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The weathering test of polypropylene composites

RAPID COMMUNICATION

Summary — Commercial Malen P polypropylenes (i) pure, (ii) filled (20%) with chalk or talc, and (iii) UV-stabilized with 0.2 or 0.4% of a hindered amine light stabilizer, Tinuvin 791, were studied in laboratory weathering tests. The samples were exposed to UV-irradiation at doses of 0—950 MJ/m^2 with moisture cycles and programmed temperature and relative humidity in the test chamber. Progress in composites photodegradation was studied by measuring *M* and *MWD* determined by gel permeation chromatography and mechanical properties like elongation, tensile stress and notched impact strength. For white composites resistance to yellowing under irradiation was studied. Chalk was found to be the better filler than tale; it stabilized mechanical properties and enhanced color resistance. Additional application of a UV-stabilizer increased the light stability of tested samples, presumably by forming a protective coat on a filler surface that prevented the adverse effect of metals contained in the filler.

Key words: photodegradation, weathering test, polypropylene, additives, HALS UV-stabilizer.

Polymeric products exploited outdoors are usually exposed to weathering factors which give rise to aging processes worsening their service properties.

The fundamental parameters of a weathering test are light, heat and moisture. There may be other weathering factors such as pollution or biological attack, but these are not present in every environment. In a basic outdoor exposure test, weather conditions cannot be controlled. Laboratory instruments allow to perform simulated weathering tests under more controlled and accelerated weathering conditions than those of a real-time exposure. Laboratory weathering tests speed up the weathering process by increasing the intensity or the level of the operating factor. The response of a polymeric product to the weathering factor will vary not only with the combination and intensity of the factor applied but also with the material composition.

This paper sets out to describe the effect of the type and concentration of additives such as a filler and a UV-stabilizer used in polypropylene on the course of a laboratory weathering test of polymeric composites.

EXPERIMENTAL

All laboratory weathering studies were performed by using a Xenotest Alpha HE apparatus equipped with a xenon arc lamp, because the spectral power distribution of this light source (Fig. 1) has been recognised to give the best available simulation of sunlight.

In Fig. 2, the ultraviolet part of sunlight is seen to have the greatest effect on the degradation of PP material. To eliminate the unwanted range of UV radiation of the xenon lamp, which does not exist in the sunlight (wavelength below 300 nm), and the principal part of IR radiation, a set of Xenochrome 300 filters with a Suprax cylinder was used. Infrared radiation does not cause polymer photodegradation, but it can warm the polymer and thus give rise to its thermodegradation.

The basic polymer was a commercially available Malen-P type polypropylene produced by Polski Koncern Naftowy ORLEN SA, Płock. Test-ready samples of the pure polymer and its composites, prepared according to PN-88/C-89012 [2] by injection molding, are listed in Table 1.

The weathering test was performed according to [3, 4] by applying programmed moisture cycles (102-min long "dry" phase followed by 18-min long rain phase),

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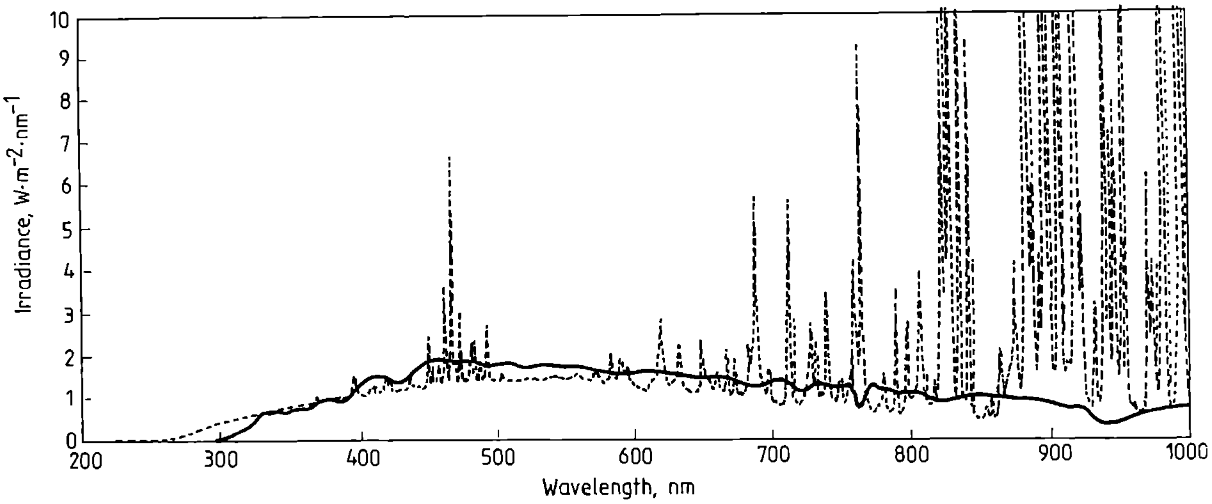

