

# Ageing and Stabilization of Polystyrene Plastics. III.\* Nature of the Carbonyl Functional Groups Formed during the Photo-oxidation of Rubber Modified Polystyrene

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The formation of carbonyl compounds during the photo-oxidation of rubber modified polystyrene has been studied by means of infrared spectroscopy. A significant portion of the photo-oxidation products has been found to be soluble in methanol. The technique of difference spectra in the combination with the specific chemical reactions of carbonyl compounds with ammonia, sodium hydroxide, potassium tetrahydroborate, thionyl chloride, and hydrogen chloride was used to detect the nature of carbonyl groups in solid polymer films and in low-molecular products extracted by methanol from the oxidized samples. The presence of both esters and free acids in the photo-oxidized rubber modified polystyrene has been qualitatively proved. Aldehydes and ketones were further present but could not yet be distinguished one from another.

Rubber modified (high impact) polystyrenes have very good mechanical properties especially excellent impact properties. However, the presence of double bonds introduced into this system by the modifying unsaturated elastomer (polybutadiene or styrene-butadiene rubber is usually used) affects adversely the ageing characteristics. These materials are therefore particularly sensitive to the light initiated deterioration both in weathering and in photo-oxidation tests. Under these conditions relatively rapid decrease in the impact strength takes place [1–3]. The decrease of the double bonds content of the elastomer component as well as the increase of carbonyl and hydroxyl absorption bands have been found by means of the infrared spectroscopy [4–6].

The exact structure of the oxygen compounds produced by photo-oxidation is little known. However, the knowledge about the nature of oxygen groups present in the polymer is very valuable not only for the elucidation of the photo-oxidation mechanism but also for solving the technical problems of ageing and stabilization of these materials. The presence of carbonyl compounds (*e.g.* ketones) absorbing radiation in the near u.v. region and forming excited states is frequently considered to be the source of low resistance of many industrial polymers against the photo-oxidation. In the case of the other oxygen compounds (acids, esters) such adverse effect need not always occur and the excellent ageing resistance, for instance of poly(methyl methacrylate) [7], is well known.

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There have been reported some attempts to distinguish individual types of carbonyl compounds following the changes of the infrared absorption bands after the reaction of oxidized polymers (*e.g.* polybutadiene [8], polypropylene [9], polyethylene [10], and styrene homopolymer [11]) with selective agents. We have tried similar method for the identification of various types of carbonyl compounds found at advanced stages of photo-oxidation in rubber modified polystyrene.

### Experimental

The rubber modified polystyrene was prepared using the well-known polymerization technique. About 6.0% of the polybutadiene (Plioflex AET 5000) was dissolved in styrene monomer which was subsequently bulk polymerized. Nonpolymeric substances (*e.g.* residual monomer, antioxidants of elastomer component) were removed by reprecipitation of the unstabilized and unpigmented polymer from the benzene solution with the excess of methanol. Other changes caused by the reprecipitation were insignificant, as measured by infrared spectrometry, viscometry, phase contrast microscopy and oxidative degradation in the presence of osmium tetroxide.

The films of thickness about 0.1 and 100 mm in diameter were prepared by freely evaporating benzene solution of the reprecipitated polymer on the level of mercury containing 0.01% of tin [12]. The films were further dried *in vacuo* for several days at a temperature of 30°C and the removal of the last traces of benzene was followed by means of absorption band at 675 cm<sup>-1</sup>. Then the films were cut into 8 mm by 50 mm samples and according to the intensity of the absorption band at 1603 cm<sup>-1</sup> the films with perfectly equal thickness were selected for the difference spectra measurements.

The photo-oxidation took place in air at 30–35°C. The Tesla mercury vapour lamp (400 W) placed in a distance of 40 cm from the samples served as the source of light. The wave lengths shorter than 300 nm were suppressed by means of the Pyrex glass filter. The intensity of the radiation incident on the sample surface (estimated using a ferri-oxalate actinometer [13, 14]) was about  $1 \times 10^{16}$  quanta cm<sup>-2</sup> s<sup>-1</sup>. The films used for reactions with chemical agents were exposed to the radiation dose of  $9.0 \times 10^{21}$  quanta cm<sup>-2</sup>.

