar moieties

grafted in each case, and also to the crosslinking that occurred when the SBS was modified with DBPH. J. K. Kim et al. showed that a decrease of peel strength on SBS copolymers could be attributed to increasing crosslinking.³¹

4. Concluding remarks

SBS was modified by reaction with NCMA employing BPO and DBPH as radical initiators that contribute to enhance its wettability and adhesion properties. Under the experimental conditions adopted in this study, NCMA was grafted onto the SBS macromolecules when using BPO as can be deduced from FT-IR spectra analysis, while NCMA derivatives having similar functional groups to NCMA were grafted when using DBPH. The highest grafting level was achieved at a concentration of peroxy groups of 3×10^{-4} mol%.

The information derived from contact angle measurements agree with those obtained from T peel tests in showing the concentrations of 1.5×10^{-4} and 3×10^{-4} mol% of peroxy groups as the optimum amount to initiate this grafting reaction.

The comparative analysis of the influence of initiator on surface and adhesive properties let us establish that BPO is far more effective than DBPH.

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Table 1. Grafting efficiency and relationship between the absorption bands corresponding to carbonyl ($A_{C=O}$), double bonds (A_{1634} and A_{910}), and a reference band (A_0) of samples modified with BPO.

Concentration of peroxy group ($\times 10^{-4}$ mol%)	$^1A_{C=O} / A_0$	2 Efficiency, %	A_{1634} / A_0	A_{910} / A_0
0	---	---	1.5 ± 0.2	10.5 ± 0.1
0.75	0.8 ± 0.3	24	1.6 ± 0.2	9.9 ± 0.4
1.50	1.2 ± 0.1	35	1.5 ± 0.1	9.8 ± 0.3
3.00	1.8 ± 0.4	53	1.8 ± 0.3	10.1 ± 0.2
6.00	0.9 ± 0.2	27	1.6 ± 0.1	11.3 ± 0.1

$^1 A_0$, absorption of the reference band at 1950 cm^{-1} corresponding to overtone of styrene ring and $A_{C=O}$ absorption of carbonyl band centred at 1720 cm^{-1}

2 Efficiency calculated as $[(A_{C=O} / A_0) / 3.4] \times 100$. The value of $A_{C=O} / A_0$ for unpurified materials is 3.4

Table 2. Relationship between the absorption of carbonyl band ($A_{C=O}$) and the absorption of the reference band (A_0) of SBS modified with DBPH.

Concentration of peroxy group ($\times 10^{-4}$ mol %)	$A_{C=O} / A_0$
0.75	1.0 ± 0.1
1.5	1.8 ± 0.1
3.0	2.5 ± 0.1
6.0	1.5 ± 0.2

Table 3. Peel strength as a function of concentration of peroxy group for the modified SBS.

Concentration of peroxy group ($\times 10^{-4}$ mol %)	T-peel Strength (N/m)	
	BPO	DBPH
0	530 \pm 30	
0.75	1080 \pm 40	980 \pm 60
1.50	2900 \pm 90	1000 \pm 80
3.00	2600 \pm 100	1250 \pm 40
6.00	1500 \pm 40	1000 \pm 70

