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INFLUENCE OF ABS LOW MOLECULAR WEIGHT SPECIES ON ABS PROPERTIES

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Key Words: ABS, SAN, Low Molecular Weight Species, PC/ABS Blends, Extraction

ABSTRACT

A commercial ABS has been treated with methanol in a Soxhlet apparatus, at the boiling temperature of the solvent, for various procedures and times, in order to extract from it different amounts of low molecular (MW) weight species, a very important parameter in determining the final properties of PC/ABS blends.

Thermal, mechanical, dynamic mechanical, and impact properties have been performed on the obtained samples as a function of the amount of the extracted species.

The molten state results seem to be very sensitive to the subtraction of low MW species from the ABS, as shown by the viscosity, increasing with enhancing the extraction extent.

The glass transitions, detected by dynamic mechanical tests, show that both SAN and B low MW species are extracted from the ABS. Other low MW additives, such as antioxidants and sta-

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bilizers, are extracted from the ABS as well, giving rise to degradative effects, particularly effective for the materials undergoing processing treatments for prolonged times at high temperatures (i.e., for large extraction amounts).

Tensile performances, at a temperature just below the SAN T_g (100°C), show a sensitive influence of this parameter as well as of the above mentioned degradative effects at such a temperature.

Impact properties slowly worsen with increasing low MW extracted amounts, and, for high extraction amounts, they exhibit a brittle behavior.

INTRODUCTION

ABS (acrylonitrile-butadiene-styrene) copolymers are well known commercial materials with properties suitable for a variety of end-uses (1-3). They can be obtained by different techniques, each of which imparts different characteristics to their processing and properties. They are made of three components, acrylonitrile, butadiene and styrene, in the form of copolymers, styrene-co-acryonitrile (SAN), butadiene-g-SAN, whose ratios can vary to a certain extent. Therefore, they represent a large family of commercial polymers. ABS are often blended with Polycarbonate or other polymers, in which case a good compensation of properties of the two components can be achieved in such alloys, giving rise to new families of commercial blends (4).

It is known from the literature (5, 6) that SAN copolymers contain a small percentage of low molecular (MW) species, which plasticize the materials and lower their glass transition (T_g) and their impact properties as well (7). These low MW species may have a certain influence on the structure and properties of ABS and of PC/ABS alloys as well: they tend to migrate during the melt mixing toward the PC through the boundary between the dispersed ABS particles and the PC matrix. In this way, PC is plasticized and therefore, its T_g is lowered, whereas, in the ABS the free volume is decreased by their loss and its T_g is enhanced (8-10). Furthermore, the inward shift of PC and ABS T_g's for PC/ABS alloys appears to be greater than the one observed for PC/SAN materials, suggesting that low MW species of polybutadiene are likely to contribute to this phenomenon as well (9, 12, 13).

The aim of the present paper is to investigate the effect of low MW species contained in the ABS on rheological, thermal, and mechanical and impact properties of such materials as a necessary step of knowledge to successively understand their influence on more complex systems, such as PC/ABS alloys.

EXPERIMENTAL

Materials

The ABS used is a commercial copolymer manufactured by ENIC, Inc. with the trade name of Sinkral B32, having weight ratios AN/B/S = 27/22/51 and a melt flow index MFI = 4 g/10min (measured according ASTM-D-1238).

This copolymer underwent successive operations in order to extract from it low MW species as explained in the next paragraph.

Low MW Species Extraction

The extraction of SAN, PS and PB low MW species was carried out in a Soxhlet apparatus at the boiling temperature of the used solvent, methanol (85°C), for different times of extraction:

The ABS copolymer was first finely powdered in a mill manufactured by Retsch Inc. (mod ZM 1000) then, two different procedures were followed:

1) About 6 g of ABS were charged in a cellulose thimble (23 mm internal diameter and 100 mm external diameter) and put in a soxhlet apparatus for 24 hours, obtaining an extraction of 6.8 wt%. However, the amount treated in this thimble was too small for producing enough material for all the designed tests and therefore, it was necessary in the following of this work to use a thimble of a larger volume.

