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Oxidation and colour development in AES resins

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Summary

The structural changes connected with the beginning of colour development during thermal oxidation of a AES polymer blend have been investigated. The yellowing behaviour of AES has been compared with that of the different components of the blend, and the influence of oxygen partial pressure on the polymer degradation has been determined. Colour changes have been shown to be correlated with the early stages of oxidation, and at the same time the different stabilities of the blend components were verified.

Introduction

AES resins are formed by a glassy matrix of styrene-acrylonitrile (SAN) copolymer in which a rubbery phase of ethylene-propylene-diene (EPDM) is dispersed together with SAN grafted onto EPDM chains (EPDM-g-SAN). The graft copolymer acts as a compatibilizer. The use of a rubber without unsaturations on the main chain gives a material comparable to ABS as mechanical properties are concerned, but with better thermal and thermooxidative resistance [1].

Ageing of polymeric materials may be defined as a progressive deterioration of physical properties due to the action of heat, oxygen, radiation or mechanical work, either separately or in combination. Ageing may be effective from the very beginning of polymer life. In the case of styrene-based polymers, for example, immediately after the polymerisation reaction some plant operations may be run at temperatures between 200 and 250°C, for short times, in order to remove residual monomers and any low molecular weight compound. Unproper control of the vacuum conditions may lead to

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partial oxidation of the macromolecules, with unwanted polymer coloration. Processing operations as well may induce thermomechanical oxidation which can shift the polymer properties out of the suitable range for technological uses.

In another paper we have reported the results of an investigation about the thermal oxidative behaviour of an AES blend and of its components, both under conditions of total volatilisation and lower temperatures prior to decomposition [2]. Particularly, it has been pointed out that the oxidation reactions start on the EPDM chains at temperatures below those of polymer decomposition. Higher reactivity towards oxidation has been also found in the grafted EPDM, compared to the pure rubber. In the present communication the structural changes connected with the yellowing of an AES blend during thermooxidation and its dependence on the oxygen concentration are investigated. Results on the yellowing behaviour of unstabilized AES in air are discussed first, followed by those on the behaviour of the components of AES resins heated under different partial oxygen pressures.

Experimental

Materials. AES was an industrial sample (Enichem, Italy), obtained by radical copolymerization of styrene and acrylonitrile in the presence of EPDM rubber (weight composition: ethylene 60%, 5-ethylidene-2-norbornene 9%). The material was a mixture of SAN copolymer (acrylonitrile weight content: 25%), unreacted EPDM and EPDM-g-SAN graft copolymer. The overall rubber content in the AES was 25%. The composition of AES as determined by fractional extractions, was 60% SAN, 9.5% EPDM, 29.5% EPDM-g-SAN and 1% insoluble fraction. From elemental nitrogen analysis the acrylonitrile content was determined and the weight composition of the EPDM-g-SAN calculated as 57% EPDM and 43% SAN. Apart from the original AES polyblend and the EPDM-g-SAN obtained by extraction, the other samples employed were the same EPDM rubber (Dutral 046-E3, Enichem Elastomeri, Italy) used for AES synthesis and an azeotropic SAN copolymer (Kostil AF600, Enichem, Italy).

Ageing and characterization. Yellowing treatments were carried out in a forced-air circulation oven at fixed temperatures. The experiments at low pressures were run in an all-glass high vacuum apparatus, previously evacuated to 10^{-2}-10^{-3} mbar. The samples were exposed to different oxygen pressures while the temperature was kept constant. All the experiments were performed with polymer films of 80±10 μm thickness obtained on KBr plates by evaporation of chloroform solutions. The effect of treatments on the structure of the polymers was measured with a Perkin Elmer 1710 FTIR Spectrometer.

Results and discussion

Samples of unstabilized AES were subjected to oven-ageing at constant temperatures and the colour formation in the films was followed visually. In Figure 1 the starting time for yellowing is plotted in a temperature range between 150 and 300°C. The reported values may be considered as induction times for colour development. In the enlarged section of the figure the behaviour at the higher temperatures may be better appreciated. The shape of the curve shows a noteworthy decrease of induction time around 200°C, in agreement with the temperature where beginning of polymer oxidation was revealed by DSC measurements [3]. In Figure 2 the IR spectrum of oven-aged AES (5.5 min at 225°C) is compared with that of the original polymer in the region between 2000 and 1500 cm^{-1}. The appearance of a weak absorption around 1715 cm^{-1}, which can be attributed to carbonyl groups, indicates that the oxidation process has already started in the polymer.

In order to obtain more information on the yellowing mechanism and on critical conditions of oxidation, the components of AES polyblend were subjected to oven-ageing at 250°C for constant time (5 and 10 min) under different pressures of oxygen.