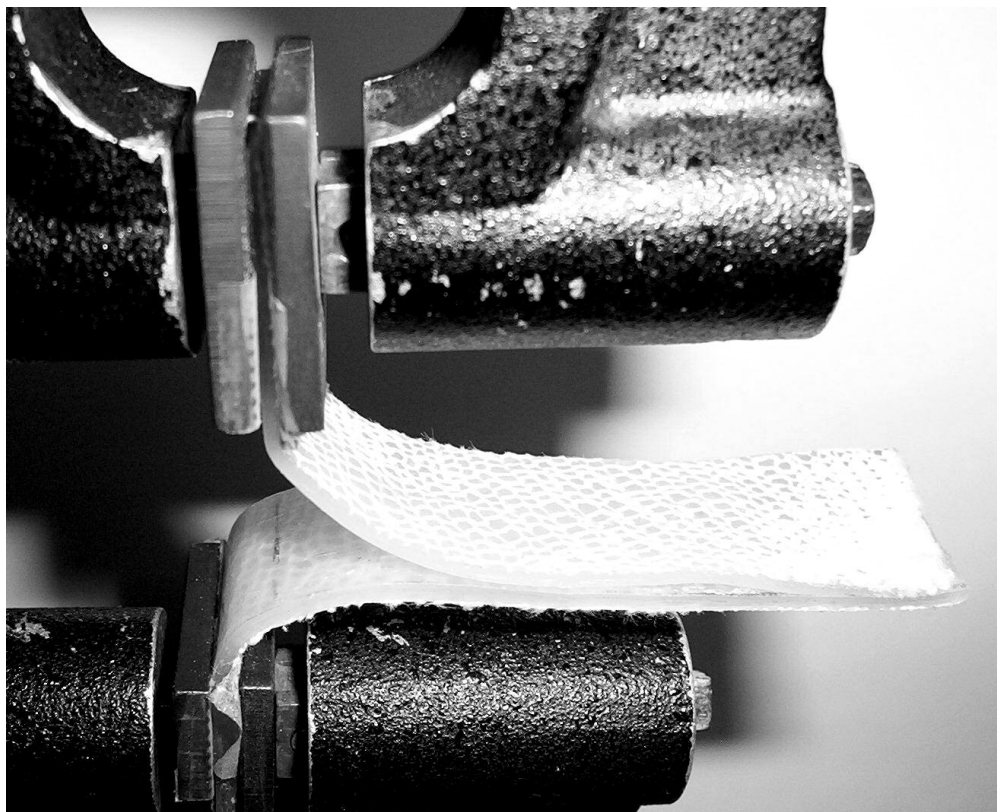


Figure 1. Picture showing a polymer/adhesive/polymer joint in a T peel test.