2) About 30 g of ABS were charged in a larger cellulose thimble (43 mm internal diameter and 123 mm external length). The ABS powder amount was subdivided in 20 parts, separated by as many filter discs of the same internal thimble diameter, in order to avoid during the extraction the powder packing which tended to lower the efficiency of the extraction; A period of time of two hours yielded an extraction of 2.3% in weight of low MW species; 24 hours yielded a 3.6% of extracted materials.

Higher amounts of extraction (5%) required a renewal of the procedure: the discs of ABS obtained by the first extraction were dried, milled again and underwent a second extraction process for further 24 hours.

Specimen Preparation

The discs obtained from the solvent extraction were cut in small pieces and dried under vacuum at a temperature of 60°C for about 90 hours. Then the material were compression molded at a temperature of 200°C at a pressure of 100 atm.

From the molded sheets obtained, different types of specimens were cut at a temperature of 90°C by suitable punches: a) dumbbell ones for tensile mechanical tests (DIN 53504 type S3A); b) rectangular ones for Charpy impact tests (LxWxT = $64 \times 6 \times 3$ mm^3); c) discs for wide angle X-rays diffraction (DxT = 35×1 mm^2).

Thermal Treatments

The small specimens to be thermally scanned, already inserted into normal aluminum DSC pans, were annealed at 90°C, below the glass transition temperature, (T_g) of the ABS for 96 hours, in order to age the materials and develop an enthalpic peak over the T_g. This technique improves the T_g reading.

Techniques

Rheological Properties

Viscosity tests were performed by a Rheometrics rotational viscometer at a temperature of 220°C in a range of shear rates from 10^{-2} to 4×10^{-1}. The tests were made on the ABS discs directly obtained from the Soxhlet apparatus' extraction, without any further compression molding process.

Thermal Properties

Thermal differential scanning and DSC scanning were performed on Mettler equipment from 20 up to 180°C at a rate of 20°C/m, in order to detect the T_g of the ABS's.

Tensile Tests

Mechanical tensile tests were performed by a Daventest Testometric 500D at a temperature of 100°C and a cross-head speed of 20 mm/m. From the stress-strain curves the Young modulus, the yield stress, the stress and the elongation at break were measured on an average of 6 specimens.

Impact Tests

Charpy impact tests were performed on parallepipedal specimens, notched in the middle by a razor blade. From the curves of impact stress versus time, the energy, the stress at rupture, and the stress intensity factor were calculated.

Dynamic Mechanical Tests

Dynamic-mechanical flexural tests were performed on a Polymer Laboratories equipment (DMTA) at a scanning rate of 3°C/min and at a frequency of 1 Hz.

RESULTS AND DISCUSSION

Rheological Properties

The viscosity of the ABS, from which low MW species were extracted in different amounts, is reported as a function of the shear rate in Figure 1.

All the curves show the usual pseudoplastic behavior of the viscosity as a function of shear rate with absolute viscosity values increasing with the percentage of extraction. This effect is clearly due to the loss of low MW species which, decreasing the free volume existing in the materials, enhances the internal friction, giving rise to higher viscosity values. From a different point of view the presence of low MW species tend to dilute the concentration of molecular

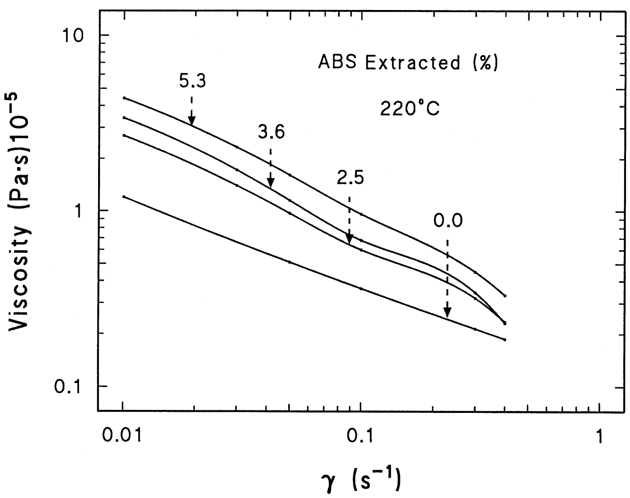

Figure 1. Viscosity versus shear rate for ABS's with various extracted amounts of low MW species (wt%), as indicated.

