Study on the Recycling of ABS Resins: Simulation of Reprocessing and Thermo-oxidation

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ABSTRACT

Processability, morphology, optical, and mechanical properties of acrylonitrile-butadiene-styrene (ABS) polymers were studied by simulation of its reprocessing and service life. A series of ABS samples were prepared by melt-mixing of SAN and γ-ABS. All specimens were characterized by melt mass-flow rate (MFR) measurements, tensile testing, impact strength (Izod), Fourier transform infrared (FTIR) spectroscopy, colour spectrophotometry (data of L*, a*, and b*) and transmission electron microscopy (TEM) techniques. Reprocessing and thermo-oxidative ageing clearly alter the elongation-at-break, impact strength and yellowness index of the polymers. These changes observed at a macroscopic scale have been related to chemical alterations in the structure of ABS. TEM Micrographs indicated no significant changes in the status of rubber (PB) phase. The PB phase was demonstrated to be the initiation point of the degradative processes induced by processing, service life, and recycling. The results of the FTIR showed that upon processing of ABS, cross-linking and chain scission of rubber phase was the governing degradation and yellowing mechanisms. Thermo-oxidative ageing degradation has affected the degree of yellowing of the polymer more severely. Thus, it may be deduced that the changes occurring during service life of ABS are part of the life cycle which mostly affect its further recycling possibilities and performance in second-market applications.

INTRODUCTION

Acrylonitrile-butadiene-styrene (ABS) is an engineering thermoplastic which consists of an amorphous, heterophase polymer with very good mechanical properties, especially high impact resistance. Poly (styrene-co-acrylonitrile) (SAN) copolymer forms the continuous phase. The second phase consists of dispersed polybutadiene, or butadiene copolymer; these particles have a layer of SAN grafted onto their surface which makes the two phases compatible [1]. The properties of ABS are given by the composition, thermoplastic and rubbery phase characteristics, and their corresponding interactions
with each other. Thus, the content, molecular weight, and composition of SAN control properties such as processability, heat resistance, surface hardness, and chemical resistance. Meanwhile, rubber content contributes mainly to toughness. The main applications of ABS are in automotive industry, telecommunications, business machines, and electric/electronic casing. The wide range of ABS application is due to both the properties and price which are intermediate between the lower priced commodity thermoplastics and the more expensive high performance engineering plastics. ABS is also an interesting plastic material for recycling [2,4,5].

According to this, three key properties have been proposed in order to guarantee the quality of the recycled plastic materials: (1) degree of mixing (composition), (2) yellowing, and (3) the presence of low-molecular weight compounds (degradation products, contaminants, etc.) [3]. In order to investigate the degradation of polymeric materials, several approaches can be considered by taking into account the changes in their macroscopic or microscopic properties. The functional group changes by Fourier transform infrared (FTIR) spectroscopy, the alterations in the mechanical properties by tensile tests, the thermal properties such as the glass transition temperature (Tg) or the degree of crystallinity by differential scanning calorimetry (DSC) are some of the physical, chemical, and mechanical analyses which are commonly employed to monitor alterations in polymer [2-7].

Several studies have been carried out on the mechanical recycling of ABS. For example, Potente et al. [8] studied the recyclability of injection moulded lamp-shade parts based on ABS. They found that, after regrinding and injection moulding, the mechanical properties were not significantly affected, apart from a slight reduction in the notched Izod impact strength. Gel permeation chromatography (GPC) investigation showed that only slight molecular degradation occurred during the injection moulding and/or regrinding. Thus, they considered that the main reason for the reduction in impact strength could be the volatilization of some of the additives used in the virgin material.

In another study, pieces of ABS from computer monitor casings were granulated followed by thermal processing in a torque rheometer [9]. Then, the material was regranulated followed by injection moulding into mechanical test specimens. This method was used to simulate a typical commercial recycling procedure. After this reprocessing, tensile strength decreased only by a few MPa, tensile modulus increased slightly, strain-to-failure decreased from about 11% to 6%, and un-notched impact strength decreased from 44 to 31 kJ/m². It was thought that polymer degradation might have caused the reduction of impact strength and it has slightly increased the stiffness of the recycled material.