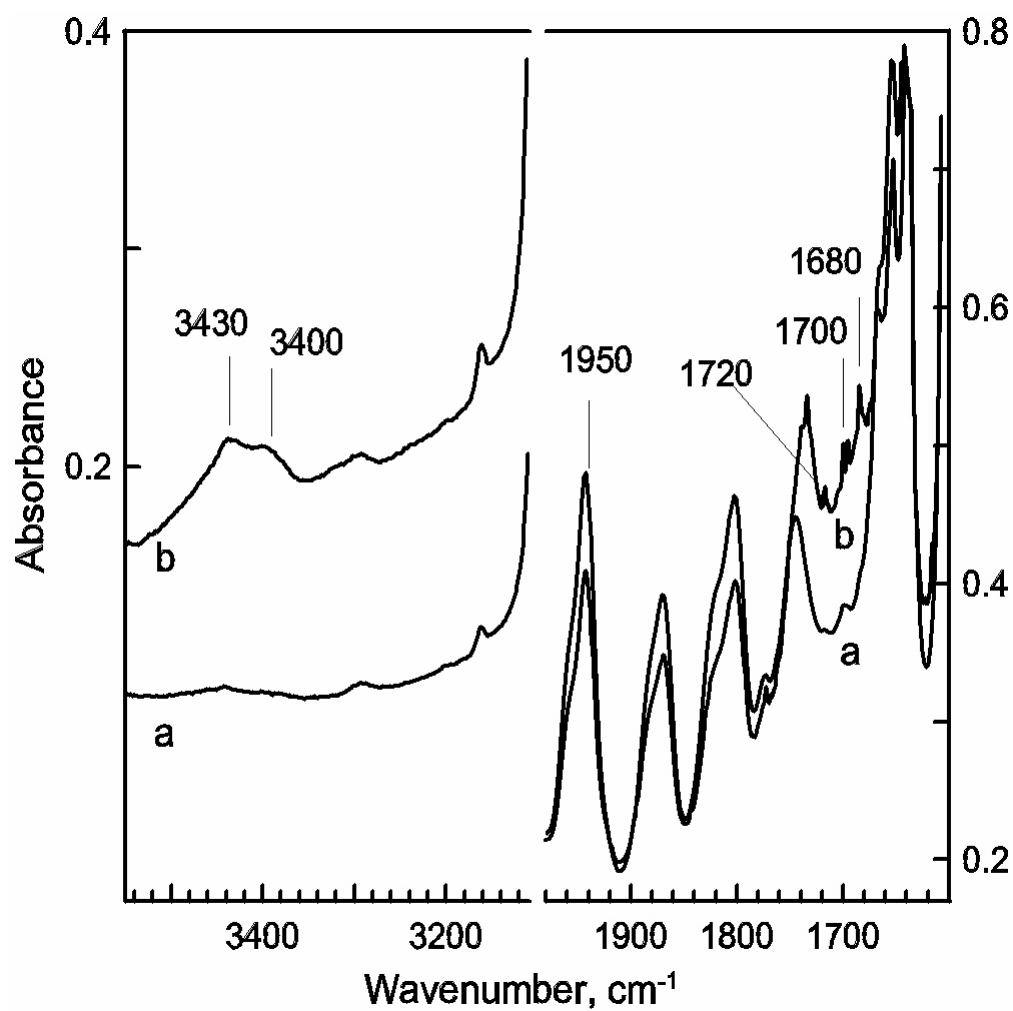


Fig. 2. Regions between 3600–3100 cm^{-1} and 2000–1500 cm^{-1} of the FTIR spectra of: a, SBS; and b, physical mixture of SBS and 0.5 wt% of NCMA. The spectra were slightly shifted along the y-axis.

