

Application of plasmochemical processes in treatment of properties of macromolecular materials

II. Surface treatment of polypropylene by oxygen-nitrogen plasma in the fluidized bed

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Received 25 January 1984

Surface treatment of powdered isotactic polypropylene (PP), accomplished by action of the low-temperature O₂—N₂ plasma ($V(\text{O}_2)/V(\text{N}_2) = 1:4$) of the high-frequency discharge in the fluidized bed, has been studied. The reaction product has been characterized by IR, NMR, and ESR spectra. The influence of the exposition time on the variations in some of the properties has been examined.

Была исследована поверхностная обработка порошкообразного изотактического полипропилена под действием низкотемпературной плазмы O₂—N₂ ($V(\text{O}_2)/V(\text{N}_2) = 1:4$) разряда высокой частоты в псевдооживленном слое. Продукт реакции был охарактеризован с помощью ИК-, ЯМР- и ЭПР-спектров. Был исследован эффект продолжительности экспозиции на изменения некоторых свойств.

One of the characteristics of nonpolar polymers is their low water-wetting ability of the surface. This fact causes the problems arising in the practical use of these materials within the packaging technique, textile industry, printing art, etc., in a word, wherever the successive treatment by dyeing and bonding (sticking) is required, or where the bound-water ability is demanded [1].

For treatment of the surface polymer properties were used chemical etching, alpha radiation [2], ultraviolet light [3], and plasma [4]. A survey of plasmochemical processes applied to the surface transformation of materials may be found in *Holland's* summary [5].

In using oxygen plasma, primarily the polymer surface oxidation at a depth of 10–1000 nm [2] takes place, leading eventually to a decrease in the bonded hydrogen content and to the relative increase in the carbon content (compared with thermal degradation) [6]. The peroxy radicals, alkyl radicals, and other active groups formed may act as the initiators of successive radical reactions proceeding at the stage of additional treatment. These reactions make further modification of surface properties and a hydrophilic rise in the processed polymer possible, e.g. by means of graft copolymerization involving a convenient hydrophilic monomer [7]. The peroxides of powdered isotactic polypropylene were successfully used as the initiating centres for the emulsion polymerization of styrene [8].

The processing of polypropylene in both the air and oxygen plasma brings about an increase in the wetting ability and, accordingly, an improvement in the adhesive properties and dyeing ability as well [9]. In addition to these variations, the oxygen plasma is responsible also for crosslinking. During a long-term plasma effect, the degradation of the surface polypropylene layers, a decrease in the molecular mass, and a drop in the polypropylene sample absolute mass occur. After having used N₂O the change in the adhesive properties was identical to that found in the case of oxygen plasma. No changes in the processed polypropylene behaviour were noticed when the rare gases, H₂S, NH₃, and CO₂, respectively [10], were employed.

In literature we have not met so far with plasmachemical modification of powdered polypropylene (PP) being utilized for the preparation of sheets or fibres.

Experimental

For the processing of powdered PP was used an equipment, the scheme of which can be seen in Fig. 1.

The fluidization column 0.9 m in length and 2.2 cm in diameter was produced of glass SIAL. The upper part of the reactor column was separated from the bottom by a grid made of sintered glass S2. The high-frequency discharge was excited in the reactor part of the column inserted in the cavity of the inductance coil. The column was evacuated by the rotary oil pump RV-5 through the cyclone and filter systems. The operating gas flow was controlled by a needle valve. The atmospheric air was used as an operating gas. The gas flow was kept on the value of $2.5 \times 10^{-3} \text{ m}^3 \text{ h}^{-1}$, which is a tenfold of the threshold speed under working conditions (the column pressure of 330 Pa, the laboratory temperature of 293 K). The value of the threshold fluidization speed of $5.256 \times 10^{-2} \text{ m s}^{-1}$ was evaluated in accordance with [11].

For the experimental measurements was used the sample of isotactic powdered PP TATREN, manufactured by the national corporation Slovnaft. The PP properties indicated by the producer are: fusing temperature ranging from 165 °C to 175 °C, density of the polymer 902 kg m⁻³, a minor nondefined content of volatile fractions, humidity, hexane, and other organic substances used in the polymerization, the ash content 0.05 %, and the

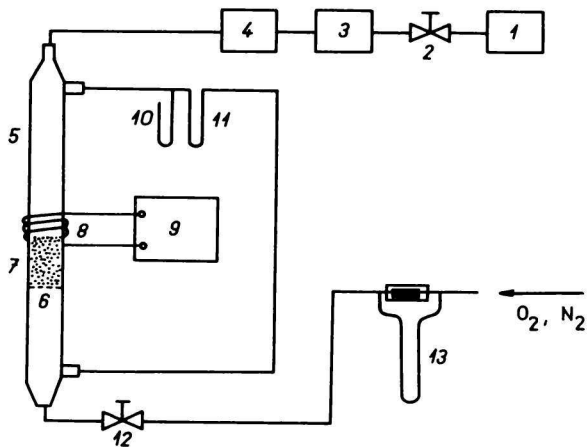


Fig. 1. Scheme of the equipment for the plasmochemical processing of powdered PP.