Some basic studies on multiple recycling of ABS have been carried out. For example, the effects of reprocessing conditions on the mechanical properties of ABS have been evaluated by varying temperatures and dwell times [10]. In this case, the material was grinded and remoulded five times. It was found that the mechanical properties varied with reprocessing temperature. Following the use of higher temperatures, Izod impact strength decreased but there were increases in tensile strength and modulus. Also, the variations of these mechanical properties increased with longer processing dwell times. There was a good correspondence between the changes in mechanical properties and the observed structural variations. Degradation of the rubber phase (evidenced by infrared spectroscopy) was thought to be the main reason for the decrease in toughness. Following the most severe moulding conditions, toughness reduction was even greater, perhaps because of the degradation of the styrene-acrylonitrile (SAN) phase.

In another study, an ABS material was injection moulded and recovered for five cycles [11]. During this multiple reprocessing, the strain-to-failure showed a very slight tendency to decrease. Failure strength slightly increased after five processing cycles. The toughness measured by notched impact strength reduced continuously. The changes of these important properties were probably due to the degradation of the soft polybutadiene component, which was seen from infrared and dynamic mechanical analysis results.

Kim et al. reprocessed three ABS resins five times using an extruder [12]. After extrusion, the glass transition temperature of the SAN phase was not changed. The effect of repeated extrusions on mechanical prop-
erties such as tensile strength, strain-to-failure, and hardness was small. However, impact resistance of all materials decreased after recycling, especially the impact resistance of ABS with the highest polybutadiene content. The reason for the decrease in the impact strength was again thought to be the degradation of the polybutadiene component in ABS.

The purpose of this study was to investigate the processability, morphology, optical, and mechanical properties of ABS during its reprocessing and thermo-oxidation to develop a detailed knowledge on how and to what extent, processing, service life, and mechanical recycling affect the performance of ABS. The processing and recycling of the plastic material were moulded by multiple processing, while the yellowing processes occurring during the service life was simulated by thermo-oxidative ageing in a forced-ventilation oven at 120°C. The samples were characterized by transmission electron microscopy, data of colour spectrophotometry (L*, a*, b*), melt mass-flow rate (MFR), tensile impact strength, notched impact strength (IZOD) and Fourier transform infrared spectroscopy (FTIR) to determine the changes in chemical composition, processability, morphology, optical, and mechanical properties induced by the recycling-related processes. This paper reports the results of the study.

EXPERIMENTAL

Materials
The materials used in this work were ABS resin (g-ABS coded RB) and styrene–acrylonitrile (SAN coded APH) copolymer made by Tabriz Petrochemical Complex (Tabriz, Iran). Magnesium stearate (acid scavenger) and ethylene-bis-stearamide (processing lubricant), were kindly supplied by Tabriz Petrochemical Complex (Tabriz, Iran). Tetrahydrofuran (THF) and OsO4 were supplied by Merck (Darmstadt, Germany).

Sample Preparation
The ABS compounds, used for these studies, were prepared via melt-mixing the SAN (66 phr), g-ABS (34 phr), acid scavenger (0.4 phr) and processing lubricant (0.4 phr) using SM twin-screw laboratory extruder set at 160 rpm (L/D=36, co-rotating, intermeshing) (Korea). The six heating zones were set at 180, 190, 210, 210, 210, and 225°C. The extruded strands were quenched immediately in water at room temperature and chopped into granules by using SM pelletizer (Korea). The obtained granules were dried at 80°C for 2 h in an air oven before processing in order to avoid possible moisture degradation reactions. Some material was kept for analysis whereas the remaining was reintroduced again for further extrusion. The specimens for calculating tristimulus values and impact tests were moulded using LG injection moulding machine (Korea) at injection temperatures varying from 180 to 205°C. All processing was done with the same equipment by the same operator. Moulded part consisted of both, length: 90 mm width: 50 mm, thickness: 2.5 mm flat plaques, length: 63.5 mm, width: 12.7 mm, thickness: 3.17 mm sheet for measurement of yellow index and Izod impact strength properties, respectively. For evaluation of tensile properties dogbone-shaped samples were prepared. In order to simulate thermo-oxidation during service life, injection moulded parts were introduced into a forced-ventilation oven under air atmosphere at 120°C. The samples were removed for analysis after different ageing times.