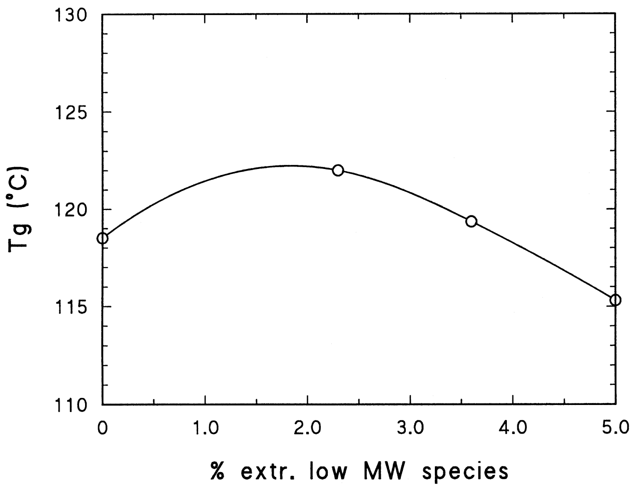

Figure 2. Glass transition temperature versus wt% of extracted low MW species from ABS.

entanglements or topological restraints among the macromolecules, reducing the terminal relaxation times (14).

Thermal Properties

In Figure 2, the T_g, evaluated by DSC, is reported a function of the amount of the low MW species extracted from the ABS. Starting from pure ABS (0%), the T_g first increases for an extraction of 2.3% in weight and then decreases with further extraction values.

The initial increasing effect of the SAN T_g, with enhancing the extraction percentage, is certainly due to the subtraction of S and AN low MW species from the ABS, as already found in literature by Guest and Daily (5). More difficult is the understanding of why the ABS(SAN) T_g decreases with further extraction amounts: a tentative explanation is that the prolonged exposure to the methanol vapors at a temperature of 85°C, during the soxhlet extraction, may have induced some kind of slight degradative effect into the material. An additional cause can be attributed to the second milling necessary to reduce in powder the ABS to be subjected to the second Soxhlet operation as well as to the extraction of some stabilizer and antioxidant additives originally added to the commercial ABS. As a matter of fact, the ABS exhibited, after the successive molding process and the cutting at high temperature, a yellowing effect, the more pronounced the higher the extraction time. Therefore, during the operations following the extraction some kind of degradation may have produced some additional low MW species, replacing, in the final extracted ABS, the initial ones originally present in the commercial ABS. The above results seem to be in contrast with the viscosity data, for which the larger the extent (and time) of extraction in the ABS, the higher the viscosity, indicating a clear plasticization effect due to the original low MW species. It is to be noted however, that the contradiction is only apparent since the discs of materials, obtained from the soxhlet have not undergone any further processing (compression molding and cutting at a high temperature) after the extraction, since they were directly used for viscosity tests.

Mechanical Behavior

In Figure 3, stress-strain curves of ABS specimens with various extracted amount of low MW species (LMW%), subjected to classical tensile tests at a temperature of 100°C and a cross-head speed of 20 mm/m, are reported.

All the curves show typical trends with increasing the deformation extent: an initial Young modulus, a yield peak, followed by a rather large elongation of the gauge length of the specimens and by a final breakage. It is evident a certain dependence of the shape of the curves from the low MW% parameter.

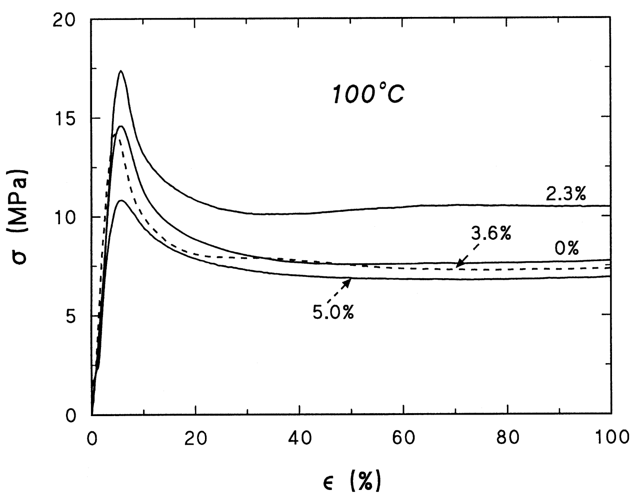

Figure 3. Stress-strain curves of tensile tests obtained at 100°C on ABS's specimens with various extracted amounts of low MW (wt%), as indicated.

