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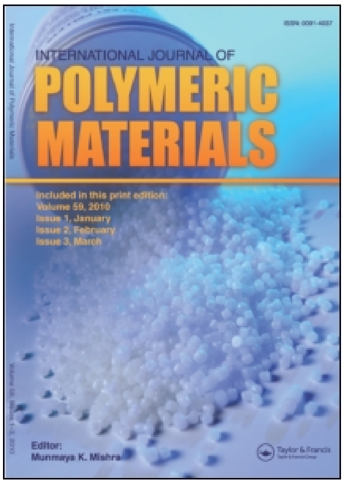

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The Distribution of Irradiation-Grafted Acrylic Acid in the Cross-Section of Polypropylene Fibers

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The Distribution of Irradiation-Grafted Acrylic Acid in the Cross-Section of Polypropylene Fibers

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The relative efficiency of grafting of acrylic acid (AA) in the surface layer and in the bulk of pre-irradiated polypropylene fibers was studied by combining the ATR and transmission IR techniques. At graft percentage from 41 to 98, the surface layer contains 2–3 times higher concentration of the grafted chemical groups than the fiber bulk. At 140% of AA, the surface of the host polymer becomes screened by the grafted material.

KEY WORDS Polypropylene fibers, acrylic acid, grafting irradiation.

INTRODUCTION

The graft polymerization of vinyl monomers to polyolefine fibers and films results in increase of strength and heat resistance, in enhancement of hydrofility and colour ability[1]; the grafting can induce completely new properties of polymeric materials, such as bactericide, complex-forming and ion-exchanging ones.[2] The osmotic stability of grafted fiber ionites justifies their application for air filtration against toxical impurities of both alkaline and acid character.

At the practical using of grafted polymers as ion-exchange materials, the essential characteristics of host polymer modification are connected not solely with the newly acquired chemical properties (number and nature of functional groups, exchange capacity etc.) but also with the homogeneity of grafting in the fiber cross-section.

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The latter characteristic is closely related to the efficiency of ion-exchange and sorption processes.

In dependence of the mode of grafting, the surface (e.g. plasma-chemical processing) or homogeneous (e.g. pre-irradiation of host polymer by electrons) functional group distribution can predominantly be obtained.[3] In the present work we investigated the distribution of grafted acrylic acid (AA) in the cross-section of γ-irradiated polypropylene (PP) fibers. To determine the relative concentration of grafted AA in the bulk and in the surface layer of fibers, the transmission and attenuated total reflection (ATR) infrared spectra were measured.

EXPERIMENTAL

The IR measurements were performed on the commercial non-woven needlelepunchered material FIBAN K4, manufactured by processing of AA-grafted PP fibers. The grafting has been effectuated due to radicals produced by reaction between peroxidal and hydroperoxidal groups of previously γ-irradiated PP, and Fe ion introduced in the AA solution:

$$\mathrm{PP}^{60} \xrightarrow{\mathrm{Co_2O_2}} \mathrm{PP{-}OOH,\ PP{-}OO{-}} \xrightarrow[\mathrm{t^0,\ Fe^{2+}}]{\mathrm{CH_2{=}CHOOH}} \text{PP grafted with AA.}$$

Grafting was carried out from the 30% monomer solution in distilled water at boiling point and at Fe^{2+} content 0.3 g/l. The graft percentage (G) was measured gravimetrically from a weight increase of initial PP as compared to washed and dried at 80°C (to constant mass) grafted polymer. G was varied from 28 to 140%. The exchange capacity of grafted fiber was found from curves of potentiometric titration by 0.1 n NaOH solution. The swelling was given by the weight difference between the swelled and centrifugated at 55 g during 15 min. fibers.

IR spectra were obtained on a DS-403G grating spectrophotometer equipped with an ATR attachment. In view of great troubles arising when recording the ATR spectra of non-woven material, the "melting" ATR element was used. This technique allows to gain many times the contrast of ATR spectra of rough surface specimens.[4,5] The advantage is reached by substitution of the solid optical material (KRS5, Ge or other) by IR-transparent chalcogenide glass IKS35 which being heated up to 60–80°C, becomes softened. A portion of glass is placed into a mould formed for needed ATR-element, e.g. semicylinder. The sample with rough surface relief is attached onto the free plane of heated softened glass and tightened to obtain the optical contact. Despite the parasitic light scattering on fibers, the gain in band intensity appeared to be quite significant due to removal of the air gap.[5]

RESULTS AND DISCUSSION

In Figure 1, a curve of potentiometric titration of AA-grafted PP by NaOH solution is presented. A single overbending of the curve indicates the monofunctionality of obtained fiber ionite.

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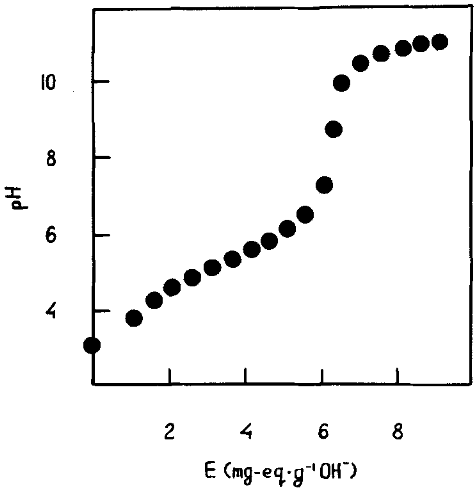

FIGURE 1 Curve of potentiometric titration by 0.1 n NaOH solution of PP fibers grafted by 98% of AC.

