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Formation of Polymer Nanolayers with Special Properties at Polymer Surfaces

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Summary: A principal possibility of the utilization of polymer peroxides for the modification of polymer surfaces that provides an immobilization of the tailored quantity of peroxide groups at them has been established. The processes of polymer surface activation with following "grafting from" or "grafting to" utilizing immobilized peroxide groups has been studied using a FTIR-ATR spectroscopy, ellipsometry and measurements of contact angles. The proposed technique of polymer surface activation is based on the universal ability of carbon chain polymer to participate the free radical reactions.

Keywords: hydrophilic polymers; nanolayers; polyolefins; polyperoxides; surface modification

Introduction

Surface properties of polymers are not less important than polymer bulk properties since their interaction with environment proceeds just through the surface. Providing desired properties to the surface of polymers: hydrophilicity; bio- and hemocompatibility; bactericidity; electric conductivity and others, – increases significantly the variety of their application.[1–3] An urgency of corresponding studies is challenged by the rising applications of modified polymer surfaces in nanotechnologies utilized in biotechnologies, medicine, micro- and nanoeletronics. One of the general methods of surface modification is an intentional grafting of surface polymer layer.[2] Today, various techniques have been developed for such grafting realization with the most widespread ones utilizing free radical mechanisms. UV- or γ-irradiation and plasma treatment of polymer surfaces with following grafting of polymer layers are applied widely for this.[4–6] Alternative technique of surface activation is a utilization of low molecular weight peroxides that generate macroradicals at polymer surfaces at the expense of radical reactions.[7–9] Peroxidized surface allows to perform the known techniques of "grafting to" and "grafting from" polymer nanolayer formation. Thus, the possibility of managing the grafted nanolayer structure to the state of polymer brushes or 3D-crosslinked structures appears.

In this work, we present a novel approach to the peroxidation of polymer (carbon chain) surfaces using polyperoxides – polyperoxide modifiers of polymer surfaces. The universal ability of carbon chain polymers to participate the free radical reactions is utilized. A covalent grafting of polyperoxide to the surface with the formation of polymer layers carrying peroxide groups is performed at the expense of controlled decomposition of polyperoxide -O:O- groups.

We have synthesized polymer peroxides incorporating: ditertiary peroxide groups[10]; peresteric[11]; hydroperoxide[12]; or peroxide and hydroperoxide groups together at controlled ratios[13], – that can be applied for the modification of polymer surfaces.

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Experimental Part

As polymer modifier of the surfaces, the copolymer of peroxide monomer 2-*tert*-butylperoxy-2-methyl-5-hexene-3-yne (VEP) with octyl methacrylate (OMA) (VEP-OMA, incorporating 24%mol of VEP units and M_n ca. 6500), which was synthesized using technique[14], have been utilized.

Monomers: hydroxyethyl methacrylate (HEM), acryl amide (AAm), vinyl acetate (VA), butyl acrylate (BA), acrylic acid (AAc), were utilized after preliminary purification using standard techniques.

Heparin sodium, dextran, dextran sulphate (ICN Biomedicals Inc.) was utilized as received.

Grafting of the monomers was performed by the thermostatting of peroxidized substrates in degassed 1%wt solution of monomers at 120 °C during 62 hours except for specially described cases.

Ellipsometric mapping was carried out using a high-speed in-situ-44-wave lengths ellipsometer (Woollam Co.) with incident angle of 75^0 at ambient conditions.

FTIR-ATR studies were performed using an IFS55 spectrometer (Bruker, Germany) from the surfaces of two identically prepared specimens simultaneously.

Results and Discussion

Activation of polymer surface at the expense of physical sorption and free radical grafting of polyperoxides has been studied at the peroxidation of polyolefine substrates.

Modification technique consist of two stages: (1) polyolefin substrate activation (peroxidation) by heterofunctional polyperoxide (VEP-OMA) at the expense of physical sorption and free radical peroxide grafting; (2) activated surface modification, using "grafting from" technique, in other words, using polymerization of functional monomers, initiated from surface, and "grafting to" technique.

We have conducted the studies of polypropylene surface by means of null-ellipsometry, atomic force microscopy, FTIR-ATR spectroscopy, measurements of contact angles. Ellipsometric mapping of polyperoxide layer (Figure 1a) confirmed polyperoxide grafting on PP surface. It has been found that the height of polyperoxide layer grafted to polypropylene is of 18 ± 3 nm.

