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Changes to polymer morphology caused by u.v. irradiation: 1. Surface damage

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The influence of u.v. irradiation on the surface morphology of some commercial polymers was investigated using scanning electron microscopy (SEM). The photodegraded samples exhibited a high degree of surface damage. The formation of cracks and holes resulting from the degradation and evolution of volatile products was observed. In polymers undergoing photocrosslinking, the agglomeration of particles was clearly seen. Polymer photodegradation in the presence of hydrogen peroxide as an acceleration agent revealed its etching action.

(Keywords: morphology; degradation; u.v. irradiation)

INTRODUCTION

Physical and mechanical properties of plastics depend not only on the chemical structure of polymers but also on their morphology. Polymer macrochains can be completely disordered (amorphous) or partially ordered. The amorphous phase consists of more or less entangled macrochains – sometimes only linear, in other cases branched or crosslinked – forming tridimensional, interpenetrating networks. Ordered structures have a tendency to crystallization although fully crystalline polymers appear very rarely. Crystalline forms (fringed micelles, fibrils, folded lamellae, spherulites) existing in ordered polymers are interconnected by amorphous regions. In order to improve mechanical properties, crystallinity is induced in amorphous polymers by stretching the sample at room temperature (cold drawing) or at a temperature above its glass transition. The higher the degree of crystallinity, the more pronounced the properties[1].

The characterization of polymer morphology contributing to properties and behaviour of plastic products is very important from the practical point of view. In many technical applications, the observation of changes in polymer structure allows the best polymer composition and preparation conditions to be chosen to achieve the desired properties of the final products.

Over the past few decades, the morphology of polymers has been extensively investigated as a result of the fast development of various sophisticated microscope techniques[2–5].

Polarized light optical microscopy is used for the investigation of crystalline polymers[4,5]. Spherulites show the typical maltese cross in polarized light, which is caused by the birefringence effects.

Transmission electron microscopy (TEM) is used to observe the internal microstructure of polymers[3,6,7]. TEM requires very thin sample sections (10^{-7}–10^{-8} nm) which can be obtained using an ultramicrotome knife. Electron irradiation frequently damages thin polymer film therefore the sample should be stabilized. One possible method for investigating polymers that are unstable to an electron beam is surface replication, but information obtained by this method is not always representative of the internal structure. In order to improve the contrast of images, the shadowing of specimens with a heavy metal or sample staining with osmium tetroxide and ruthenium tetroxide is often used.

Scanning electron microscopy (SEM) is a very powerful tool for studying the morphology of surfaces. The surface of non-conductive samples must be coated with a thin layer (10–50 nm) of gold or platinum. Sometimes, a surface pretreatment (ion sputtering or chemical etching) is carried out to reveal structural details. Moreover, brittle fracture of samples (in liquid nitrogen) can give information about the internal morphology of bulk specimens.

The following applications of SEM have been made: study of surface microstructure of polymer films, fibres and powders (amorphous[8,9] and crystalline[10,11]); investigation of liquid crystals[12,13]; control of the polymerization process[14,15]; study of the structure of copolymers[16,17], polymer blends and networks[18,19] (investigation of miscibility and adhesion of components); observation of structural defects[16] and sample roughness[20]; changes in the structure of polymers during stretching and upon loading (formation of crazes and cracks)[21,22]; fracture surface morphology[23]; grafting processes[24]; chemical agent transport processes through membranes (porosity of membranes)[25,26]; the mechanism of plastics toughening by resins[27,28]; testing of polymers used as fillings in dentistry[29,30].

There also exist very modern microscopic techniques such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), which allow examination of polymer samples from the scale of micrometres down to angstroms. The arrangement of individual polymer chains is visualized, and in some cases the observation of single atoms is possible[31,32].

Although microscopic methods are so popular and frequently used in the investigation of polymers, very little is known about their application to the study of the degradation processes in polymers[33–36].

The purpose of this work was to investigate by SEM the changes in polymer morphology caused by photodegradation processes.

