

INFLUENCE OF ADDITIVES ON POLYOLEFINS' DEGRADATION STUDIED BY INFRARED SPECTROSCOPY

Ivana Šeděnková, Jan Pilař, Danuše Michálková

*Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovský Sq. 2, 162 06 Prague 6, Czech Republic
(author@email.address, www.imc.cas.cz)*

Degradation of polypropylene (PP), polyethylene and poly(ethylene-co-norbornene) stabilized by set of hindered amine stabilizers was followed by infrared spectroscopy to study changes in the molecular structure of the materials. The attenuated total reflectance technique was used to obtain spectral series during the photooxidation experiment. Relative occurrence of the oxidation products in the material was determined. Additionally, the statistical method, factor analysis, was applied on the sets of measured spectra to clarify degradation process in the dependence on the chosen commodity polymer and stabilizer. The evaluation of ATR FTIR experiment is illustrated on the PP samples in presented text.

After weathering, the spectra of all PP samples exhibit similar changes, typical of material oxidation. Three new bands were found. The complex peak in carbonyl region with maximum located at 1717 cm^{-1} in the case of irradiated and at 1735 cm^{-1} in the case of non-irradiated surface, broad band with maximum about 1150 cm^{-1} and weak band at about 3350 cm^{-1} . In both spectra the carbonyl band has a pronounced shoulder at 1650 cm^{-1} , which is better defined in the spectrum taken on non-irradiated surface.

A deconvolution of the carbonyl peak showed four main absorbing bands composing the spectrum. Their maxima are at 1652 (vibration of vinyl group), 1716 (carbonyl vibration in carboxylic acid and ketones), 1745 (ester carbonyl vibration) and 1764 cm^{-1} (vibration of γ -lactones) in the spectrum of the irradiated side.¹ The additional band at 3350 cm^{-1} is typical of -OH vibrations in carboxylic acid, the broad band at about 1150 cm^{-1} is connected with vibration of C-O-O group.

The relative intensities of the bands are dependent on the set of additives and WOM exposition time. The tool which can be used to compare the course of degradation in different materials is factor analysis. The factor analysis substitutes the original series of n experimental spectra by their equivalent orthonormal base of vectors. The vectors of the orthonormal

base are called “subspectra” S_j . The statistical importance of each subspectrum is expressed by the set of singular numbers w_j .² The second subspectrum S_2 should indicate the main changes in the samples’ spectra and the interpretation of the subspectrum S_2 leads to understanding of the main degradation process occurring in the sample. The main advantage of the factor analysis is the possibility to distinguish independent degradation processes in the material and follow the various degradation processes in time.

Further, the evaluation of the singular numbers w_2 and w_3 than indicates the relative intensity of the degradation process (Tab 1). The higher value w_2 in proportion to w_1 signifies higher amount of the arising oxidation products in the whole course of the degradation process.

Tab: Singular values w_j , polypropylen, A- irradiated, B – non/irradiated site of the sample

additives	Tinuvin® 770		Tinuvin® 123		Chimasorb® 119	
time [day]	124		143		112	
	A	B	A	B	A	B
w_1	14.613	15.390	14.605	13.754	15.435	14.979
w_2	0.648	0.654	0.816	0.510	2.539	0.676
w_3	0.516	0.469	0.488	0.295	0.714	0.428
additives	Tinuvin® 116		Tinuvin® 371		none	
time [day]	112		112		112	
	A	B	A	B	A	B
w_1	14.593	14.817	14.817	15.016	16.251	14.769
w_2	0.743	0.531	0.531	0.592	2.840	2.155
w_3	0.374	0.406	0.406	0.378	0.674	0.374

The values w_2 in the table confirm the effectiveness of the used stabilizers. The only exception is Chimasorb 119. The degradation of PP with this stabilizer is then the significantly lower on the non-irradiated site in comparison to the nonstabilized PP.

1. Philippart J.L.; Sinturel C.; Arnaud R.; Gardette J.L., Polym. Degrad. Stab. 64:213, 1999.
2. Henry E.R., Hofrichter J., *Methods in Enzymology*, 210, 129-192, 1992.