Infrared spectra were taken with a Unicam spectrometer SP 100 using the NaCl prism and diffraction gratings 1500 and 3000 lines/inch in the region 650–3650 cm<sup>-1</sup>. The sector scan repetition device enabled to record spectra of several samples on a single chart of paper.

The rubber modified polystyrene films, unexposed or photo-oxidized, were treated with gaseous ammonia or hydrogen chloride, with the solution of sodium hydroxide in methanol or isopropanol (concentration 10 g/100 ml) or with saturated KBH<sub>4</sub> solution in dry ethanol, respectively. The reaction time between 48 and 240 hours has been found sufficient at a temperature of about 25°C in most cases.

The extraction of the oxidation products was carried out in separate experiments. About 10 g of the photo-oxidized rubbermodified polystyrene in the form of thin film (approximately 0.1 mm) was cut into small pieces and extracted with a minimum volume of the cold methanol anal. grade (50 ml) in the nitrogen atmosphere for 96 hours. The extract was concentrated by evaporation in the nitrogen stream at a temperature of 30°C. The films of suitable thickness were prepared by casting the concentrated extract on the NaCl window and evaporating to dryness. The remaining extract was treated with gaseous ammonia, hydrogen chloride, thionyl chloride vapours, or KBH<sub>4</sub> solution in ethanol, respectively. The reaction products were dissolved in chloroform or methanol

and a film with approximately equal thickness was prepared for the recording of difference spectra.

### Results and Discussion

During the photo-oxidation of rubber modified polystyrene essential changes occur in the infrared spectrum. The intensity of the  $970\text{ cm}^{-1}$  absorption band assigned to double bonds very quickly decreased. The formation of oxygen compounds is demonstrated with the increase of absorption bands in the region of  $3400\text{ cm}^{-1}$  (hydroxyl groups) and  $1700\text{ cm}^{-1}$  (carbonyl groups).

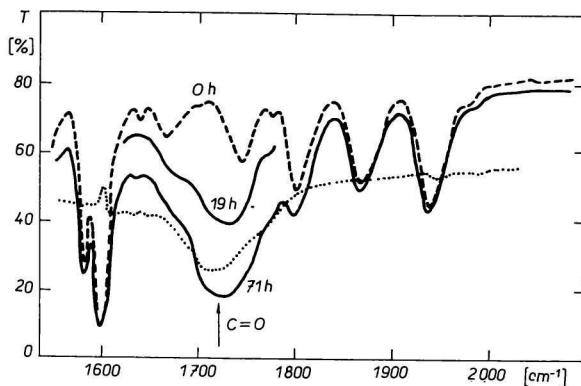


Fig. 1 Infrared spectrum of the photo-oxidized rubber modified polystyrene film in the carbonyl region.

The dashed line refers to the unexposed sample, the full lines to the exposure time 19 hours and 71 hours respectively, the dotted line is the difference spectrum.

The shape of the absorption band of the carbonyl groups in the region  $1720\text{--}1740\text{ cm}^{-1}$ , the broadening of the band and the shift of the maximum from  $1735\text{ cm}^{-1}$  to lower wavenumbers in the advanced stages of oxidation (Fig. 1) indicate the presence of many different types of carbonyl compounds. Moreover the absorption band of carbonyl groups is distorted because of overlapping with the absorption band of the polystyrene at  $1745\text{ cm}^{-1}$ . When eliminating the influence of this band in the difference spectrum the position of the absorption band of carbonyl compounds was  $1725\text{ cm}^{-1}$ . The broad band with maximum at  $1170\text{ cm}^{-1}$  can be assigned to the vibration of the  $\text{—C—O—}$  bond in several structural groups. The other very weak bands in the spectrum could not be reliably interpreted.

