



Formation of hydrophilic nanolayers on the surface of polypropylene microfibers

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Introduction

Immobilization of macromolecules and formation of thin polymeric films on solid surfaces is a promising contemporary method of improving the properties of polymeric materials. Surface modification enhances conductivity, wettability, stability, adhesion, antithrombogenicity, and antibacterial properties of polymeric surfaces without impairing the material's bulk properties. Polymer surface modification is conventionally achieved by targeted covalent polymer attachment (grafting), resulting in thin films with interesting properties. In many cases, radical polymerization is considered a useful approach for polymer grafting on a solid surface.

Polymeric surfaces were peroxidized by employing plasma treatment, UV-irradiation, oxygenation and ozonation, and radical initiators and then further modified by the grafting of surface polymer films. Alternatively, polyperoxide macromolecules can be used for substrate surface activation.

Methods

Materials - Polypropylene microfiber 6 mm long, 0.1 mm in diameter. Polypropylene plates produced by Hostalen 0180 D, Elenac, Germany. A copolymer of N-[(tert-butyl peroxy)methyl]acrylamide with octyl methacrylate (PA-OMA) was synthesized according to the methods described in [1].

Modification of the surface of polypropylene microfiber: grafting PA-OMA and grafting polyacrylamide chains were performed according to the methods described in [1].

Water retention. Samples of microfiber (0.2 g) were placed in a perforated polypropylene cylinder. The microfiber was compressed in the cylinder to the specified volume by means of a rod. A microfiber cylinder was placed in a Dogadkin device and the amount of water absorbed was determined. Measurements were performed every 15 minutes and stopped when the difference between the previous and next measurement was absent.

The free surface energy of polypropylene planar surfaces was determined by measuring the wetting angle by the method of two liquids (water and methylene iodide) by the method described in [2].

Results

In this work we studied the processes of microfiber modification grafting PA-OMA and grafting polyacrylamide chains. Covalent attachment of polyperoxide macromolecules to a polypropylene surface occurs due to the radical processes initiated by thermolysis of the peroxide groups. Covalent bonds between polyperoxide and a polypropylene surface are formed by the reaction of chain transfer to the polymer surface macromolecules, followed by recombination between the surface macroradicals and polyperoxide macromolecules. Chemical functionalization of a polymeric substrate, as a rule, results in increasing surface energy. Peroxide groups of the grafted polyperoxide macromolecules on a polymeric substrate can be used for surface hydrophilization (grafting polyacrylamide chains).

To control the modification processes we used to estimate the value of specific water retention at different stages of modification, ATR FTIR spectroscopy. At the same time under the same conditions were modified and monitored changes in surface properties of planar polypropylene samples.

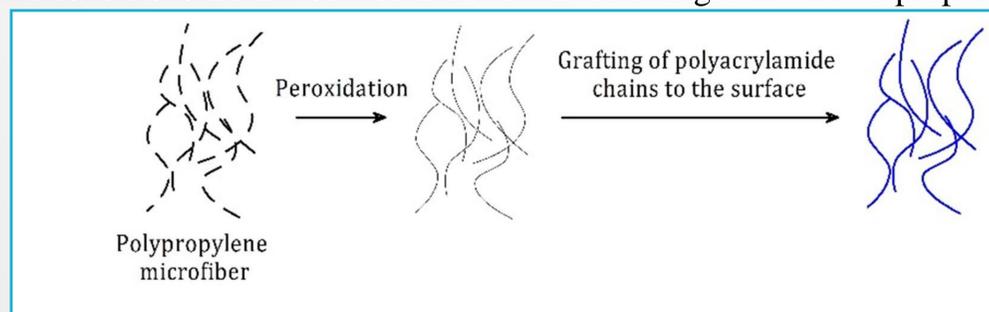


Fig. 1. The scheme of modification of polypropylene microfiber

The scheme of modification of polypropylene microfiber (Fig. 1) includes the following stages: • modification (peroxidation) of the surface of polypropylene with copolyperoxide PA-OMA; • grafting of polymer chains of polyacrylamide.

Changes of the free energy parameters of the surface of planar samples, value of specific water retention for the fiber at different stages of its modification (Tab1.) ATR FTIR spectroscopy (Fig. 2) and elemental analysis clearly confirmed the successful surface modification of polypropylene microfibers.

Table 1
Surface characteristics of planar samples of polypropylene and microfiber

| | The nature of the surface | Components and total free surface energy, mN / m | | | The share of the modified surface, % | Water retention, $g_{\text{water}} / g_{\text{fiber}}$ |
|---|----------------------------|--|---------------|-------------|--------------------------------------|--|
| | | λ_s^d | λ_s^h | λ_s | | |
| 1 | PP | 30.60 | 2.83 | 33.43 | - | 0.3 ÷ 0.5 |
| 2 | PP→PA-OMA | 31.62 | 5.25 | 36.88 | 97 | 0.6 ÷ 0.8 |
| 3 | PP→PA-OMA → polyacrylamide | 9.33 | 29.81 | 39.15 | 95 | 8.0 ÷ 8.6 |

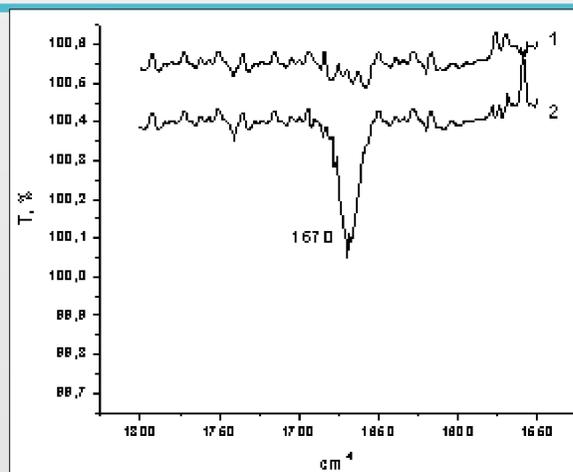


Fig. 2. ATR FTIR spectrum of polypropylene microfiber: 1) unmodified; 2) modified with polyacrylamide.

The presence on the spectrum (Fig. 2) the absorption bands with maxima of 1670 cm^{-1} and 1644 cm^{-1} (which can be attributed to the valence vibrations of the carbonyl group $=\text{C}=\text{O}$ and $=\text{NH}$ in the amide group) suggests the grafting of nanolayers of polyacrylamide to the activated by PA-OMA surface of polypropylene.

Conclusions

The results of the conducted research have shown that the possibility of activating the surface of polypropylene microfibers when using polyperoxides with subsequent modification of the peroxidized surface. The hydrophobic surface of polypropylene acquires hydrophilic properties due to the grafting of nanolayers.

References: 1. Nosova N., Roiter Y., Samaryk V., Varvarenko S. and other. Polypropylene surface peroxidation with heterofunctional polyperoxides // *Macromolecular Symposia*. – 2004. – Vol. 210. – P. 339–348.
2. Samaryk V., Voronov A., Tarnavchik I., Varvarenko S. and other. Formation of coatings with tailored properties on polyperoxide-modified polymeric surfaces // *Progress in Organic Coatings*. – 2012. – Vol. 74. – No.4. – P.687–696.

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