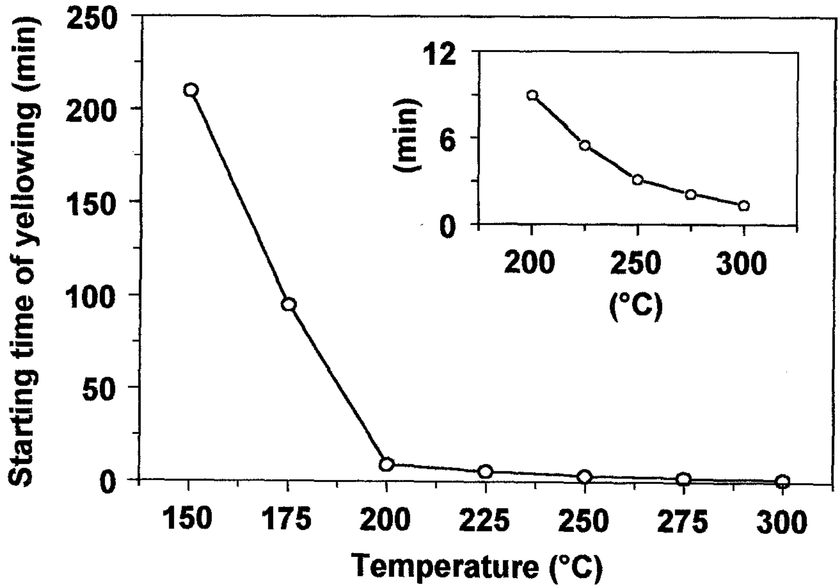

Fig. 1. *Yellowing curve of unstabilized AES in air.*

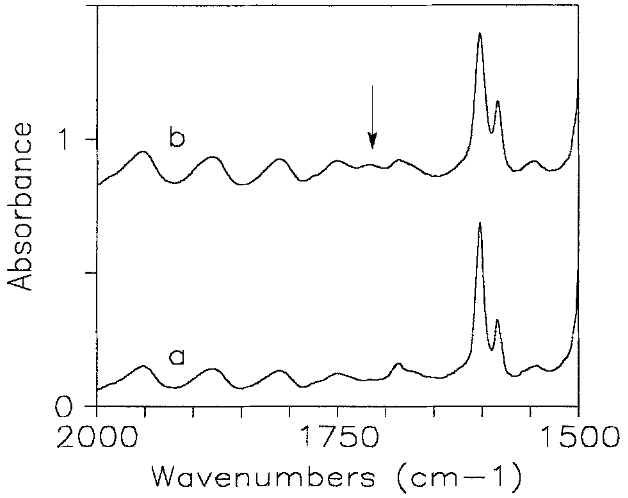

Fig. 2. *IR spectrum of untreated (a) and oven-aged AES (b).*

The spectra of both an EPDM film treated 5 min at 212 mbar and an untreated sample are shown in Figure 3. The major spectral changes resulting from oxidation occur in the hydroxyl region between 3600 and 3100 cm^{-1}, in the carbonyl region between 1800 and 1600 cm^{-1} and in the C-O region between 1200 and 1000 cm^{-1}. Similar

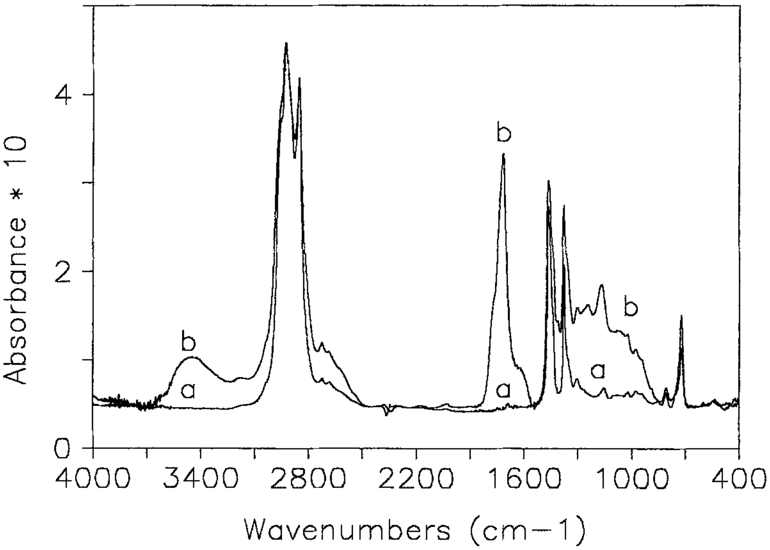

Fig. 3. *IR spectrum of untreated (a) and oven-aged EPDM (b).*

structural modifications are also reported in other studies dealing with thermal- and photo-oxidation of EPDM rubbers [4-7]. The IR spectra of EPDM-g-SAN films treated under the above conditions showed the same changes, whereas on SAN samples no effect could be found. Therefore, it may be concluded that the EPDM chains represent the initial site of oxidation in the AES resins.

The evolution of carbonyl absorptions on the samples subjected to the above treatments was also measured. Absorbance readings were expressed as indexes and the peak at 1377 cm^{-1}, corresponding to the C-CH_3 symmetrical bending, was used as a reference. The trends of carbonyl groups in free EPDM and in the rubber part of EPDM-g-SAN, for treatments of 5 minutes at 250°C, are plotted as a function of oxygen pressure in Figure 4. The curve of EPDM shows an induction pressure of ca. 4 mbar with an initial fast building-up, followed by a slower growth of the index until the pressure reaches the value corresponding to that of oxygen in air. The rubber portion of the graft copolymer presents a similar behaviour with a lower induction pressure (ca. 3 mbar).

