The effect of ultraviolet light and temperature on the degradation of composite polypropylene

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Selected from International Polymer Science and Technology, 40, No. 8, 2013, reference PM 12/12/55; transl. serial no. 17091

Translated by P. Curtis

Articles of polymeric materials are exposed to light outside, leading to their ageing, which is associated with polymer chain rupture by the action of UV light with a wavelength of 300-400 nm. Under real conditions, the effect of air oxygen, which promotes photo-oxidation of the polymer, must also be taken into account. The photochemical reaction in the polymer proceeds by a radical chain mechanism and depends on the duration and intensity of exposure to light. Thus, polyethylene breaks down under exposure to light over a period of 2-3 years. Polypropylene does not absorb light quanta with wavelengths in the range 2900-4000 Å, i.e. in the entire UV part of the solar spectrum. Therefore, photochemical degradation of polypropylene is possible only if it is partially oxidised, in which case groups capable of absorbing UV light appear. Degradation is intensified in the presence of moisture (photohydrolytic degradation) and air oxygen (photo-oxidative degradation). The quantum energy of UV radiation exceeds the energy of the C-C bond of the polymer macromolecules and does not depend on temperature. Therefore, photodegradation may also develop at relatively low temperatures, accelerating and deepening in the presence of oxygen. Polymers with groups C=O, C≡N, C=C=C, C=O, etc., which contain groups of chromophore atoms, degrade particularly rapidly [1]. Photochemical degradation is a radical chain process and, by virtue of the poor penetrating capacity of UV radiation, occurs mainly in the surface layers of the polymer [2]. It is assumed that premodification with UV light of mixtures of polyolefin and natural rubber can lead to an increase in their biodegradation. A synergistic effect of certain factors affecting the reactivity of the polymer was found. Thus, exposure to UV light and heat treatment comprise a simple method leading to the formation of functional groups in the hydrophobic polymer chains, which makes them sensitive to subsequent microbial attack [3]. However, there are many contradictory reports concerning the behaviour of degradable composite polymers during their storage and exposure to environmental factors.

It has been shown that temperature is also the most important factor affecting the rate of thermo-oxidative degradation of polymeric materials, whereas oxygen concentration has little effect on the oxidation rate, at least in the 5-20\% range [4]. By measuring the rate of thermo-oxidative degradation at different temperatures, it was shown that the activation energy of polyethylene films reaches 106 kJ/mol. Heating generates different oxidised products of polyethylene, which have a direct influence on the biodegradability of the polymer. Heat treatment at 70°C caused more rapid breakdown of the polymer chain [4]. After exposure to heat, the degrading plastics can undergo many chemical and physical changes. In a short exposure time to elevated temperature, the length of the induction period of oxidatively degradable plastics, during which there is a reduction in the content of antioxidants and stabilisers, is reduced. The tensile strength, impact strength, elongation, and elastic moduli can change during this induction period. However, these changes are not due to reduction in the molecular weight but are only a reaction to the temperature dependence related to increase in crystallinity, loss of volatile substances, or both. Normally at elevated temperatures, moisture, solvents, and plasticisers may be removed, the pressing stress is removed, solidification of the thermoplastic increases,
crystallinity increases, and certain changes in colour of the plastics occur. Polypropylene and its copolymers at elevated temperature become very brittle on account of loss of plasticisers or molecular breakdown of the polymer. However, detailed investigations of the effect of UV light and temperature on composite polypropylene have not been carried out prior to the present work. The aim of the present work was to check the effect of UV light and temperature on the degradation of polypropylene with different composite additives during the treatment of specimens with different times of exposure.

Specimens of films and other materials with oxybiodegradable additives ECM, PDQ-H, and UV-H (ECM Biofilms and Masterbatch Pellets, USA) were obtained by extrusion of polypropylene of grade Kaplen 01130 and 01250 with the addition of 1, 2, or 3% composite additives. It was shown that additions of ECM are broken down by microorganisms, additions of PDQ-H by microorganisms and UV light, and UVH by UV light alone [5]. Tests were conducted in a laminar box using a UV lamp with a radiation power in the 300-400 nm range of 30 W/m² with different exposure times. During the test, film specimens (50 × 100 mm) were flipped twice per day. The working temperature in the box was 20°C, and the humidity was 50 ± 5%. Tests were repeated 3 times. Experiments to investigate thermal degradation were carried out on an IKAR unit (Vologodsk Optical Factory). Test specimens were exposed 3 times to each chosen time and temperature. The degradation of specimens was judged from their loss of weight [6]. In figures showing no controls, degradation of the polymeric materials did not occur.

The conducted investigations on the effect of UV light on the degradation of polypropylene showed that, in the course of the first 10 days, in the period from 27 June to 8 July 2008, the most active degradation, measured from weight loss, was seen in films of 50 µm thickness containing 3% PDQ-H (Figure 1). It is known that the photochemical degradation of polypropylene is possible only if it is partially oxidised, in which case groups capable of absorbing UV light appear in the polymer [1]. Such a role seems to be played by biodegradable composite additives PDQ-H and UV-H added to polypropylene. It is also known that the degradation of polymers is accelerated in the presence of moisture and air oxygen [7]. Taking these facts into account, the test was continued until 25 July, as a result of which the films were brittle or completely broken up into fine parts. Films of 50 µm thickness containing PDQ-H degraded most strongly.