The direct identification of different types of carbonyl groups from this spectrum is not possible. Therefore we tried to use several specific chemical reactions of carbonyl groups [15] and we followed the changes in the difference infrared spectra caused by these reactions.

Methanol used in some reactions as a solvent was able to extract a significant portion of oxygen compounds. The fraction of the original rubber modified polystyrene film soluble in methanol was only 0.1% of the weight of polymer. With the increase of the exposure time also the portion of polymer extractible by methanol increased according

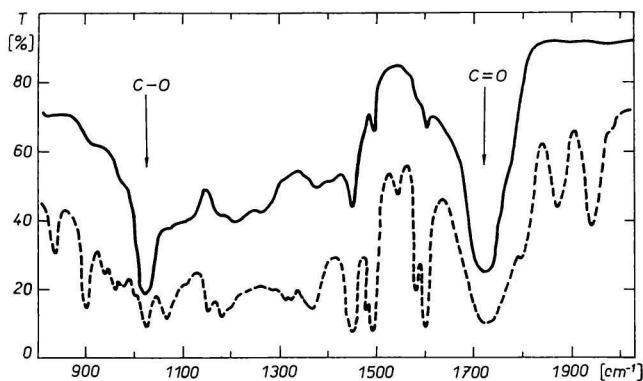


Fig. 2. Infrared spectrum of the methanolic extract of the photo-oxidized rubber modified polystyrene (full line) and of the photo-oxidized solid sample (dashed line).

to the degree of oxidation. For instance, after an exposure of sample to radiation dosis from  $3.0$  to  $6.0 \times 10^{21}$  quanta  $\text{cm}^{-2}$  it was possible to extract 3–4% of the polymer weight. The number average molecular weight of this methanol soluble fraction determined by means of vapour pressure osmometry was 580. An appreciable decrease of the carbonyl and hydroxyl absorbance ratios in the film samples (*e.g.* before the extraction the absorbance ratio  $A_{1725}/A_{1945}$  characteristic of the carbonyl groups content was 2.795 whereas after the extraction it was only 1.648) and the infrared spectrum of the extract (Fig. 2) indicate that a great portion of the photo-oxidation products is present in the extract. Thus it was feasible to reach considerably higher relative concentration of oxygen compounds in the extract than in the solid film and the changes in the spectra could be measured more distinctively.

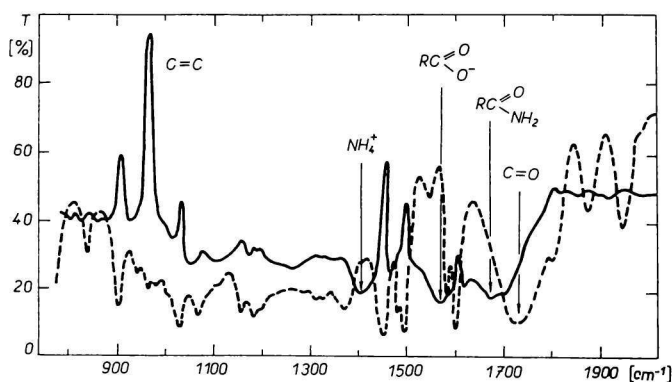


Fig. 3. Infrared spectrum of the photo-oxidized film after the treatment with gaseous ammonia.

The dashed line is the spectrum of the oxidized film before the chemical treatment without the compensation in reference beam, the full line is the difference spectrum.

In the infrared spectrum of the methanolic extract (Fig. 2) it is possible to prove the presence of substances with monosubstituted aromatic ring according to the absorption bands at 700, 760, 1495, and 1603  $\text{cm}^{-1}$ . The broad absorption band with maximum at 3440  $\text{cm}^{-1}$  demonstrates the presence of hydroxyl groups. Sharp absorption band at 1028  $\text{cm}^{-1}$  is characteristic of the vibration of  $-\text{C}-\text{O}-$  group in various oxygen compounds, the precise correlation is difficult [17]. The strongest absorption band is again the band with maximum at 1725  $\text{cm}^{-1}$ . The shoulder at 1770–1780  $\text{cm}^{-1}$  probably gives evidence of the presence of keto-acids or their esters [20, 21].