Melt Mass Flow-rate
The melt mass-flow rate (MFR) measurements of the reprocessed ABS plates were performed on a modular melt-flow series: coded 7026.000, Ceast (Pianezza, Italy). The procedure was followed according to the ASTM D-1238. The test temperature was set at 200°C and the nominal load was 5 kg. The measurements on each sample were repeated five times and the average values and standard deviations were calculated.

Impact and Tensile Testing
The impact properties were also carried out in Izod mode according to ASTM D-256 standard on five rectangular specimens of dimensions 63.5 mm length × 12.7 mm width × 3.17 mm thickness obtained by injection moulding using a Resil impactor coded 6967.000, Ceast (Pianezza, Italy).

Tensile testing was carried out on a Shimadzu, 20 kN (Japan) testing machine according to ASTM D-
638 standard on five dogbone-shaped samples of dimensions 115 mm length × 12.7 mm width × 3.17 mm thickness obtained by injection moulding. Average values and standard deviations were calculated for at least 5 samples.

**Transition Electron Microscopy**

The morphology of cross-sections was studied with a Philips CM200 FEG (Germany) electron microscope. The sample surface was first smoothed using a glass knife, followed by staining in the vapour of 2 wt% OsO₄ aqueous solution for 48 h. Staining helps to increase the brittleness of the rubber particles and to enhance the contrast between the rubber particle and the matrix. The stained samples were microtomed using a diamond knife at ambient temperature to obtain thin sections of ~ 50 nm in thickness.

**Fourier Transform Infrared Spectroscopy**

Fourier transform infrared (FTIR) spectroscopy, Bruker (Ettlingen, Germany) was used to monitor the loss of unsaturation during reprocessing and thermal oxidation of ABS.

**Yellowness Measurement**

Yellowness index (YI) was determined in accordance with ASTM E-313 by reflectance measurements using a Spectra flash SF450 data color (Germany) together with a selected standard illuminant (D65) observer (10°) to determine the CIELAB color coordinates (colour system defined by the International Commission on Illumination): L* (measure of lightness/darkness), a* (measure of redness/greenness), and b* (measure of yellowness/blueness) [10]. The instrument is designated to give YI values. Several values of YI obtained from different parts of the samples were used to obtain an average value of the yellowness index.

**RESULTS AND DISCUSSION**

**Processability**

The melt mass-flow rate (MFR) is a common property employed in the recycling industries for quality control of the final recycled material, in order to guarantee its further processing capability for the manufacture of secondary products from these recyclates. Figure 1 shows the slight increase in the MFR of the ABS subjected up to seven extrusion cycles. One reason for the slight increase of MFR may be attributed to the consumption of antioxidant stabilizers in the extrusion reprocessing giving rise to a less protected ABS. The degradation of the grafted polybutadiene can lead to a degrafting of SAN, which would be in line with the observed increase of MFR. Viscosity of SAN reduces due to the reduction of molar mass of SAN after multiple reprocessing at high temperature [14,15]. From a recycling point of view, ABS seems to be a promising material for mechanical recycling, since the MFR values only increase approximately 1.8% in the first reprocessing step and a total of 37.5% after seven extrusion cycles. This small variation of the MFR with a large number of recycling steps would guarantee the processability of the recyclates during the mechanical recycling processes [16].

**Impact and Tensile Properties**

The impact properties of ABS polymers during reprocessing and thermo-oxidative ageing are shown in Figure 2. Figure 2a shows the notched Izod impact strength evolution with the number of reprocessing cycles. There was relatively a large reduction in the first cycle, from approximately 40 kJ/m² to 34.5 kJ/m² and for the following reprocessing cycles the impact strength values decreased slowly to a more
or less 28 kJ/m². This impact property degradation was associated with the lower molecular weight and entanglement density of the SAN matrix, and to the degraded butadiene particles. Previous investigations have also recognized the substantial deterioration in impact properties as a result of recycling [12, 16-18].