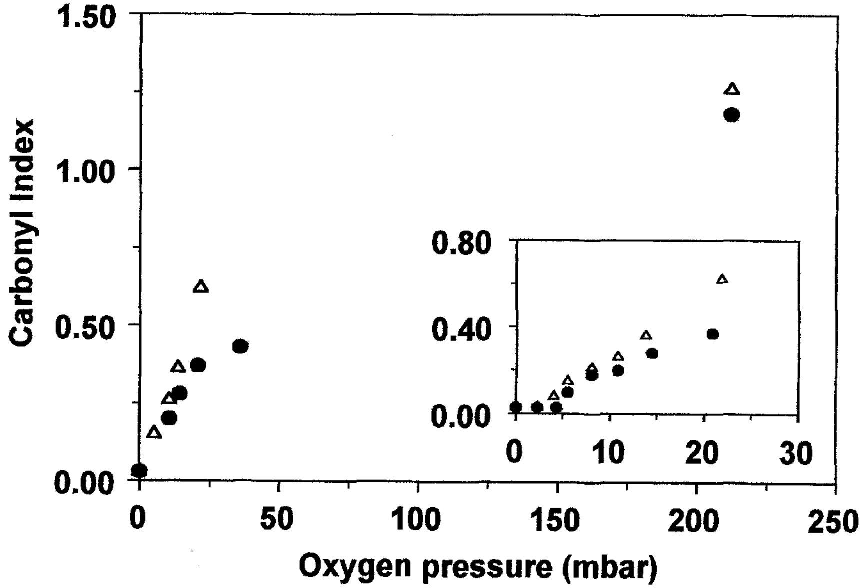

Fig. 4. *Carbonyl indexes of EPDM (●) and EPDM-g-SAN (△) for treatments of 5 minutes at 250°C.*

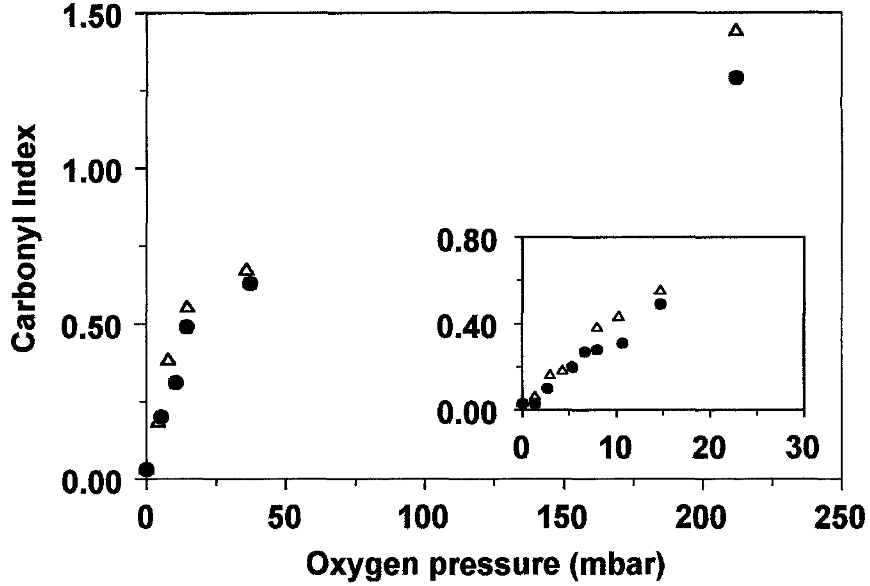

Fig. 5. *Carbonyl indexes of EPDM (●) and EPDM-g-SAN (△) for treatments of 10 minutes at 250°C.*

The curves relative to treatments of 10 minutes (Figure 5) also show a similar trend. The induction pressure is 1 mbar for EPDM and lower than 1 mbar for EPDM-g-SAN. In all the samples aged at pressures higher than the induction one, yellowing arised and colour intensity was proportional to oxygen pressure and time of ageing. Similar results have been reported in a study about the thermal-oxidation of EPDM, in which the colour changes of the rubber were closely related to the end of the induction period [6].

From the analysis of structural changes and from the comparison of the carbonyl curves it may be inferred that the same mechanism of oxidation acts in free EPDM and in the graft copolymer. However, in EPDM-g-SAN oxidation reactions start at lower pressures in respect of pure EPDM, and the degradation process takes place at higher rates reaching higher conversions.

The exact structure of the products which originate yellowing in oxidised polymers is difficult to be determined. It is generally supposed that secondary degradation reactions give rise to structures containing conjugated unsaturations, which absorb visible light. In the case of AES, though polymer yellowing cannot be used as a convenient and direct degradation criterion, colour changes are clearly correlated with the early stages of oxidation, and their appearance during plant operations would be an indication of non desired structural changes. The characteristics of thermal-oxidation at partial oxygen pressures of EPDM-g-SAN are essentially similar to those of free EPDM and the lower stability of grafted rubber is to be associated with the presence of SAN chains linked to the norbornene units [2].

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