The results of FTIR-ATR spectroscopy studies obtained from the surface of industrial PP Hostalen 0180 D points to

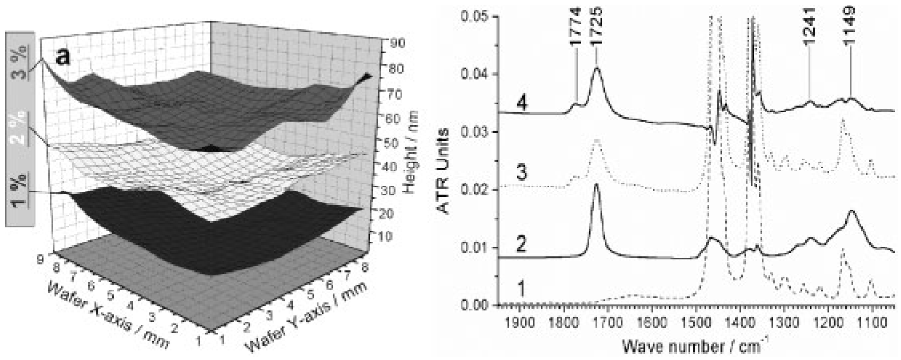
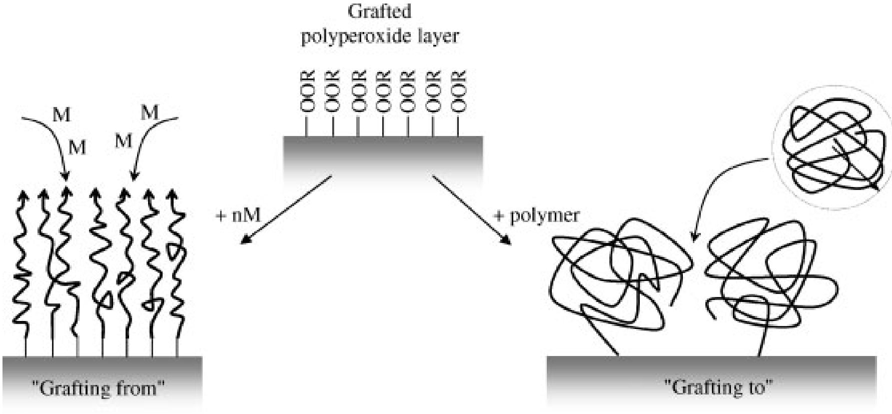


Figure 1.

Ellipsometric mapping of VEP-OMA layer (**a**) grafted to PP surface at different concentrations of VEP-OMA in spincoated solution: 1%wt; 2%wt; 3%wt, – at 130 °C for 20 hours; and (**b**) FTIR-ATR spectroscopy study of industrial PP Hostalen 0180 D surface (**1**), VEP-OMA surface (**2**), PP surface modified with VEP-OMA (**3**), and difference between the spectra of modified and virgin PP surfaces (**4**).



Scheme 1.

the presence of immobilized polyperoxide on it (Figure 1b). Curve 4 in this figure represents the difference between spectra of polypropylene surface modified with polyperoxide (curve 3) and virgin PP surface (curve 1). One can see that the modification of polypropylene with polyperoxide results in the appearance of absorption bands at 1725 cm^{-1} (carbonyl groups), 1241 cm^{-1} and 1149 cm^{-1} (ester groups) that are characteristic for virgin polyperoxide (curve 2).

As a result of peroxidation, one can observe surface characteristics changes and peroxide groups, able to initiate radical processes, immobilization is sued. Schema of surface modification with ''grafted from'' technique and ''grafted to'' technique is showed on Scheme 1.

Modification of peroxidized polypropylene by acryl amide, acrylic acid and other functional monomers, heparin,dextran and dextran sulphate was followed by ellipsometric study and determination of free surface energy components.

Peroxidized surface of polypropylene at its heating in monomer solution initiates its ''grafting from'' radical polymerization. Thus, covalent grafted nanolayers of different polymers are formed and their height depends on monomer concentration in solution and grafting conditions. For example, ellipsometric mapping of grafted polyacrylic acid is showed (Figure 2a)

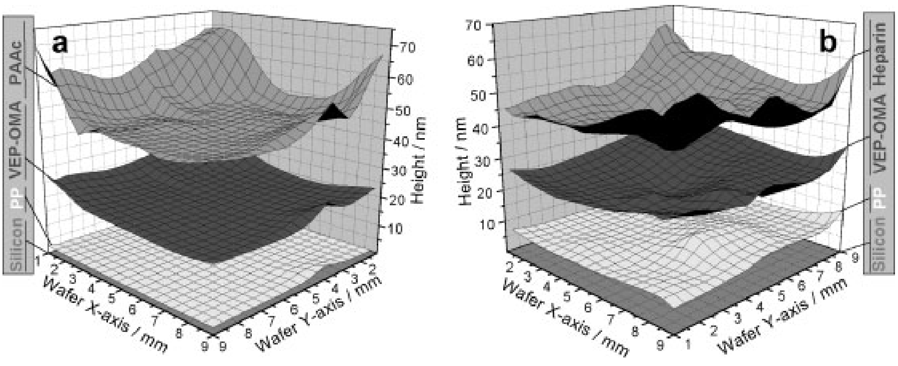


Figure 2.
Ellipsometric mapping of model PP specimen peroxidized with copolymer VEP-OMA with following modification by AAc ''grafting from'' (**a**) or heparin ''grafting to'' (**b**) (reactions were performed in 1%wt water solution both of AAc and heparin, at 130 °C heating for 20 hours). (PAAc – poly(acrylic acid).