From Figure 2b, it is particularly evident that the impact strength slightly reduced with thermo-oxidative ageing. Since notching after heat ageing removes the surface structure of a specimen, the results in the Figure 2b indicate that failure under impact is critically dependent on the condition of the surface layer in ABS. In contrast, however, the impact strength of notched ABS specimens before heat ageing at 120°C decreases rapidly during ageing time of four days, as shown in Figure 2c where initial impact value of 40 kJ/m² drops to approximately 16 kJ/m². Various factors have been involved in reduction of impact strength, including chemical changes in the PB microstructure, which are attributed to chain scission and cross-linking. Furthermore, degradation of the PB phase at the surface forms hydroperoxide species [19,20,21]. Degradation of PB phase by cross-linking would also reduce polymer chain mobility and decrease free volume [19]. Ageing at 120°C produces an increase in T_g due to molecular chain cross-linking in PB phase in consistent with the decrease in impact strength shown in Figure 2c [17, 22, 24].

The influence of reprocessing and thermo-oxidative ageing on the tensile modulus, yield stress, and elongation-at-break was analyzed by tensile testing. Figure 3 shows Young's modulus of reprocessed ABS against the processing step. As it can be observed, the Young's modulus remains practically unaltered during the five reprocessing cycles with slight deviations from mean value of 2.3 GPa, indicating that the degradation of ABS did not have any effect on the low-strain mechanical property. The lack of influence of consecutive reprocessing on the Young's modulus was usual in styrenic polymers such as high impact polystyrene and ABS [12,17]. However, the yield stress and elongation-at-break are clearly influenced by the successive processing steps, with a progressive diminution of the elongation-at-break and stress-at-yield. The decrease in the elongational properties of ABS coincided with a slight increase in material stiffness, which could be seen by an increase in the tensile
Figure 3. Tensile properties of ABS subjected to multiple processing: (a) Young’s modulus; (b) Stress-at-yield; (c) elongation-at-break.

Kim et al. have investigated the NMR sequence before and after recycling of ABS specimens. The colour of SAN may be varied by the sequence of styrene and acrylonitrile. Yellowing occurs according to the content of sequence AN-AN-AN. However the results of their experiment show that the content of the sequence AN-AN-AN was not much changed by recycling and the total molecular weight of ABS was not changed [12]. Therefore, it is presumed that the butadiene component affects the yellowing process which may introduce alterations in the chemical structure of the polymeric chains, resulting in a slightly more brittle material with lower ductility. These structural changes in the components of the ABS material will be studied in more detail in the discussion of the infrared spectroscopy results.

Figure 4 shows the influence of thermo-oxidative ageing at 120°C on the tensile properties of ABS. It can be observed that the effect of ageing on the mechanical properties of ABS is more severe than the one reported for reprocessing. The elongation-at-break and yield stress drastically decrease with the ageing time, after 4 days of exposure to thermo-oxidative degradation. On the other hand, the Young’s modulus shows a slight increase in their values during the initial ageing times (after 1 day) but after 8 days of exposure the increase is more pronounced. The explanation to this complex behaviour could be obtained from the different processes that are involved in thermo-oxidative ageing. The influence of cross-linking in the PB phase is evident in the Young’s modulus of aged ABS specimens.

From Figure 4a, it is particularly evident that the Young’s modulus increased with thermo-oxidative ageing. Similar to the reducing of Izod impact strength at Figure 2c, this ageing (and subsequent cross-linking in the PB phase) increases Young’s modulus also influences failure mode at relatively low loading and results in ductile-brittle transition in failure mode.

As a conclusion, the elongation-at-break and impact strength appear to be the mechanical properties that should determine the recycling possibilities.
and the second-market application for ABS recyclates. It was observed that reprocessing up to 5 cycles does not affect the mechanical properties of ABS to high percentages, with a decrease of 27.5% in elongation-at-break and 23.75% in Izod after three extrusion steps, and a total decrease of about 50% in the elongation-at-break and 30% in Izod after 5 cycles. On the other hand, the thermo-oxidative ageing at 120°C may be considered to be quite severe on the mechanical properties of ABS, since it remarkably affects the elongation-at-break and Izod impact strength of ABS, with a decrease of 75% and 77%, respectively after only 16 days of exposure.