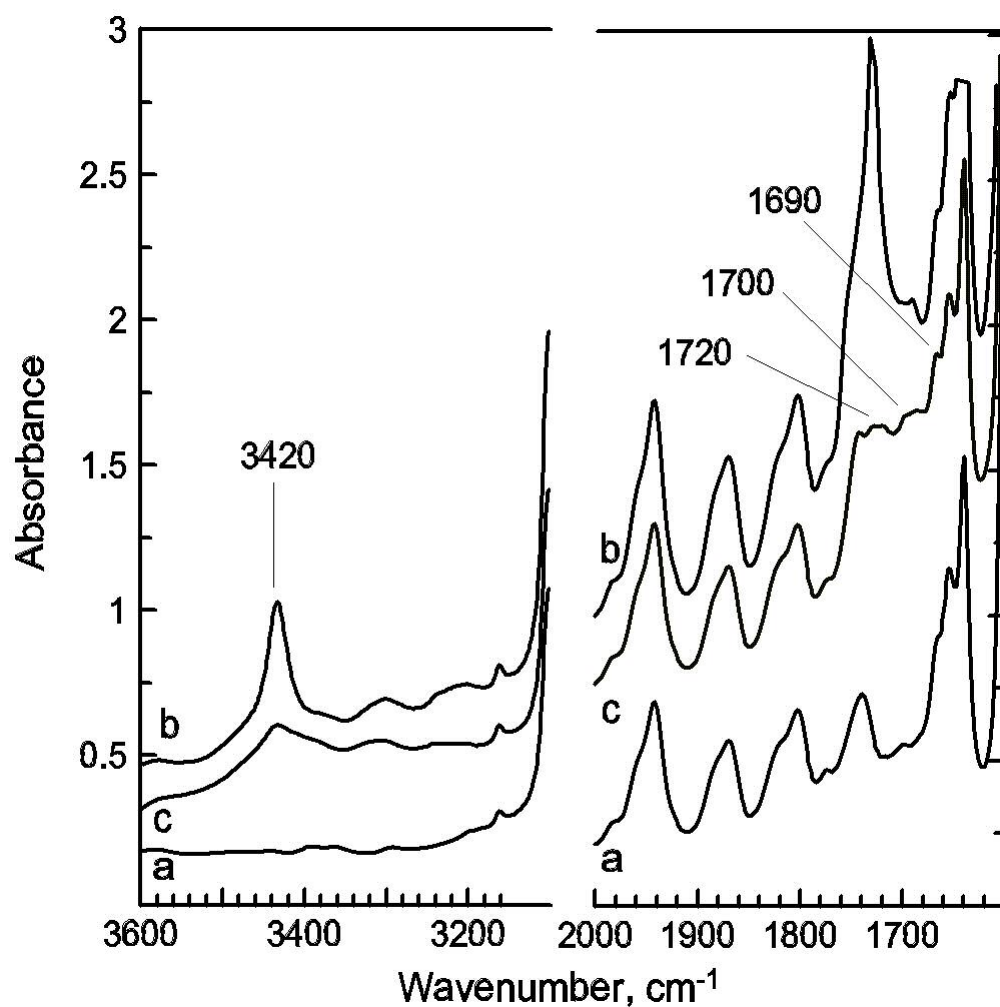


Figure 3. Regions between 3600–3200 cm^{-1} and 2000–1600 cm^{-1} of the FTIR spectra of: a, SBS; b, unpurified polymer; and c, SBS-g-NCMA obtained using 3×10^{-4} mol% of peroxy groups from BPO. The spectra were slightly shifted along the y-axis.

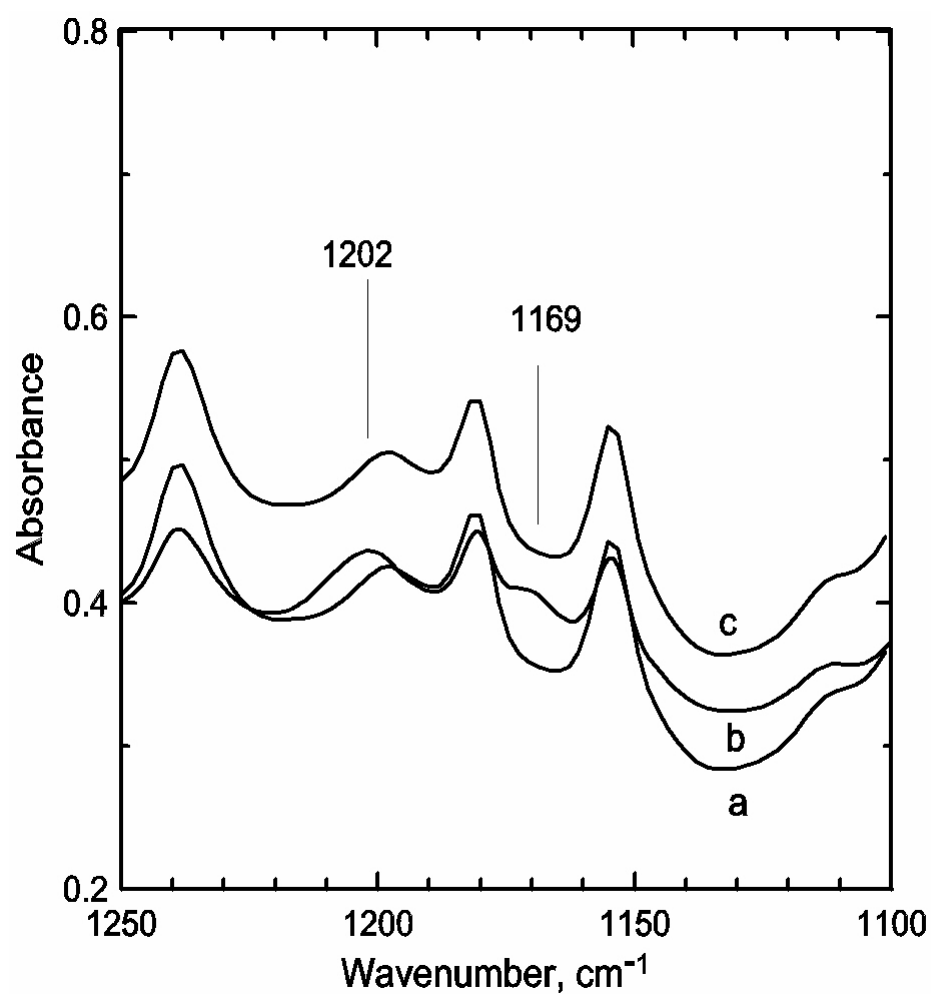


Figure 4. Region between 1300-1100 cm⁻¹ of the FTIR spectra of the SBS modified with 3 x10⁻⁴ mol% of peroxy groups from BPO: a, SBS; b, unpurified polymer; and c, purified polymer. The spectra were slightly shifted along the y-axis.