1. Rotary oil pump; 2. control valve; 3. cyclones; 4. filters; 5. fluidization column; 6. grid; 7. fluidized bed; 8. inductance coil; 9. high-frequency generator; 10. pressure gauge; 11. differential pressure gauge; 12. needle valve; 13. capillary flow indicator.

trace amounts of Ti and Al (lower than 10^{-3} %). For the purpose of measurements the screen fraction of $(315-355) \times 10^{-6}$ m was employed.

Experimental measurements were carried out with the power value of 1000 W supplied in the HF generator section. The exposition time varied from 5 to 180 s.

The hydroperoxides concentration was determined by the modified iodometry method [12, 13]. The free radicals concentration was measured on the ESR spectrometer. The structural bulk changes of the processed PP were studied by NMR spectra (PW 40). The chemico-structural changes in the surface of the processed sample were studied by IR spectra. The measurements were made on the Perkin—Elmer IR Spectrometer equipment, model 599, a wavenumber range of $200-4000 \text{ cm}^{-1}$.

Results and discussion

The amount of bonded oxygen in the form of hydroperoxides depends on the exposition time of the $\text{O}_2\text{—N}_2$ plasma, which is illustrated in Fig. 2. The dependence reveals that the highest hydroperoxides concentration may be found in the processed PP sample when exposed for 30 s. As we have pointed out in our previous study [14], the plasma oxidation process of PP is accompanied by surface roughening.

In Fig. 3 is shown the dependence of free radicals concentration on the exposition time leading to the periodical exposure of the subsurface particles of the

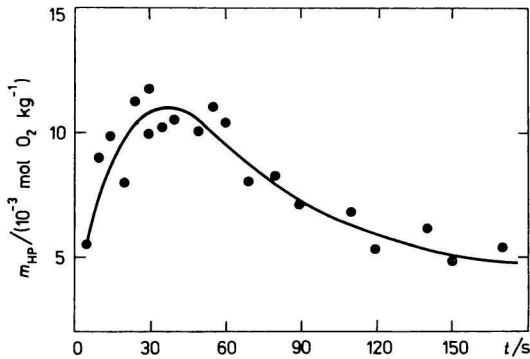


Fig. 2. Hydroperoxides concentration m_{HP} dependence on the exposition time t (air, flow rate of $6.9 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$, pressure of 330 Pa).

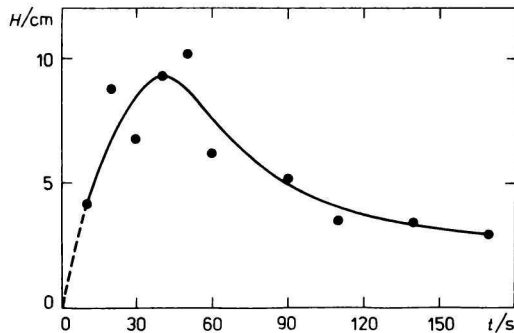


Fig. 3. Dependence of free radicals concentration, expressed as the ESR intensity of the spectrum H , on the exposition time t (air, flow rate of $6.9 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$, pressure of 330 Pa).

sample examined. By comparing the standard measurements, the value of free radicals specific number, amounting to $3 \times 10^{18} \text{ kg}^{-1}$, was obtained. The reciprocal correspondence with the position of relative extremes, shown in Figs. 2 and 3, indicates the radical mechanism of the surface destruction of PP. In Fig. 4 is illustrated the dependence of free radicals concentration on the inertial time in the aerial atmosphere after exposing the sample. An exponential drop in the radicals concentration is caused by bimolecular successive reactions.

From the dependence shown in Fig. 5 it follows that the hydroperoxides concentration increased within 30 days — since the PP powder had been exposed to the plasma effect — approximately threefold. This fact is in agreement with the

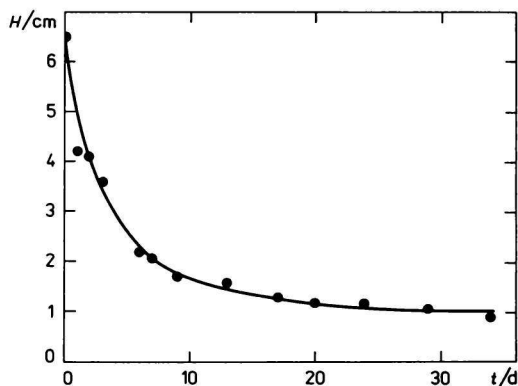


Fig. 4. Dependence of free radicals concentration, expressed as the ESR intensity of the spectrum H, on time after irradiation (air, flow rate of $6.9 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$, pressure of 330 Pa, exposition time of 30 s).