Fig. 1. Sunlight (—) and xenon arc lamp (...) spectrum comparison [1], normalized to 665 W/m² (300—800 nm)

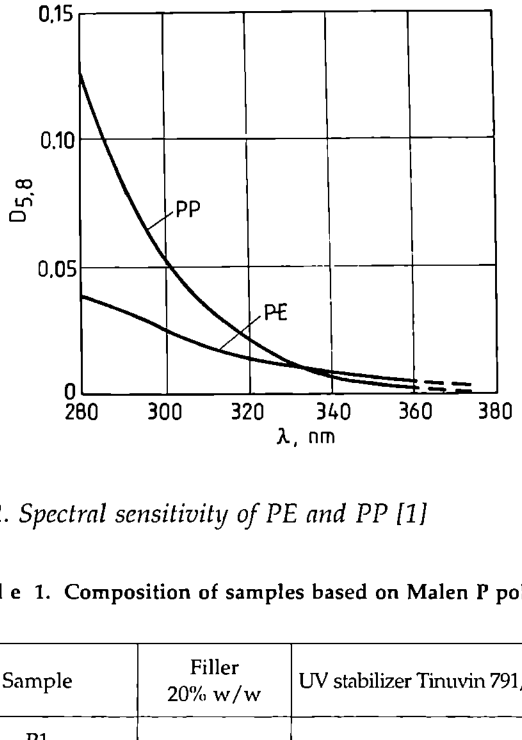

Fig. 2. Spectral sensitivity of PE and PP [1]

Table 1. Composition of samples based on Malen P polypropylene

Sample	Filler 20% w/w	UV stabilizer Tinuvin 791, % w/w
P1	—	—
P2	chalk	—
P4	chalk	0.20
P6	talc	—
P7	talc	0.20
P9	talc	0.40

at a temperature of 30°C and relative humidity of 50% in the test chamber. The criterion for finishing a period of the weathering test was the UV-irradiation dose.

The progress of photodegradation of the polymer was observed by following changes in the molecular weight and molecular weight distribution as well as in mechanical properties and in the yellowness index. The results obtained for modified PP were compared with the data on pure PP samples received under the same conditions. It should be stressed that some tests (mainly examination of mechanical properties) destroyed the samples; therefore, each programmed exposure dose required a new polymer samples. The aged polymers were conditioned and then examined.

Measurements

Molecular weight (*M*) and molecular weight distribution (*MWD*) were determined by gel permeation chromatography by using a HT GPC Waters 150-C instrument. Trichlorobenzene containing a stabilizer was used as a solvent.

Mechanical properties of paddle- and beam-shaped samples (elongation, tensile stress, notched impact strength) were determined according to Polish Standards PN-81/C-89034 [5] and PN-85/C-89050 [6].

The yellowness index was evaluated by colorimetric measurements carried out in an X-Rite 968 spectrophotometer within the range of visible light, 400—700 nm, at 20 nm intervals [7].

RESULTS

Of all the tested samples, pure polypropylene was found to be the least resistant to the weathering conditions. This polymer showed a more than double decrease of the elongation coefficient as compared with the non-aged one, already after having been exposed to a 190 MJ · m^{-2} dose (Fig. 3). The mechanical properties changed only slightly but, as the test was prolonged, the worsening tendency was found to intensify (Table 2).

The decrease of the elongation coefficient may be explained by changes in the structure of macromolecules, which occur during degradation. As the irradiation dose was increased, each sample exhibited a decrease

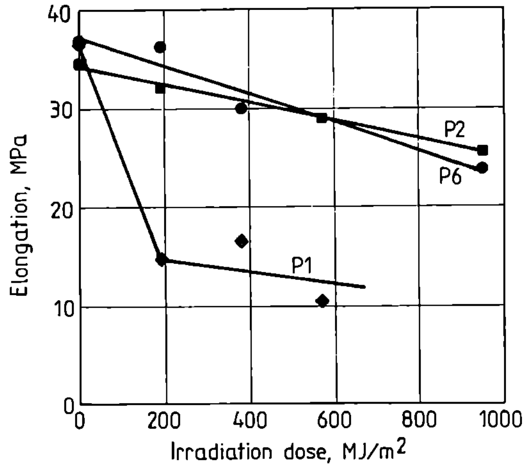

Fig. 3. Elongation in relation to irradiation dose

Table 2. Properties of aged polymers

Sample*)	M_w	*MWD*	Tensile stress, MPa	Notched impact strength, kJ · cm^{-2}
P1/0	235 400	4.35	25.3	0.38
P1/190	181 000	4.92	28.2	0.27
P1/380	207 000	4.67	27.8	0.26
P1/570	168 300	7.53	27.4	0.24
P2/0	232 400	3.33	22.7	0.36
P2/190	216 300	3.95	24.6	0.37
P2/380	235 900	4.57	25.1	0.30
P2/570	221 500	5.07	24.6	0.33
P6/0	227 700	3.61	24.7	0.34
P6/190	206 300	3.75	26.8	0.31
P6/380	103 700	5.95	28.8	0.27
P6/570	111 700	9.42	29.6	0.36