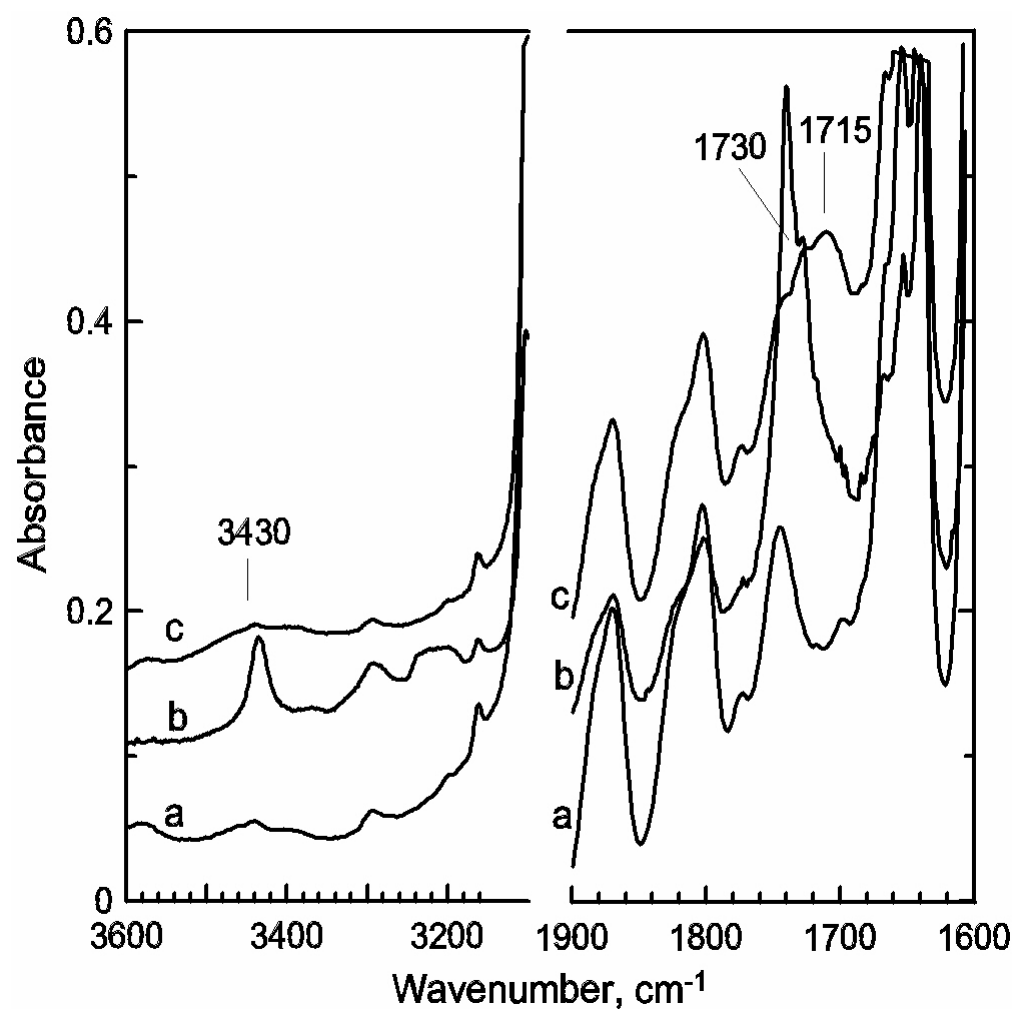


Figure 5. Regions between 3600-3200 cm⁻¹ and 1900-1600 cm⁻¹ of the FTIR spectra of: a, SBS; b, unpurified polymer; and c, SBS-g-NCMA obtained using 3x10⁻⁴ mol% of peroxy groups from DBPH. The spectra were slightly shifted along the y-axis.