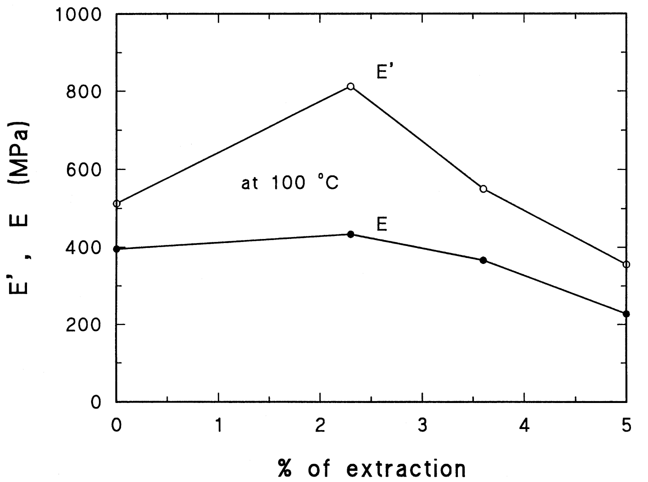

Figure 4. Young's and storage moduli versus wt% of extracted low MW species from ABS.

In order to better quantify this influence, classical mechanical parameters calculated from the curves, have been plotted in the following figures.

In Figure 4, the Young modulus, calculated from the curves of Figure 3, is reported as a function of the extracted amount of low MW species and compared with the storage modulus obtained at the same temperature on these materials. The trend of both parameters is rather similar to the one already observed for the T_g: first an increase and then a decrease of the E and E' moduli with increasing the extraction amount.

An analogous trend is also observed for the yield stress and the stress at break in Figure 5, whereas the elongation, reported as well, exhibits a continuous decrease with increasing low MW%. The tentative explanation is the same provided for the behavior of T_g: the ABS first increases its rigidity (moduli) and also its resistance to large deformations (yield and breakage stress) and shows high elongation values at a temperature close to its T_g with values decreasing at higher extraction amounts of low MW species.

Impact Properties

In Figure 6, curves of impact stress against time of deformation, obtained by Charpy mode, are reported for ABS's from which various amount of low MW

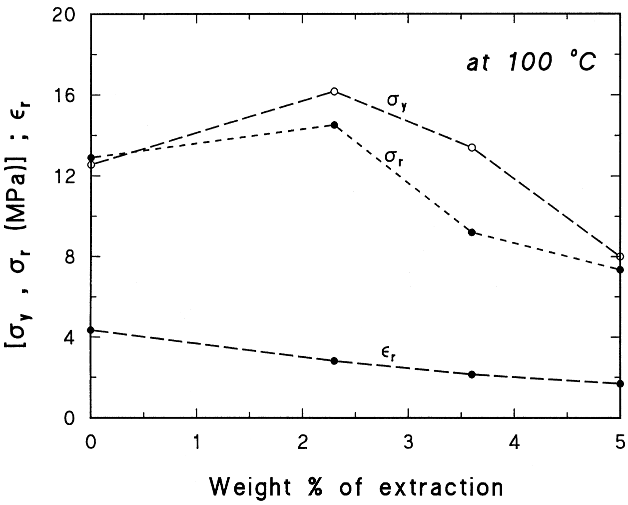

Figure 5. Yield stress, stress and elongation at break versus wt% of extracted low MW species from ABS.

species have been extracted. The behavior becomes the less ductile the larger the extent of extraction, reaching a brittle one for the sample with 5% of extraction. The trend of the curves indicates a progressive worsening of the impact performance of the ABS due to the loss of SAN species, as already evidenced by the T_g trend of Figure 2.

This is clearly shown in Figure 7, where the maximum stress reached by the curves of Figure 6 and the relative calculated stress intensity factor, are reported against the extracted low MW%. Both the parameters show a decreasing trend with increasing the amount of extraction from ABS. Furthermore, from a visual inspection of the fracture surface of the specimens it appears that. beyond a certain value of extraction. the ABS looses its good impact properties and becomes more and more brittle, as already seen by the curves.