Using gas chromatography [16] it was possible to distinguish clearly the extract obtained from the photo-oxidized polystyrene modified with polybutadiene (presence of 8 various substances minimum) from the extract of polystyrene modified with styrene–butadiene copolymer (presence of 15 various substances minimum). The more complicated structure of the latter elastomeric component may be the cause of greater variety of low-molecular oxygen compounds resulting from the scission of polymeric chains. By that time only benzaldehyde and acetophenone were reliably identified in the substances formed in this way, they are most probably produced in the photo-oxidation of the polystyrene phase because both substances were present even in the extract of polystyrene modified with polybutadiene. After the reaction of the extract with various agents the selective disappearance of some peaks on the chromatogram was observed and some new peaks appeared corresponding to the reaction products [16]. These results also support the statement about the presence of several types of carbonyl compounds in the extract.

The treatment with gaseous ammonia caused relatively great changes in the infrared spectrum of the photo-oxidized film sample (Fig. 3). Original absorption band of the carbonyl groups disappeared almost entirely. New bands appeared in the difference spectrum at 1670, 1570, and 1410  $\text{cm}^{-1}$ , from which the band at 1670  $\text{cm}^{-1}$  can be assigned to the  $\text{C}=\text{O}$  group in primary amides [17, 20] formed relatively easy when esters reacted with ammonia. The absorption band at 1570  $\text{cm}^{-1}$  gives evidence of the formation

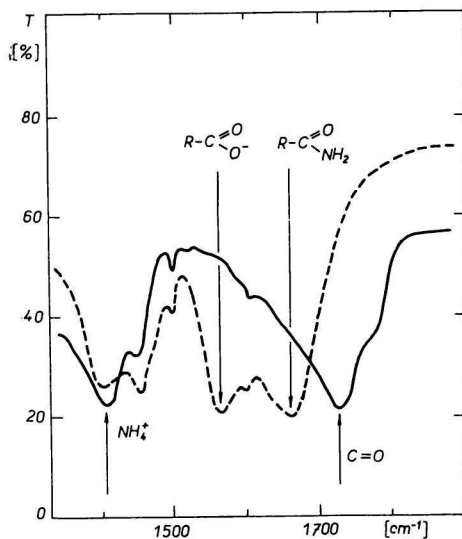


Fig. 4. Infrared difference spectrum of the methanol soluble extract of oxidized sample treated with gaseous ammonia (dashed line) and subsequently treated with gaseous hydrogen chloride (full line).

of the carboxylate ion [9] produced in the reaction of acids with ammonia. The presence of very strong absorption band at  $1410\text{ cm}^{-1}$  confirms the presence of the  $\text{NH}_4^+$  ion. This band may be present also in the spectrum of primary amides [17]. In the region of stretching vibration the original absorption band of hydroxyl groups decreased and a broad band characteristic of primary amides as well as of the  $\text{NH}_4^+$  ion was formed at  $3200\text{ cm}^{-1}$ . It was not succeeded to prove in the spectrum of ammonia treated film the presence of ketimines as the products of reaction of ammonia with aldehydes and ketones.

After the reaction of the methanol soluble extract with gaseous ammonia a complete disappearance of the original absorption band of carbonyl compounds took place (Fig. 4). The absorption band at  $1670\text{ cm}^{-1}$  and the development of a new absorption peak at  $3200\text{ cm}^{-1}$  again give evidence of the formation of primary amides [17, 20]. A strong absorption band at  $1570\text{ cm}^{-1}$  belongs to the  $-\text{COONH}_4$  group together with another strong absorption band at  $1410\text{ cm}^{-1}$ . After subsequent hydrogen chloride treatment the free acids were regenerated from their ammonium salts and the absorption band of carbonyl group of acids reappeared again.