It is assumed that premodification of polyolefin with natural polymer can lead to an increase in their degradation in the presence of UV light. Investigations conducted by the present authors on 200 and 500 µm thick polypropylene films not modified with composite additives showed that their degradation did not occur over the period of a month-long experiment.

Checking of the effect of sunlight on films of composite polypropylene placed on the surface of soil (Figure 2) confirmed the degrading action of UV light. It was shown that composite films containing additives that can degrade when exposed to UV light (1% PDQ-H or 3% UV-H) broke down most actively. Thus, the sensitivity to photodegradation of composite polypropylene depends both on its ability to absorb UV lamplight and on its ability to absorb part of dangerous tropospheric solar radiation. Solar radiation includes UV-B surface radiation (~295-315 nm) and UV-A radiation (~315-400 nm) responsible for direct photodegradation (photolysis, initiated photo-oxidation). The visible part of sunlight

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**Figure 1.** The effect of UV light on the degradation of polymer films with different additives over a 30 period: 1 - PP01030 + 3% PDQ-H; 2 - PP01250 + 1% PDQ-H + 50 μm; 3 - PP01250 + 3% PDQ-H + 50 μm

**Figure 2.** The degradation of film specimens on the surface of soil over a 55 day period: 1 - PP01030 + 3% ECM; 2 - PP01250 + 1% PDQ-H; 3 - PP01250 + 2% PDQ-H + 100 μm; 4 - PP01250 + 3% UV-H + 50 μm; 5 - PP01250 + 3% UV-H + 100 μm
(400-760 nm) accelerates thermal oxidation [7]. Most plastics have a tendency to absorb radiation with high energy in the UV part of the spectrum, which activates their electrons to increased reactivity and causes oxidation, rupture, or some other degradation.

For correct use of composite polypropylene in different areas, it is very important to know the processes of its thermal degradation. During the thermal degradation of polypropylene in an inert atmosphere or in vacuum, there is a reduction in its molecular weight, and volatile products are formed, consisting mainly of 2-methylpropene-1 and pentene-2. During the breakdown of unbranched polypropylene, gaseous products are formed much more rapidly than in the case of polypropylene of branched structure. The reduction in molecular weight depends on the temperature and duration of pyrolysis. The rate of formation of volatile products is also a function of temperature. However, the rate of thermal degradation of polypropylene does not depend on its molecular weight. During degradation there is a reduction in the crystallinity of the polypropylene. In contrast to other polymers, the pyrolysis of polypropylene produces only a small amount of monomeric product, which is due to the low activation energy of isomerisation of the macroradicals formed during thermal degradation [7].

Investigations conducted by the present authors in accordance with the ASTM D 5510-94 requirements to check the heat ageing of oxidatively degradable polypropylene with different composite additives showed that their degradation depends both on temperature and on the type of additives contained in them. It was shown (Figure 3) that, at a temperature of 35°C, the higher the content of composite additive (ECM, PDQ-H) in the polymer, the greater the degree of degradation of the films. Here, in a 21 day experiment, degradation occurred most actively in films containing 3% PDQ-H and 1% UV-H. In contrast to these data, in a test conducted at 70°C (Figure 4), the degradation of films containing 3% PDQ-H occurred more rapidly, and their breakdown occurred after only 2 days. Similar data were obtained by the present authors in the heating of specimens at 55°C (Figure 7), when the degradation process occurred over a longer time.

Checking of the effect of heating at 70°C on the degradation of composite polymer films (Figure 4), dumbbell testpieces (Figure 5), and sheets (Figure 6) showed that the rate of their degradation depends on the thickness of the specimen, the nature of the composite additive, and the duration of heating. Specimens degraded most rapidly at 70°C (films after 2 days, dumbbell testpieces and sheets after 8 days) and most actively with a content of 2-3% PDQ-H. Here, dumbbell testpieces and sheets changed colour, crumbled, and became brittle.

Investigation of the thermal degradation at 55°C of sheets that have previously been in sapropel and...
biohumus (Figure 7) showed that, within a 12 day period, it was higher than at 35°C, but lower than at 70°C. Here, thermal degradation was more active in sheets that had previously been in sapropel, in which their biodegradation was more active. Comparison of the thermal degradation of disposable vessels at 70°C showed (Figure 8) that, in dishes containing 2% UV-H, it was 2 times higher than in the control not containing composite additives.

Thus, the chemical reactions taking place in the thermal degradation of composite polypropylene lead to a change in the physical properties in relation to their initially specified values. Thermal degradation mainly includes changes in the molecular weight of the polymer and changes in properties such as a reduction in viscosity and brittleness, crumbling, a change in colour, and cracking, which was observed in experiments conducted with polypropylene containing biodegradable composite additives.

REFERENCES