**Morphology**

The morphology of materials were compared before and after reprocessing step, as shown in Figure 5. In the TEM micrographs the dark domains represents the PB phase in the ABS while the light region represents SAN matrix. The micrographs show that reprocessing...
had no significant changes on size, shape, and the distribution of the rubber particles [4,12].

**Fourier Transform Infrared Spectroscopy**

The absorbance spectra of the ABS samples subjected to multiple processing and thermo-oxidative ageing at 120°C were studied. In particular, the hydroxyl groups (3296.4 cm\(^{-1}\)), carbonyl groups (1723 cm\(^{-1}\)), very complex region of C-O stretching vibrations (1000-1300 cm\(^{-1}\)), and the unsaturated groups from the polybutadiene phase of ABS corresponding to the peak of trans-1,4 (966.7 cm\(^{-1}\)) and vinyl-1,2 (911.6 cm\(^{-1}\)) were analyzed in detail. Moreover, in order to obtain a quantitative picture of the structural changes caused by reprocessing and ageing, the relative absorbance ratios of the peaks corresponding to the maximum of the hydroxyl region (3296.4 cm\(^{-1}\)), carbonyl region (1723 cm\(^{-1}\)), the maximum of the C-O regions (1000-1300 cm\(^{-1}\)), trans-1,4 group (966.7 cm\(^{-1}\)), and vinyl-1,2 group (911.6 cm\(^{-1}\)) were determined, related to the height of a reference peak at 1602.3 cm\(^{-1}\) corresponding to the styrene moieties (stretching absorbance of aromatic ring) which remains unchanged during reprocessing, in order to make their results comparable and to eliminate the effect of the thickness of the films [4,12,14].

Figure 6 shows the FTIR spectra of some selected reprocessed and thermo-oxidation ABS samples. Apart from the characteristic peaks related to the aromatic ring stretching vibrations at 1493.9 and 1452.3 cm\(^{-1}\), and the peaks at 1602.3 and 1583.7 cm\(^{-1}\) caused by the aromatic C=C stretching vibration, all others originated by SAN units in the ABS [19,20] some peculiarities in the analyzed spectra could be found. It is believed that the thermomechanical degradation processes caused by the multiple processing of the ABS in an oxygen deficient atmosphere induce a series of heterogeneous and complex chemical reactions that may be responsible for the appearance of a wide range of oxidative moieties in the polymeric chains.

As it can be observed in Figure 6a, the repeated extrusion of ABS results in the decrease of trans-1,4 and vinyl-1,2 indexes corresponding to the polybutadiene phase and appearance of a peak at around 1261.3, 1156.6, 1071, and 1029.2 cm\(^{-1}\) with slight increase in the carbonyl and hydroxyl indexes. The band at 1071 cm\(^{-1}\) assigned to cross-linking ether bridges with low intensity. However, polyethers are known to be highly oxidizable structures, and easily convert to alkoxy macroradicals, and \(\beta\)-scission of alkoxy macroradicals might have occurred. In other words, the cage reaction of alkoxy macroradicals (with hydroxyl radicals) may occur, leading to \(\alpha,\beta\)-unsaturated ketones [20].

Figure 7 represents the spectroscopic results of the
analyzed functional group indexes as a function of the reprocessing steps. It can be observed that repeated processing steps induce complex changes in the absorbance of the selected functional group. As a whole, a decrease in the trans-1,4 and vinyl-1,2 indexes corresponding to the polybutadiene phase can be noticed, together with a slight increase in the carbonyl and ether indexes. This decrease in the double bond groups from polybutadiene could be caused by some cross-linking reactions occurring during the extrusion or also by some minor oxidation processes due to the interaction of the polymer with some residual oxygen which could have been present in the extruder. The diminution in the unsaturated groups, together with the possible decrease in the molecular weight of the ABS suggested by the MFR measurements (indirect value of the molecular weight) may explain the decrease in the elongation-at-break with successive extrusion steps reported by the tensile testing [15].