Potassium tetrahydroborate reduces selectively aldehydes and ketones to primary and secondary alcohols, respectively, whereas with acids and esters it does not react [18]. In the difference spectrum of the film samples (Fig. 5) the original absorption band of carbonyl groups entirely disappeared and new strong bands appeared at  $1570$  and  $1405\text{ cm}^{-1}$ . The weak bands at  $1050$  and  $1085\text{ cm}^{-1}$  might be attributed to primary and secondary alcohols. The products of the decomposition of  $\text{KBH}_4$  are probably able to react with acids and esters producing potassium carboxylates. This is confirmed by the formation of a strong absorption band at  $1570\text{ cm}^{-1}$ . The absorption band at  $1405\text{ cm}^{-1}$  belongs probably to the vibration of the  $\text{B}-\text{O}$  bond in the decomposition products of  $\text{KBH}_4$ .

When treating the extract with the alcoholic solution of  $\text{KBH}_4$  a similar effect occurred. The original band of carbonyl compounds disappeared and a band characteristic of the carboxylate ion appeared at  $1570\text{ cm}^{-1}$ . The intensity of the hydroxyl band also slightly

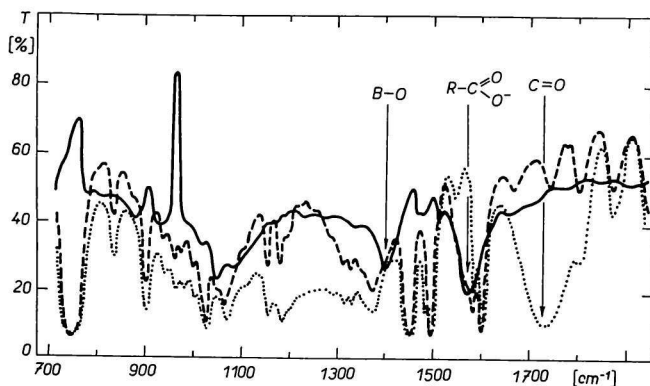


Fig. 5. Infrared spectrum of the photo-oxidized film after the treatment with  $\text{KBH}_4$  solution.

The dotted line refers to the oxidized film before the chemical treatment without the compensation, the dashed line is the spectrum after the chemical treatment without the compensation, the full line is the difference spectrum.

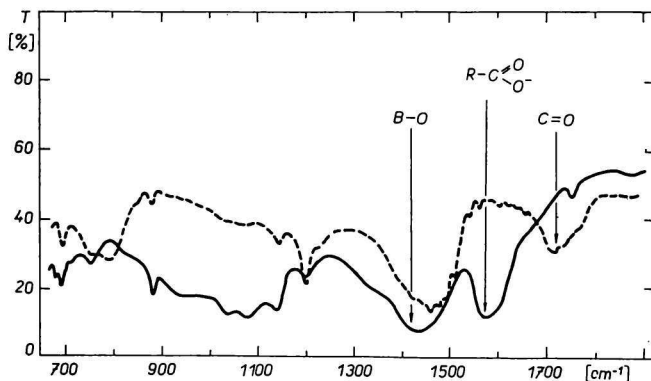


Fig. 6. Infrared spectrum of the methanol soluble extract treated with  $\text{KBH}_4$  solution (full line) and subsequently treated with gaseous hydrogen chloride (dashed line).

increased. It may be presumed that besides the specific reduction of aldehydes and ketones also in this case the reaction of the decomposition products of  $\text{KBH}_4$  (e.g. potassium borate) [19] with acids and esters takes place, while potassium carboxylates were formed. When treating the extract after the reaction with  $\text{KBH}_4$  subsequently

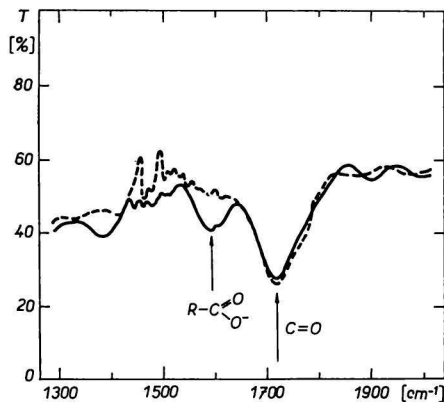


Fig. 7. Infrared difference spectrum of the photo-oxidized film sample after the treatment with sodium hydroxide solution in isopropanol (full line) and the difference spectrum of the oxidized film without the chemical treatment (dashed line).