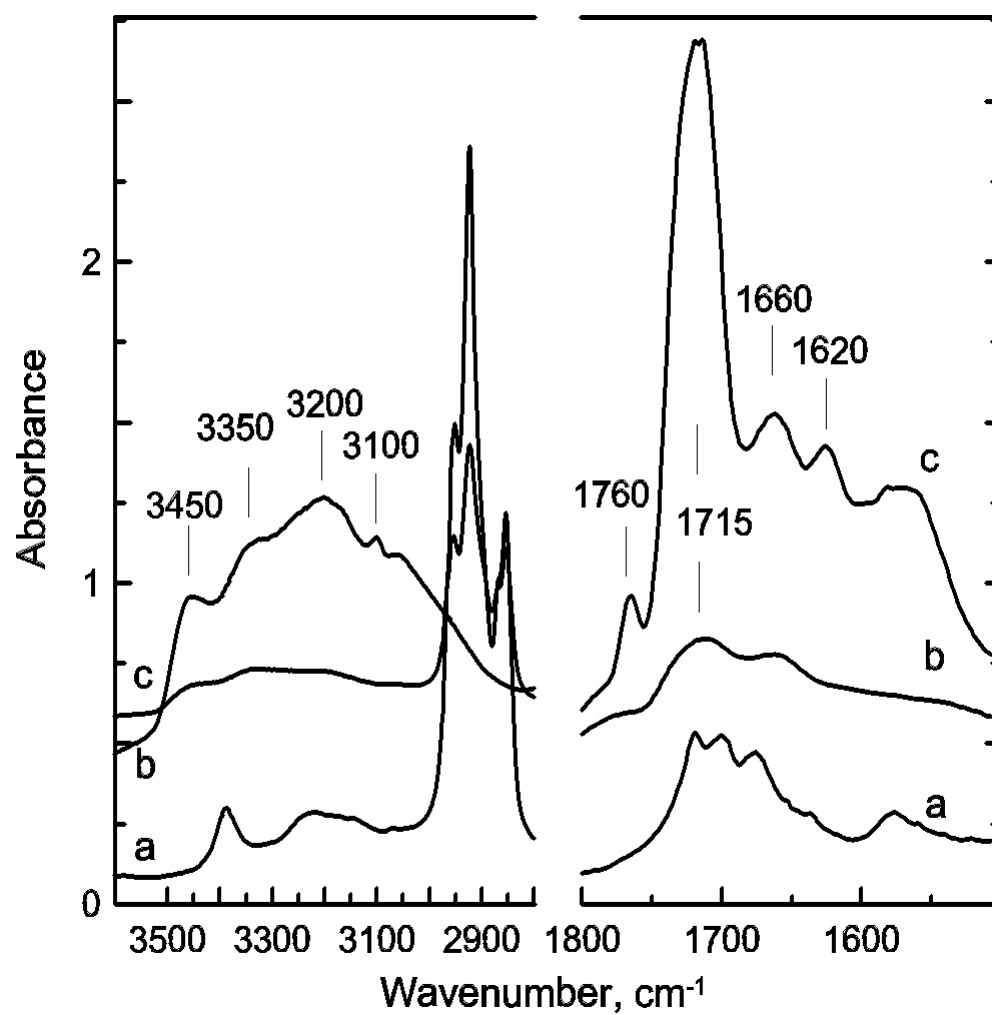


Figure 6. Regions between 3600–2800 cm⁻¹ and 1800–1500 cm⁻¹ of the FTIR spectra of: a, NCMA; b, substance I; and c, substance II.