EXPERIMENTAL

Samples of commercial polymers (supplied by Aldrich or Polyscience), were chosen for morphology studies. The abbreviations, full names (and IUPAC names) of the polymers are listed in *Table 1*.

Films about 20 μm thick of the polymers were obtained by casting 2% polymer solution onto a glass plate. After solvent evaporation, samples were dried in vacuum at room temperature to a constant weight.

Polymers were degraded in air atmosphere upon irradiation using a high pressure mercury lamp (HPK 125W, Philips, Holland) emitting polychromatic radiation within 248–578 nm. The incident light intensity at the sample position was measured by radiometer (IL 1400A, International Light, USA) to be 32 mW cm^{-2}.

Some samples were photodegraded in the presence of hydrogen peroxide (30 wt%, POCh, Poland) which is a source of free radicals. The photodegradation of water-soluble polymers in the presence of H_2O_2 was carried out in solution. The photodegradation of polymers insoluble in water was also performed in a heterogeneous, well-stirred mixture of an organic solvent and H_2O_2. Some solid samples were placed in diluted or concentrated H_2O_2 solution and then irradiated with u.v. The thickness of the layer of H_2O_2 solution on the polymer surface was about 1 mm.

Polymer specimens for SEM were covered by a 10 μm layer of platinum using (Polaron Equipment Ltd, USA). SEM microphotographs were obtained using a Jeol JSM-820 scanning microscope (Japan). The accelerating potential was 15 kV. Photographs of representative areas of the samples were taken.

RESULTS AND DISCUSSION

Disadvantageous photo-ageing processes in polymers were investigated under accelerated conditions using a u.v. radiation source to simulate the action of sunlight.

Various analytical methods, such as u.v.-vis. and i.r. spectroscopy, viscosimetry measurement and gel permeation chromatography (g.p.c.), were used to follow the processes. The results of these investigations have been described elsewhere[34–40]. All polymers investigated show great changes of the chemical structure due to u.v. irradiation. The main reaction occurring in u.v. irradiated samples are chain scission, side-group abstraction, branching and crosslinking, polyene formation, oxidation leading to the formation of ketones, hydroxy and hydroperoxide groups, and rearrangement processes. Oxidation reactions are mainly localized on the sample surface and depend on its morphology. Photodegradation products can then accelerate the further destruction of samples because of their sensitivity to light and the high activity of the intermediate free-radical products. Chemical changes cause the deterioration of physical, mechanical and optical properties of polymers. Exposed samples usually become brittle and yellow, and shrinkage of the films takes place.

Figures 1a and *b* show the SEM microphotographs of PPO irradiated for 4 h in air and for 2 h in the presence of concentrated H_2O_2, which is a source of free hydroxy (HO·) and hydroperoxide (HOO·) radicals which accelerate degradation processes in polymers[35,38]. Active free radicals are able to abstract hydrogen atoms from macromolecules and initiate efficient polymer decomposition. In both PPO samples, the growth of cracks with irradiation time was observed, but the degree of erosion is different. In PPO degraded for 4 h in air, the cracks formed on the sample surface are separated from each other. The size of the cracks, calculated from different photographs of the sample exposed for 4 h, varies from 7 to 12 μm. In PPO photodegraded in the presence of H_2O_2 some cracks are deeper, and a dense network of smaller microcracks is observed after only 2 h of u.v. irradiation. The extent of photodegradation in the presence of H_2O_2 leads to an increase of film embrittlement. It confirms earlier findings that H_2O_2 has an accelerating effect on the photodegradation of PPO[35].