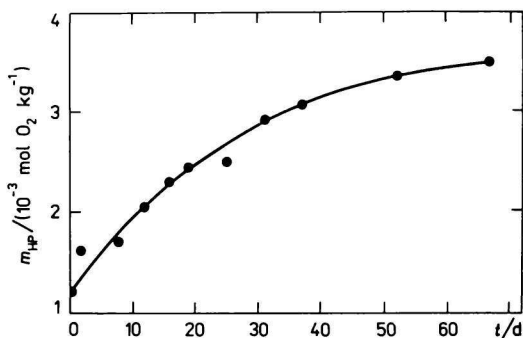


Fig. 5. Hydroperoxides concentration m_{HP} dependence on the inertial time after exposure (air, flow rate of $6.9 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$, pressure of 330 Pa, exposition time of 30 s).

measurements given in the foregoing figure, and confirms the conception of radical structures deactivation resulting from interaction of the plasma-generated free radicals, primarily by oxygen. The peroxy radicals will liberate the hydrogen out of the neighbouring polymer chain, thus generating a hydroperoxide and a new alkyl radical. The chemical reaction will mediate both the radicals approach and the radicals extinction in the fixed polymer system.

From the wide-band NMR spectra (Fig. 6) measured in the temperature range from $-120 \text{ }^\circ\text{C}$ to $150 \text{ }^\circ\text{C}$ were evaluated the second moment's square powers ΔH_2^2 dependent on the temperature T .

The variable ΔH_2^2 is characteristic of the mutual arrangement of hydrogen atoms being in the solid phase. The temperature dependence $\Delta H_2^2(T)$ enables the change

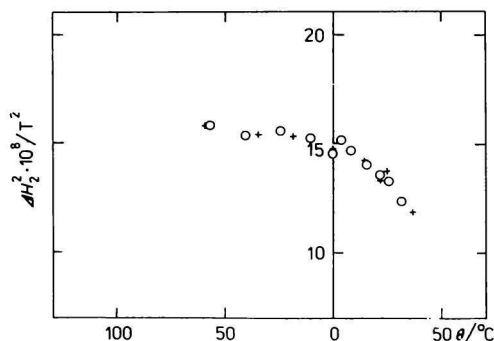


Fig. 6. Diagrammatic dependence of the second moment's square power ΔH_2^2 of the NMR band on temperature for the powdered PP sample. \circ Original, $+$ irradiated.

in some of the physicochemical properties of the processed polypropylene to be presumed. The course of the temperature dependence $\Delta H_2^2(T)$ is, in the case of both the nonirradiated sample and the PP sample exposed to the low-temperature plasma effect within 30 s, equal. This refers to the fact that the modification process proceeds only in the thin surface layer and the individual structural changes observed on the surface have no significant influence on the mechanical properties of PP in bulk.

The IR spectra measurements (Fig. 7) of the irradiated PP powder sample indicate the presence of carbonyl groups ($\tilde{\nu} = 1740 \text{ cm}^{-1}$), hydroperoxides and

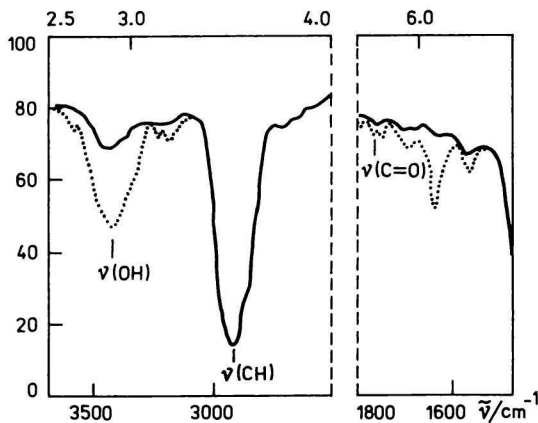


Fig. 7. Sections of the IR spectrum of the original polypropylene exposed (...) and nonexposed (—).

products of radical decay, which is noticeable as the characteristic absorption band ranging from 3300 cm^{-1} to 3600 cm^{-1} , and as a doublet lying in the region of 1000 cm^{-1} . The alcoholic groups formed by the peroxides decay bear the characteristic absorption band in the region of $1160\text{--}1300\text{ cm}^{-1}$.

Conclusion

The investigation of the plasmochemical processing of powdered PP in the fluidized bed in the air — taken as a plasma-forming gas — showed that a short time exposing for 30 s is sufficient to increase the hydroperoxides concentration within the polymer. The IR spectra measurements suggest the presence of chemical groups of the hydroperoxide type, carbonyls and other chromophores capable of reacting with other organic compounds. The presence of these makes the additional purposeful chemical changes, needed for treatment of powdered PP, possible.

The principal advantages of the fluidization technique used in the plasma modification process of PP lie in the intimate mixing of the processed material and thereby in the conditions suitable for treatment of the total surface, as well as in the possible continuation of the process as a whole.

Acknowledgements. The authors are greatly indebted to Dr. J. Plaček (Polymer Institute, Centre for Chemical Research, Slovak Academy of Sciences) for his assistance in measuring and evaluating the ESR spectra, as well as to the reviewer for his careful appraisal of the paper.

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Translated by L. Hadrulcová