This worsening of the impact properties is due not only to the loss of SAN low MW species but, what is even more important, to a simultaneous loss of low MW B species, as evidenced in the following of the paper by dynamic mechanical tests as well.

Evidence of both these losses after the extraction is given in the next figures.

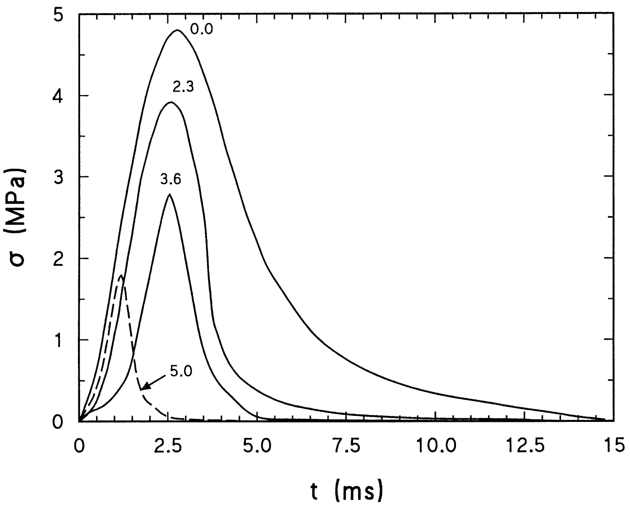

Figure 6. Curves of impact stress, obtained at room temperature, on ABS's specimens with various extracted amounts of low MW species (wt %), as indicated.

In Figure 8, a plot of tan δ versus temperature, is reported for the used commercial ABS and for a sample from which 6.8 wt% of low MW species were extracted, according to the extraction procedure n.1, described in the paragraph (Low MW Species Extraction).

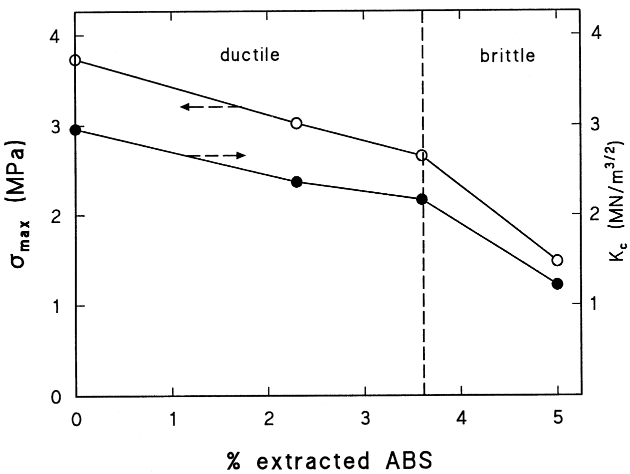

Figure 7. Maximum stress (on the left hand side) and stress intensity factor (on the right hand side), obtained by Charpy tests, versus wt% of extracted low MW species from ABS.

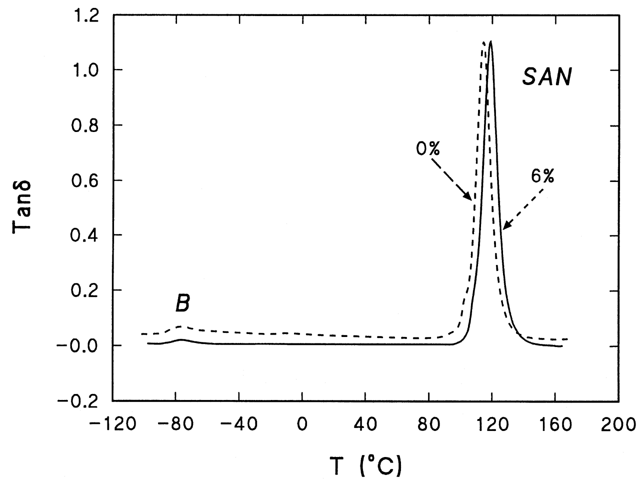

Figure 8. Curves of tan δ versus temperature, obtained by dynamic mechanical tests, for two ABS's with different wt% of extracted low MW species from ABS.