The formation of microcracks on the polymer surface is strictly connected with the chain scission reaction occurring in photodegraded samples. Breaking of polymer bonds produces fragments which occupy more volume than the original macromolecules. This causes strains and stresses which can be responsible for the formation of microcracks and damage of the u.v.-irradiated polymer film. The cracks are frequently initiated from the breakdown of crazes formed at internal defects as voids or impurities[21]. The high degree of surface erosion leads to the loss of mechanical properties of polymers. It should be noted that the undegraded PPO film (*Figure 1c*) does not exhibit any special microstructure; films are smooth, transparent, and without any visible structural defects (the scratch shown in *Figure 1c* was made intentionally on the sample surface by a knife, to demonstrate the presence of the film placed on the support).

Table 1 Polymers used in the investigation

Abbreviation	Common name	IUPAC name
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)	poly[oxy(2,6-dimethyl-1,4-phenylene)]
PB	*cis*-1,4-polybutadiene	*cis*-poly(1-butenylene)
PIP	*cis*-1,4-polyisoprene	*cis*-poly(1-methyl-1butenylene)
PAA	poly(acrylic acid)	poly(1-carboxylatoethylene)
PEI	poly(ethylene imine)	poly(iminoethylene)

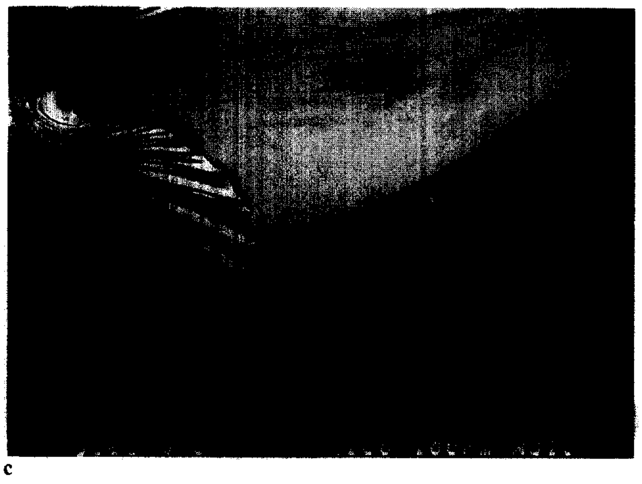
Different images were obtained in PB photodegraded in air and in the presence of H_2O_2 (*Figures 2a* and *b*). Although there are no discernible changes in the surface images of unirradiated PB and PB irradiated in air, significant changes occur when the sample is exposed to H_2O_2. The SEM microphotograph of PB irradiated for 2 h in air shows granular folded morphology (*Figure 2a*). The PB specimen degraded in the presence of H_2O_2 reveals a significant agglomeration of granules (*Figure 2b*). These agglomerates sometimes have a bead-like shape, and are sometimes irregular with a highly developed folded surface. The size of the typical agglomerates shown in *Figure 2b* is about 5–10 μm. Their diameter increases with increasing dose of irradiation. The presence of agglomerates can be explained by the free-radical crosslinking reaction of PB, leading to the formation of microgels. Indeed, about 40% of insoluble gel was obtained from PB films irradiated in these conditions. Reactions of macroradicals in a solid polymer matrix are considered to be diffusion controlled. In this case, diffusion of radicals and their recombination is facilitated owing to the high flexibility and mobility of PB macrochains.

Figures 3a–c show the results obtained for photodegraded PIP. Similarly to PPO, the formation of irregular crazes and cracks was found during u.v. irradiation of PIP in air. The formation of a crack network proceeds with increasing time of exposure, leading to damage of the whole sample. *Figure 3a* shows the PIP film irradiated for 8 h with a high degree of erosion.

An interesting phenomenon was observed in the PIP sample photodegraded in the presence of H_2O_2 (*Figures 3b,c*). The crack network was not observed in PIP during 2 h photodegradation in H_2O_2, but the deeper layer of the polymer bulk became visible. Here H_2O_2 together with u.v. irradiation acts as an etching agent. It should be mentioned that etching of the polymer surface by

a

b



c

Figure 1 SEM microphotographs of PPO: (a) after 4 h u.v. irradiation in air; (b) after 2 h u.v. irradiation in the presence of H_2O_2; (c) undegraded PPO