*) Sample description: type of composite/irradiation dose in MJ · m^{-2}.

in the molecular weight and an increase in the MWD (Table 2). Degradation of molecules does not go in parallel with worsening of mechanical properties. Only a large molecular weight drop (higher than 50% of initial value) causes a visible reduction in mechanical quality.

Chalk or talc added to PP as a filler increased the stability of mechanical properties (Fig. 3, Table 2). The filler is likely to decrease light absorption and to cause radiation reflection and dispersion. There was no difference between the results obtained with chalk or talc used as a filler.

All the composites tested were white; pure PP was transparent. On exposure to light, the white polymeric materials changed the initial color. In contrast to talc-filled samples, each chalk-filled sample was sufficiently resistant to yellowing (Fig. 4).

Application of a UV-stabilizer (Fig. 4, Fig. 5) increased the light stability of the samples. The present results, even if expected, are in conflict with the literature data [8], according to which a stabilizer in mineral-filled materials loses its protective properties on account of absorption by the porous filler surface which results in a decreased stabilizer concentration in the polymer mass. This is true mostly in the case of monomeric, low-molecular-weight stabilizers. In this work, the most recent hindered-amine light stabilizer (HALS) — Tinuvin 791 — was used. This is a composition of monomeric HALS-1 and polymeric HALS-3. The enhanced light stability of the composition containing Tinuvin 791 is presumably due to polymeric HALS-3. Moreover, the polymeric HALS molecules are large enough to fail to penetrate into the porous filler surface. Additionally, the stabilizer may well have formed a coating on the filler surface, which reduces the adverse effect of metallic impurities always present in natural fillers on polymer stability [8].

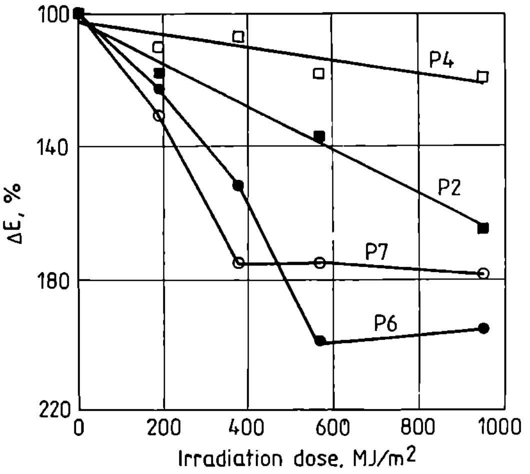

Fig. 4. Percentage changes in yellowness index in relation to irradiation dose

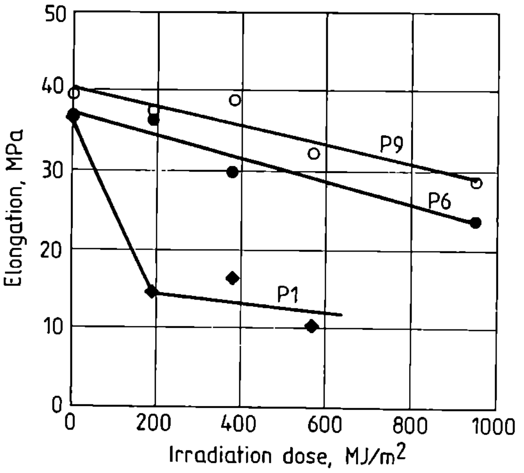

Fig. 5. Elongation in relation to irradiation dose

Concluding, a filler increases the weather resistance of polypropylene, and chalk seems to be the better filler than talc in almost all composites. A polymeric UV-stabilizer provides improved protection against degradation.

REFERENCES

1. Proc. of the Conference organized by ATLAS Company, Warsaw, May 1998.
2. Polish Standard PN-88/C-89012.
3. Polish Standard PN-85/C-89037.
4. ISO Standard 4892-2; 1994 (E).
5. Polish Standard PN-81/C-89034.
6. Polish Standard PN-85/C-89050.
7. ASTM E 313.
8. Gray R. L. in: "Plastics Additives", Chapman & Hall, London 1998, p. 360.

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Centrum Badań Molekularnych i Makromolekularnych PAN w Łodzi uzyskało status Europejskiego Centrum Doskonałości

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