Figure 8 shows the functional group indexes for the ABS samples subjected to thermo-oxidative ageing at 120°C. Quantitative study of the functional groups demonstrates that thermo-oxidative ageing induces substantial progressive changes in the functional group indexes, in contrast with the heterogeneous effects reported by reprocessing. In Figure 6b, thermo-oxidative ageing caused a marked decrease in the unsaturated groups (trans-1,4 and vinyl-1,2 groups) while asymmetric stretching of the ether bands in the C-O regions, as broad bands appears in the hydroxyl and the carbonyl regions [19,20]. The trans-1,4 group indexes showed a slight decrease at the initial ageing time due to the protective effect of the phenolic antioxidants that was added before coagulation of g-ABS latex, but after the 4th day of thermo-oxidative ageing, the reduction was considerable. Therefore, the first step in the thermo-oxidative ageing of ABS is the degradation of polybutadiene and some of the radicals formed in that degradation can act as initiators for the oxidation of ABS [19,23,25,26]. These polymer degradation products form microstructure inconsistencies which may act as stress concentration sites. Thermo-oxidative degradation of PB phase can also increase polymer density by cross-linking. The corresponding increase in Young's modulus is manifested in brittle behaviour, reducing the contribution of PB to the overall toughening mechanisms of localized shear yielding and crazing in ABS [19]. Moreover, the rapid loss in elastomeric properties of ABS as impact strength and elongation-at-break has been explained in terms of scission reactions of the graft of PB with the rest of the polymeric matrix [20].

Yellowing
Most styrenic polymers especially ABS have a weak point in regard to heat. One of the most popular methods for investigating the changes in optical properties
by heat is measuring the $L^*$, $a^*$, $b^*$, and yellowness index [13, 27].

The tristimulus values ($L^*$, $a^*$, $b^*$) of thermo-oxidative ABS samples are given in Table 1. The samples underwent rapid yellowing upon thermal ageing, yielding a measurable increase within the 2nd day. A study of the tristimulus values indicates that the observed changes in yellowing are due to variations in lightness as well as chromaticity. The $L^*$ parameter calculated from tristimulus values is a direct measure of lightness of the surface colour varying between zero (black) and 100 (white). The colorimetric data show a relatively small change in $L^*$ but significant changes in $a^*$ and $b^*$ values, indicating that discolouration is not a mere change in lightness. The positive value of $b^*$ indicates red/yellowness while the negative $a^*$ value corresponds to greenish/blueness. The starting material itself with $L^* = 79.25$, $a^* = -2.24$, and $b^* = 12.14$ may be described as having a light yellow-green surface. The value of $a^*$ decreases while that of $b^*$ increases with YI. This indicates an increase of yellow-green colour with processing. Table 1 shows the variations of yellowness index (YI) of ABS samples with thermal ageing. The YI of the ageing sample increased approximately linearly with time (up to 8 days) but the rate of increase fell thereafter. The decrease is probably a result of the slow loss of yellow brittle surface layer due to handling or leaching reactions at longer periods.

**CONCLUSION**

The results suggest that the most important factor affecting on the processability, optical, and mechanical properties of reprocessing and thermo-oxidation of ABS is degradation (chain scission and particularly cross-linking) of the rubber (polybutadiene) component. As the reprocessing and thermo-oxidation conditions become more and more severe, degradation of the polybutadiene phase seems to become progressively more significant. These changes that occur during reprocessing and thermo-oxidations alter the ABS microstructure, in particular by reducing the double bonds and cross-linking the rubber phases. These changes have significant effects on the optical and mechanical properties. Reprocessing and thermo-oxidation of ABS have a much more severe effect on impact properties and elongation-at-break than tensile properties. This is consistent with the changes outlined above, namely the degradation of the polybutadiene phase. Degradation of the rubber phase does contribute to loss of impact resistance and elongation-at-break. It has been demonstrated that the optical properties of ABS is clearly affected by thermo-oxidative ageing. In addition, the melt mass-flow rate increased slightly with the reprocessing steps, which may be related to a decrease in the molecular weight of the polymer caused by chain scission mechanisms induced by multiple processing.

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