a

b

Figure 2 SEM microphotographs of PB photodegraded in air (a) and in the presence of H_2O_2 (b) for 2 h solvents, acids or oxidants (for example potassium permanganate) is a technique used to reveal details of the internal structure. In the case of crystalline polymers, etching allows the removal of amorphous or poorly crystalline parts from the surface, and the ordered phase can be clearly seen. The investigated PIP does not appear in its typical crystalline form[41], which was checked here by X-ray diffraction, but a pseudo-ordered, underdeveloped structure is observed after u.v. irradiation/H_2O_2 etching. This snowflake-like structure, made up from central nucleation agents and particles arranged in a radical pattern, could be the precursor of spherulites. These structures are more stable against H_2O_2/u.v. action than completely disordered PIP parts; however, after long-term u.v./H_2O_2 degradation (8 h), they are also destroyed. This is in agreement with the well-known fact, that photodegradation starts preferentially in the amorphous part, and then the crystalline region is ultimately degraded. The destruction of a dense, well-ordered phase needs more energy, which can be gained after longer irradiation time. However, in some cases, even if the polymer is highly crystalline, the disappearance of ordered phases proceeds rapidly, as in the case of poly(ethylene oxide) exposed to polychromatic, highly energetic u.v. irradiation, indicating its low photostability[42]. In contrast, in photodegraded polyethylene (PE) the main chain scission induces reorganization of the amorphous phase[43]. Degraded, shortened chains are able to form more perfect crystals during relaxation processes because the amount of structural defects (for instance, branching) is reduced. This leads to an increase of the total crystallinity of PE.

Figures 4a and *b* compare the morphology of PAA photodegraded for 2 h in water solution without and with hydrogen peroxide, respectively. After degradation polymer solutions were poured onto glass plates; films of the same thickness were obtained and were microscopically investigated. A sample of PAA photodegraded