TABLE I

Physico-chemical characteristics of AA-grafted PP fibers

Graft %	Exchange capacity (mg-eq./g dry) Calc.	Exchange capacity (mg-eq./g dry) Measured	Water capacity ($g\ H_2O$)	Water capacity (eq. H_2O)	$\log(I_{1710}/I_{973})$ Bulk	$\log(I_{1710}/I_{973})$ Surface
41	4.5	4.5	0.12	1.47	3	6
58	5.0	5.0	0.16	1.78	—	—
98	6.9	6.3	0.30	2.64	4	13

The properties variation with the graft percentage increase is given in Table I. The divergence between the calculated and measured values of the exchange capacity at high G, evidences a part of functional groups are inaccessible for exchange. Moreover, while the exchange capacity increases from 4.5 to 6.3 mg-eq./g, the water capacity increases approximately by a factor of 2, although one should expect that the quantity of water molecules per one carboxyl group equivalent is independent on the number of groups. The lack of proportionality can be attributed to the relative growth of carboxyl group concentration in the surface layer as compared to that in the bulk.

The direct confirmation of inhomogeneous distribution of functional groups in the cross-section of fibers has been obtained by the IR spectroscopy technique. In Figure 2, the fragments of the ATR and transmission spectra of AA-grafted PP recorded in the range of the C=O group band at 1710 cm^{-1}, and the band at 973 cm^{-1} attributed to vibrations in PP isotactic helix are shown. The ratio of their intensities (I_{1710}/I_{973}) measured in transmission and ATR spectra characterizes the relative concentration of grafted groups in the bulk and on the surface, respectively. For all samples, I_{1710}/I_{973} was found to be greater in the ATR spectrum (Table I). With the increase of G, the inhomogeneity of C=O groups distribution grows. At G = 140%, the 973 cm^{-1} band could not be observed in the ATR spectrum.

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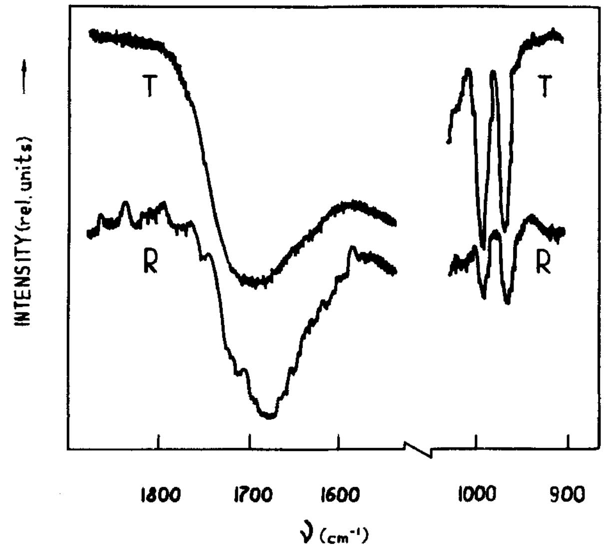

FIGURE 2 Transmission (T) and ATR (R) spectra of PP fibers grafted by 98% of AC in vicinity of the IR bands at 1710 and 973 cm^{-1}.

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Varying the angle of light incidence (ϑ) one can control the depth of the IR radiation penetration into the sample placed on a ATR-element. We varied the angle of incidence from $\vartheta = \vartheta_{cr}$ up to $\vartheta = \vartheta_{cr} + 20°$ (here ϑ_{cr} is the ATR critical angle), but no changes in the value I_{1710}/I_{973} have been found. Such a situation occurs when the modified surface layer could be considered as a "thin layer" in comparison with the minimal penetration depth.[6] The latter value in our case was about 3 μm: one can conclude, the grafting was realized predominantly in the surface layer of less than 3 μm thick.

The investigation of the analogous system (PP with irradiation-grafted AA) executed by the electron probe microanalysis[7] showed that the grafting starts from the surface and proceeds, with sharp boundary, to the bulk. In our case, the grafting process develops itself in the same manner, despite we used the preliminary γ-irradiation in contrast to simultaneous (with grafting reaction) generation of active radicals used in Reference 7.

CONCLUSION

The grafting of AA on the preliminary γ-irradiated PP allows to obtain monofunctional fibers with high exchange capacity. The grafting process proceeds from the surface into the fiber core: the surface layer contains higher concentration of the grafted chemical groups than the fiber bulk. The cross-section inhomogeneity grows with the increase of the graft percentage. At modest graft percentage, the grafted substance does not screen completely the inner regions of the host fiber. The latter point is of significant practical importance, since the penetration of grafted groups into the bulk gains the osmotic resistance and improves the strength characteristics.

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