Table 1.
Surface characteristics of industrial PP substrates at their modification

Surface nature	*Water contact angle*	*Methylene iodide contact angle*	Surface energy		
			λ_s^d	λ_s^h	λ_s
	degrees	degrees	mN/m	mN/m	mN/m
Virgin PP	91.0	54.1	31.2	0.2	31.3
PolyHEM	63.7	48.0	26.1	14.1	40.2
PolyAAm	34.5	54.4	19.0	41.5	60.5
PolyBA	49.3	50.2	23.0	29.1	52.2
PolyVL[a)]	61.0	46.3	27.3	18.7	46.0
Grafted dextran	56.2	38,2	31.3	17.9	49.2
Grafted dextran sulphate	32.6	22.5	33.8	30.7	64.5
Grafted heparin	67	55.5	23.54	15.65	39.19

[a)] Poly(vinyl alcohol) (hydrolyzed poly(vinyl acetate)).
λ - surface tension, dyne/cm; subscript indices *s*, *l* pertain surface tensions of solids and liquids, respectively; superscript indices *d*, *h* mean dispersion (London) and hydrogen bonding constituents of surface energy.

Besides, properties of the surface may be controlled by the nature of grafted to the surface polymers. The constituents of free surface energy and contact angles for the substrates of industrial PP ПП Montell Profax, on which surfaces the hydrogels of different nature were formed by "grafting from" surface.

One can see (Table 1) that the component of hydrogen binding (λ_s^h) of free surface energy can change significantly as a result of grafting polymers of different nature with diverse functional groups that allows to increase adhesion of polyolefin surfaces to hydrophilic coatings and is the first step to achieve biocompatibility of polymeric surfaces. Moreover, at the modification of peroxidized surface with dextran sulphate it is possible to achieve essential increase of total free energy (λ_s) that is the sum of λ_s^h and the component of dispersive binding.

One can see (Figure 2a) that the nanolayer of VEP-OMA peroxide copolymer (19.3 ± 2.5 nm in height) with "grafted from" it polyacrylic layer (29.2 ± 5.7 nm in height) was grafted to polypropylene layer. At the same time dextran and dextran sulphate layers "grafted to" peroxide copolymer layer are presented in Figure 3a, Figure 3b and Figure 2b correspondingly. Besides, one can see from these figures that the least grafted nanolayer was obtained in the case of dextran. This can

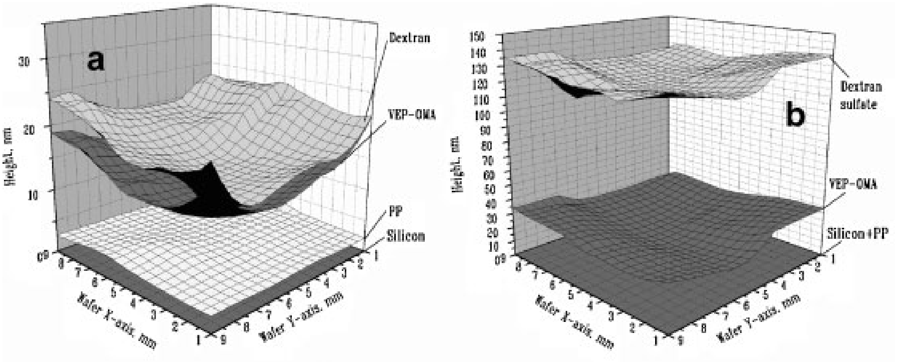


Figure 3.
Ellipsometric mapping of model PP specimen peroxidized with copolymer VEP-OMA with following modification by dextran "grafting to" (**a**) or dextran sulphate "grafting from" (**b**).

be caused by weaker electron contraction on carbon atom in position 6 in this case as compared with the case of dextran sulphate.

Thus, it has been shown that polyperoxides can be grafted to the surface of polymers capable of the participation in free radical reactions with the formation of nanolayers carrying immobilized peroxide groups. After that, immobilized peroxide groups can initiate the ''grafting from'' and ''grafting to'' reactions leading to the desired modification of polymer substrates.

Conclusions

Polymer peroxides based on peroxide and other functional monomers can be successfully utilized for the peroxidation of the surface of polymers capable of participation in free radical reactions of chain transfer and recombination. The presence of the controlled quantity of peroxide groups at the polymer surfaces allows to perform their modification via the grafting of respective monomers and polymers. This allows to provide the surfaces with such the important properties as hydrophilicity, biocompatibility and others. Peroxidation of polymer surfaces can be performed in water emulsions, melts and via the modification of polymer substrates.

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