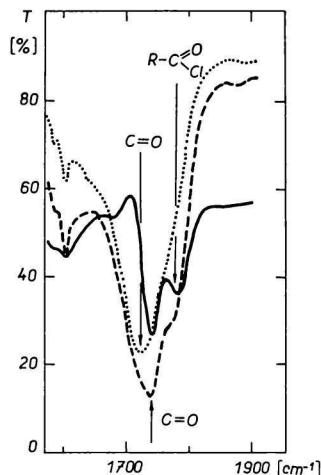


Fig. 8. Infrared spectrum of the methanolic extract of the photo-oxidized film after the treatment with thionyl chloride vapour.

The dotted line refers to the spectrum before the chemical treatment without the compensation, the dashed line is the spectrum after the chemical treatment without the compensation, the full line is the difference spectrum.

with gaseous hydrogen chloride the absorption band at  $1570\text{ cm}^{-1}$  assigned to the carboxylate ion disappeared and the band at  $1720\text{ cm}^{-1}$  of original acids reappeared (Fig. 6). However, the intensity of this band was now slightly lower compared with the original sample, as aldehydes and ketones selectively reduced by  $\text{KBH}_4$  were not regenerated by the hydrogen chloride treatment.

The decrease of the intensity of the original absorption band at  $1720\text{ cm}^{-1}$  due to the treatment of film samples by sodium hydroxide may be explained so that acids and esters are converted into sodium carboxylates. Accordingly a new band appears at the wavenumber  $1575\text{ cm}^{-1}$  assigned to the carboxylate ion (Fig. 7).

We have tried to prove the presence of free acids also by means of reaction with thionyl chloride. However, the photo-oxidized film sample was deteriorated already with the thionyl chloride vapour to such extent that it was impossible to record the infrared spectrum. In the difference spectrum of the extract after reaction with thionyl chloride vapour (Fig. 8) a new band appeared at  $1775\text{ cm}^{-1}$  which confirms the formation of acid chlorides [17]. The shift of the main absorption band to  $1740\text{ cm}^{-1}$  might again indicate the presence of esters.

The preliminary results have shown that using hydroxylamine hydrochloride or  $\text{NaHSO}_3$  the reaction conditions need to be modified and that further work is needed to interpret the complex spectrum obtained after the reaction of photo-oxidized film sample with phenylhydrazine hydrochloride.

The presence of low-molecular fragments proves that together with crosslinking also chain scission plays an important role in the photo-oxidation of this polymer.

In the reactions with used chemical agents the behaviour of solid films and methanolic extracts did not differ substantially from one another. It indicates that during the extraction the selective separation of the photo-oxidation products does not take place to a greater extent. Carbonyl groups are bonded most probably both on relative long, up to this time only slightly oxidized macromolecules, and also on extremely low-molecular fractions formed during the oxidative scission of these macromolecules.

From the results described above it can be concluded that both esters and free acids are present in the final products of the photo-oxidation of rubber modified polystyrene. The presence of aldehydes and ketones (which could not yet been distinguished one from another) can be assumed on the basis of the  $\text{KBH}_4$  treatment results. Due to the large differences in absorptivities of individual carbonyl compounds mentioned above, especially if their relative content in oxidized sample is changing in the course of oxidation, the complex nature of the carbonyl absorption band, if not taken into account, may lead to the incorrect conclusions in the quantitative interpretation of infrared spectra.

The purpose of our work in this step was to prove qualitatively the presence of various types of carbonyl compounds in the photo-oxidized rubber modified polystyrene. More experimental studies are needed to determine quantitatively the content of esters, acids, aldehydes, and ketones respectively, the kinetics and mechanisms of their formation during photo-oxidation.

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