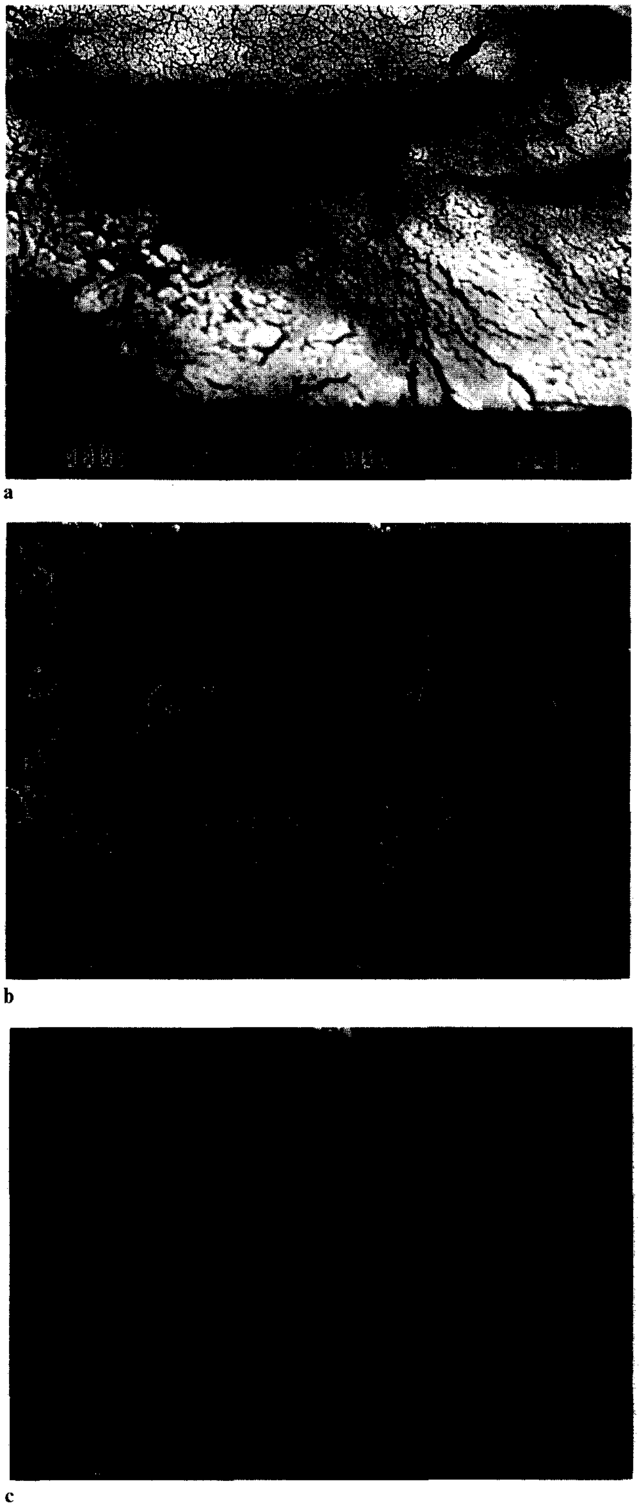


Figure 3 SEM microphotographs of PIP: (a) irradiated for 8 h in air; (b) irradiated for 2 h in H_2O_2; (c) enlargement of (b)

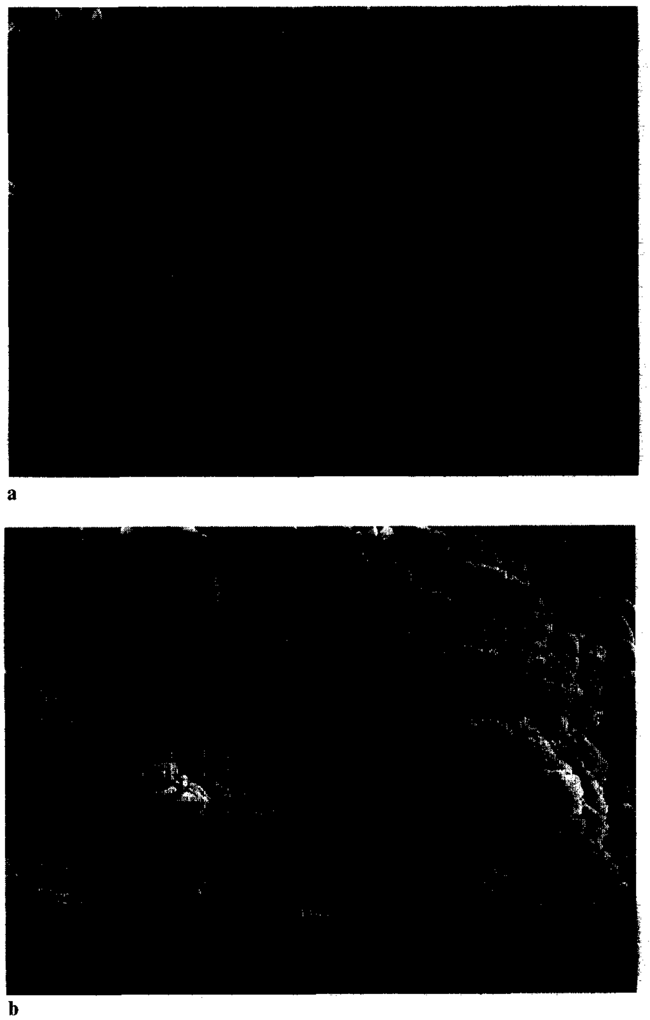


Figure 4 Morphology of PAA photodegraded for 2 h in water (a) and in H_2O_2 (b) solutions