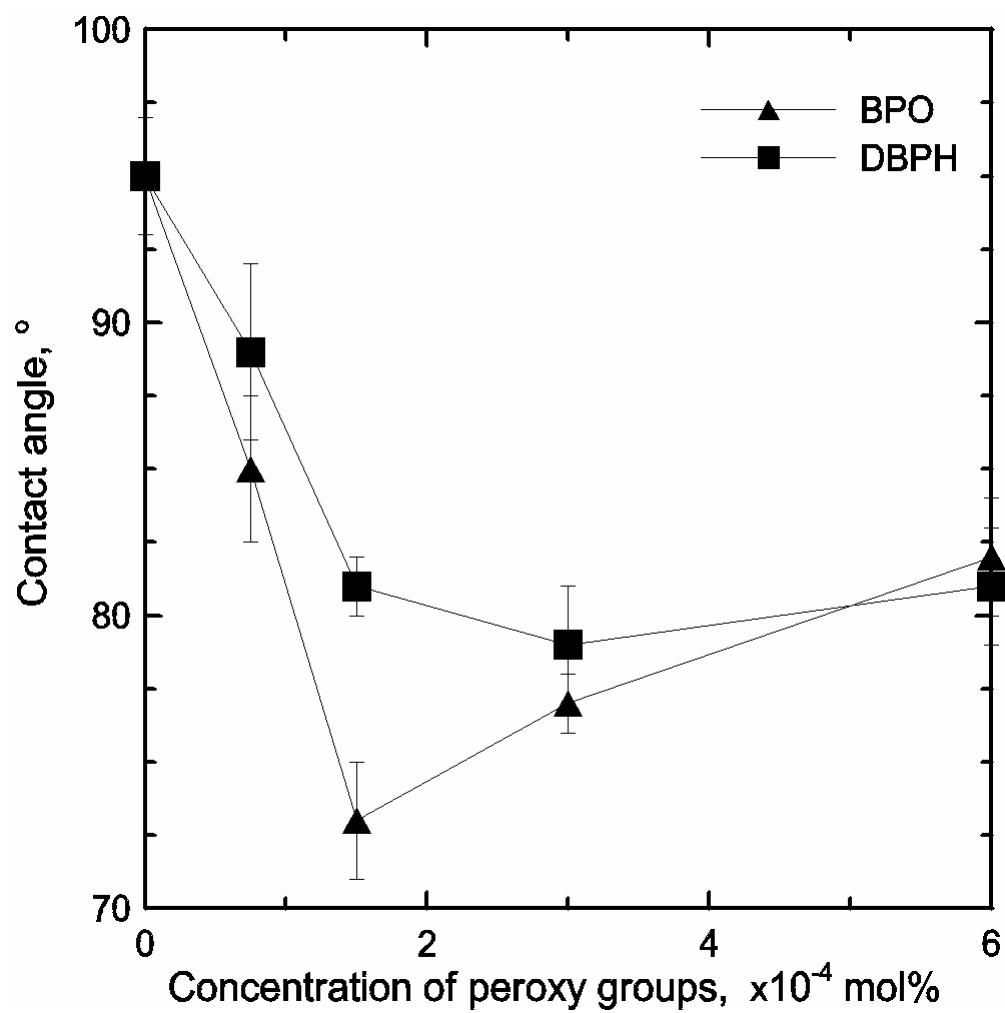


Figure 7. Water contact angle as a function of concentration of peroxy groups.