Both the curves show two classical peaks, a larger one at temperatures higher than 100°C, representing the T_g of ABS(SAN) and a smaller one at low temperatures well below 0°C, relative to the polybutadiene T_g. A magnified version of the former peaks is reported in Figure 9: the peak of pure ABS(SAN) shifts at a higher temperature when the low MW species have been extracted, as already discussed in Figure 2, showing that low MW species of SAN are taken away from the commercial ABS.

A magnified plot of the B peaks is reported in Figure 10: the peak of the extracted ABS exhibits a lower height with respect to the one relative to the commercial ABS, indicating that during the extraction a certain amount of B is extracted as well, together with the SAN low MW species.

CONCLUSION

In this paper, the influence of the extraction of low MW species from ABS by means of a Soxhlet have been investigated on a number of properties relative to the molten state, the transition from solid to melt and to the solid state, for specimens subjected to small and large deformations. The following conclusions can be drawn:

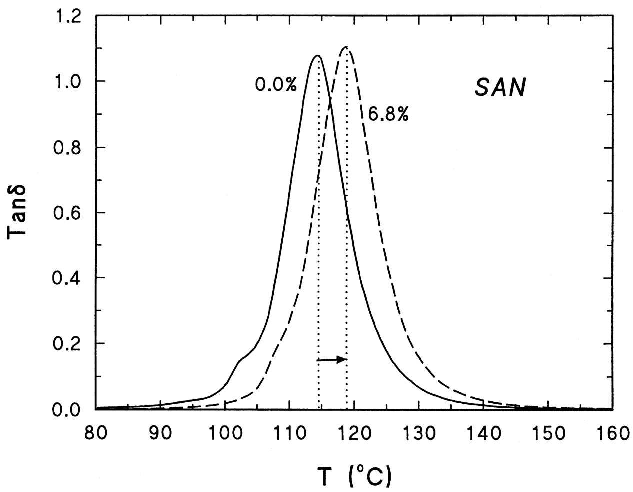

Figure 9. Magnified curves of tan δ of SAN versus temperature, replotted from Figure 8.

The molten state is very sensitive to the subtraction of low MW species from the commercial ABS used in this work: the viscosity increases with increasing the extent of extraction.

The transition zones from a glass-like to a rubber-like consistency indicates that both SAN and B low MW species are extracted from the ABS.

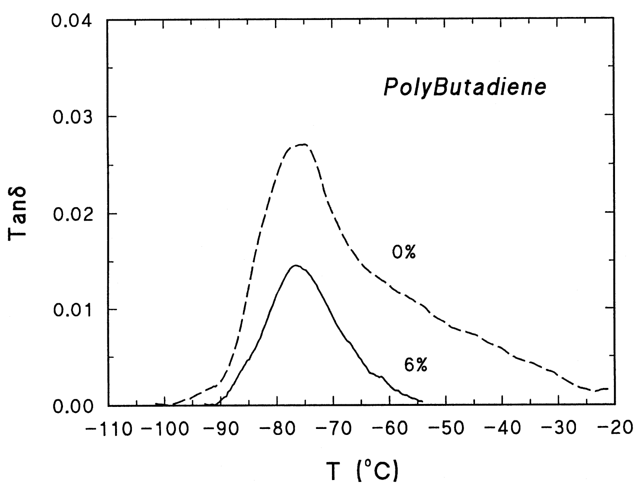

Figure 10. Magnified curves of tan δ of B versus temperature, replotted from Figure 8.

Other low MW additives, such as antioxidants and stabilizers, are taken away from the ABS, giving rise to degradative effects particularly effective for the materials undergoing prolonged time treatments at high temperature.

Tensile performances at a temperature just below the SAN Tg 100°C, show a sensitive influence of this parameter as well as of degradative effects at such a temperature.

Impact properties, such as maximum stress and stress intensity factor, decrease first slightly and then in more drastic way, becoming brittle at the highest extraction amount.

The remarkable changes in the ABS properties above investigated have a certain influence on the blend performances of PC/ABS systems as well, as it is will be shown by some preliminary results described in a next paper in preparation (15).

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