in aqueous medium is not smooth and small; individual particles with various sizes, from fractions of a micrometre to 1 μm, are seen on the sample surface (*Figure 4a*). However, the PAA exposed to u.v. irradiation in H_2O_2 solution at the same time gives a completely different microstructure. There are no visible, single particles but a dense, highly folded surface resembling 'lamb fur' (*Figure 4b*). Such a change in the surface morphology can be explained by the crosslinking reaction occurring in a relatively concentrated PAA solution (5 wt%). The amount of insoluble gel precipitated from the photodegraded PAA solution depends on the time of irradiation. In contrast to PAA, a very similar polymer, poly(methacrylic acid) (PMA), containing methyl groups instead of hydrogen atoms in each repeating polymer unit, does not form such 'lamb fur' morphology after photodegradation. It has no tendency towards crosslinking and gelation because of steric hindrance caused by the presence of methyl groups. PMA undergoes efficient depolymerization during u.v. irradiation, which was followed by viscosimetry measurements.

Very often during u.v. irradiation of polymers the volatile, gaseous degradation products coming out of the sample leave behind micropores with different shapes and sizes. This is exemplified by the photodegraded PEI film (*Figure 5*), in which holes about 1–8 μm in size are observed. PEI has a simple chemical structure, consisting of alternating ethylene and amine groups, and can therefore undergo efficient degradation due to hydrogen abstraction and main chain scission reaction[40]. The volatile, low molecular products are mainly hydrogen, aliphatic hydrocarbons and their amino derivatives. Owing to the voids and holes formed, the number of sorption sites and diffusion channels increases. Thus, oxygen diffuses rapidly into the bulk of the polymer and causes further, fast oxidation of PEI.

Similar results concerning morphology changes were reported for u.v.-irradiated, modified poly(vinyl chloride), in which numerous blisters and holes were observed on the film surface, resulting from HCl evolution[34].

Sometimes porosity is an inherent polymer feature depending on the procedure of sample preparation. Films obtained by casting may possess more or less regularly spaced micropores, depending on the solvent used[8]. Pore size is dependent on the affinity between the polymer and solvent, which can be estimated using the Flory interaction parameter and Hildebrand solubility parameter. Larger pores are formed when the affinity decreases, which is due to easier phase separation. However, in undegraded films of PEI obtained by casting from water solution, micropores were not observed by SEM.

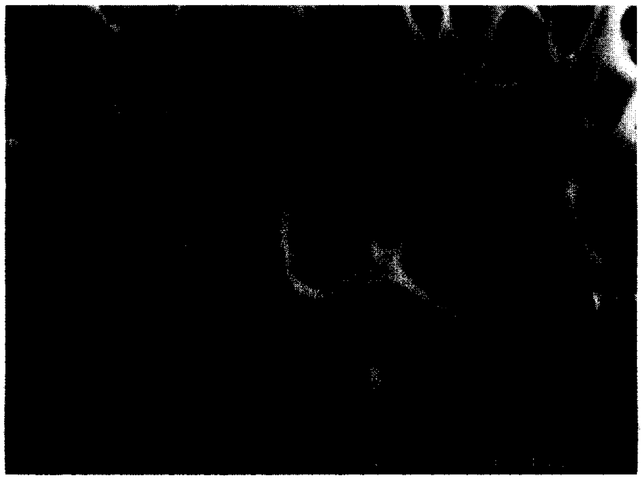


Figure 5 Surface of PEI film after u.v. irradiation for 4 h

CONCLUSIONS

The experimental results demonstrate that SEM is a very useful method for investigating microstructural changes of polymers caused by u.v. irradiation. Processes of chain scission leading to the formation of crazes and cracks are easily observed by SEM. The gelation processes due to the crosslinking reaction are also seen because of the agglomeration of particles. The formation of voids and holes by evolution of volatile, low-molecular products is also monitored on the microphotographs.

The SEM investigation of polymer photodegradation in the presence of an accelerating agent, e.g. hydrogen peroxide, reveals that etching takes place, caused by the fast destruction of the unstable, completely disordered phase.

This study confirms previous findings concerning the photooxidative degradation of polymers obtained by other methods.

SEM is a suitable technique for the study of morphology changes caused by photodegradation because the u.v. irradiation does not penetrate deeply into the polymer bulk and its action is limited to the thin surface layer.

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