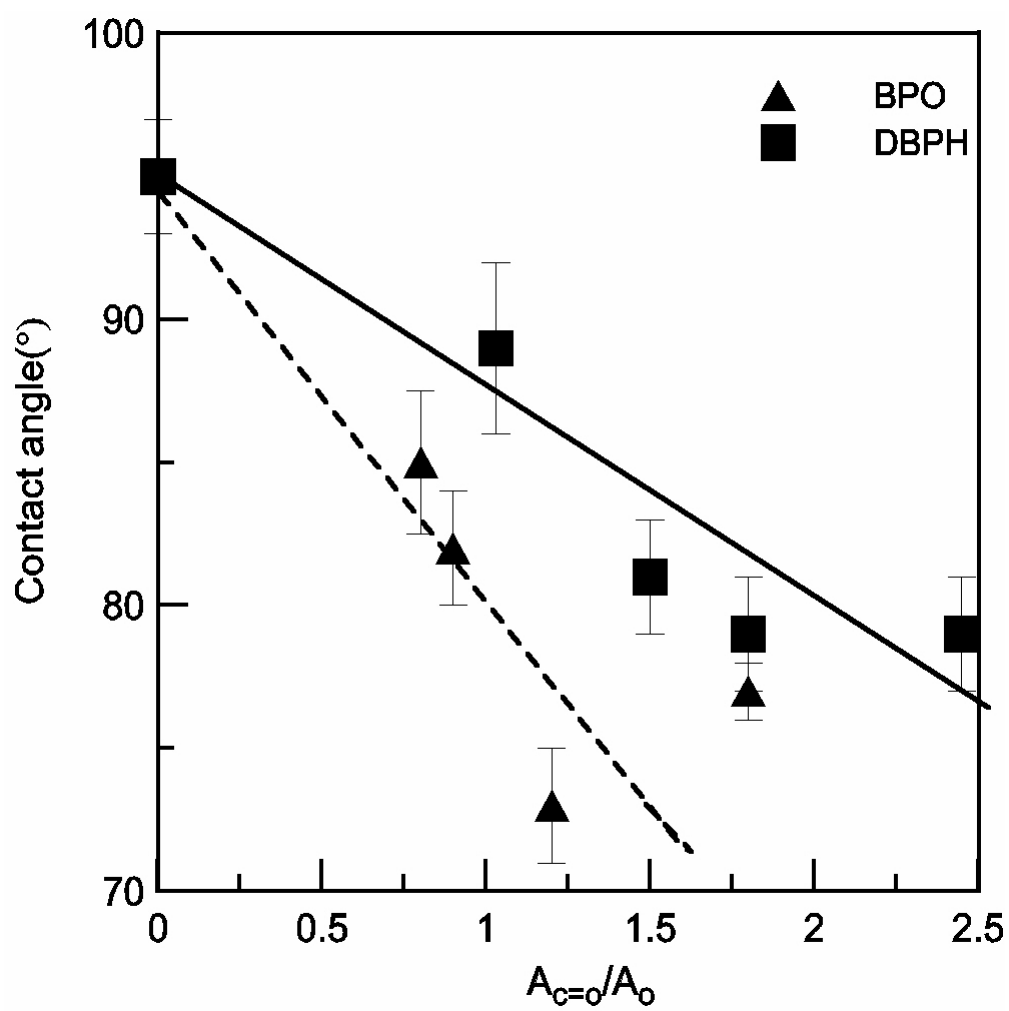
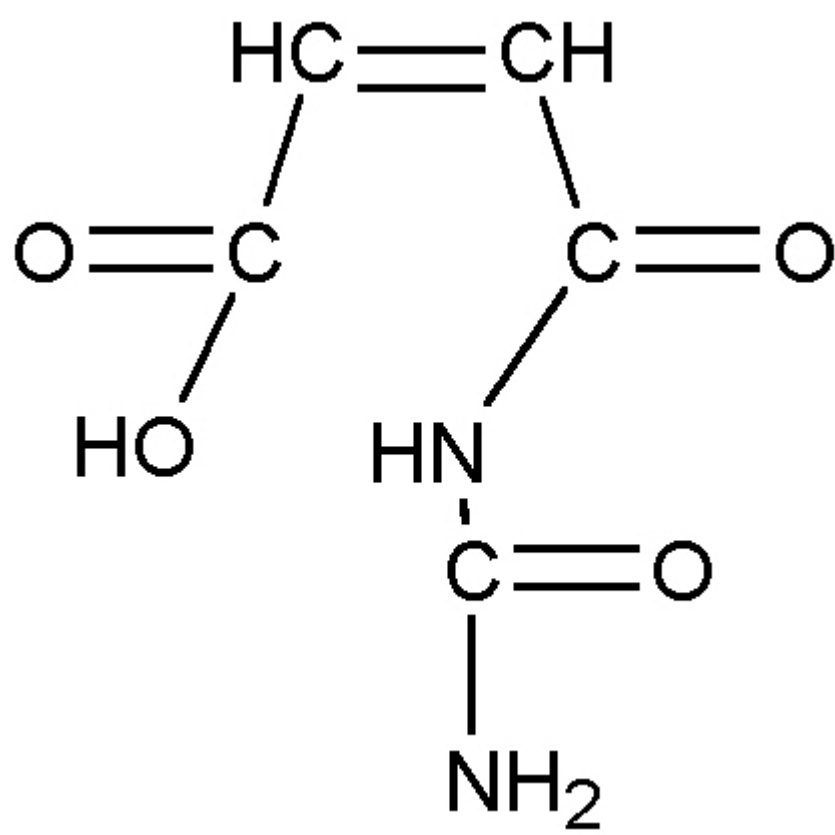


Figure 8. Water contact angle as a function of the relationship $A_{C=O}/A_0$ for both peroxides.



Scheme 1. Molecular structure of NCMA