*Macromol. Symp.* **2004**, *210,* 339-348

# Polypropylene Surface Peroxidation with Heterofunctional Polyperoxides

*Natalya Nosova,*[1] *Yuri Roiter,*[1] *Volodymyr Samaryk,*[1] *Sergiy Varvarenko,*[1]
*Yuri Stetsyshyn,*[1] *Sergiy Minko,*[2] *Manfred Stamm,*[2] *Stanislav Voronov**[1]

[1] National University "Lvivska Polytechnica", 12 S. Bandera Str., Lviv 79013, Ukraine
E-mail: stanislav.voronov@polynet.lviv.ua
[2] Institute of Polymer Research, Hohe Strasse 6, D-01069 Dresden, Germany

**Summary:** Method of polyolefin surface activation via covalent grafting of polyperoxide nanolayer by free radical mechanism has been presented. The features of such the nanolayer formation under the thermoprocessing conditions, i.e.: formation of 3D crosslinked network in polyperoxide bulk; and its grafting with complete coating of polyolefin surface, -- is considered. The method provides an availability of uniformly placed peroxide groups of one type over the polyolefin surface activated, which may further be utilized for the tailored modification of polymer surfaces using the "grafting to" and "grafting from" techniques in that time when it is necessary.

**Keywords:** covalent grafting; crosslinking; nanolayers; peroxide copolymer; peroxidation of polymer surfaces

## Introduction

The cases of contradiction in demands for certain materials, i.e.: between their bulk and surface properties, -- arise in the industry often enough. Such a situation occurs when material bulk properties, its availability and economic benefits allow an implementation of goods and surface properties of these materials do not meet the necessary demands. Especially often, this problem becomes apparent in the case of polymer materials. Their low free surface energy, hydrophobicity, scanty ability to be glued and the number of other factors restrict essentially their utilization despite of all useful physical-mechanical characteristics intrinsic to these materials due to the features of bulk structure and composition.

One of the general methods of this problem solution is a modification of surface both of virgin material and of goods on its basis. At this, the necessary change of material surface properties may be achieved under the condition of the retention of its bulk properties.

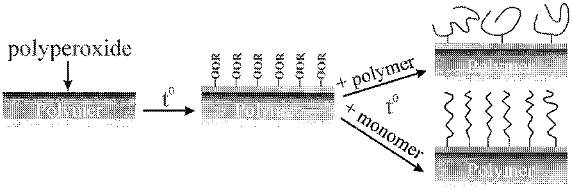
DOI: 10.1002/masy.200450638

## Theoretical grounds

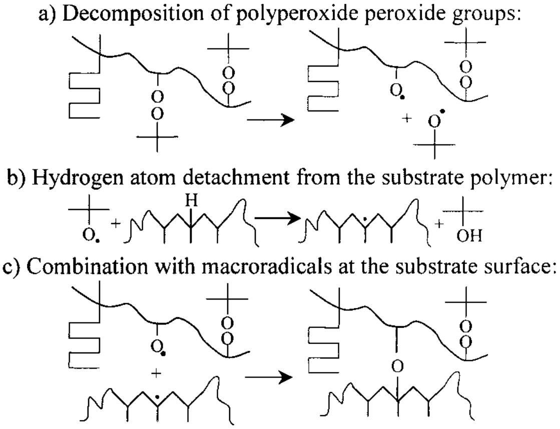
The majority of polymers relate to the materials possessing low free surface energy. That is why, a modification of their surface at the expense of physical forces of sorption is hindered. In this connection, a lot of techniques elaborated for surface modification are oriented to the covalent grafting of modifiers to the surface. In the case of polyolefins, this problem is sharpened by that their surface incorporates no functional groups capable of facilitating such the grafting. A number of techniques have been elaborated that are based, for instance, on the preliminary generation of free radicals at the surface. It provides the possibility of the creation of modifying layers via the grafting of modifier preliminary created to the surface or via the initiation of monomer polymerization from such the surface.

Among the methods, which are applied for the radical generation, one can list an irradiation with electron beam radiation, treatment with plasma and corona discharges [1-3]. Aside of the utilization complexity, restrictions imposed by surface profiles, and ecological hazard, one can add a non-uniformity of surface modification connected with the zones of different reactivity present at the surfaces to the drawbacks of these methods [4].

A method proposed here, which provides the possibility of radical generation at the polymer surface, is freed significantly from those drawbacks. This method consists in the grafting of polyperoxide layer to the surface using a free radical mechanism, and its application with further surface modification can be represented as follows:



In accordance with the method proposed, grafting to the surface can be shown in general by the Scheme 1. Grafting of surface polyperoxide nanolayer proceeds at partial (not more than 50 %) decomposition of peroxide groups. The latter fact provides further possibility of free radical generation just in that time, when it is necessary, and to graft special polymers (dextran sulfate, dextran, heparin) or to initiate a polymerization of functional monomers (acrylic acid, vinyl acetate, acrylonitrile etc.) from the surface.



a) Decomposition of polyperoxide peroxide groups:

b) Hydrogen atom detachment from the substrate polymer:

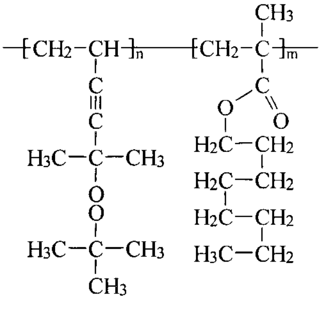
c) Combination with macroradicals at the substrate surface:

Scheme 1. Process of polyperoxide macromolecule grafting to polypropylene surface.

The demands to surface profile, necessity of the application of complicated protective and special equipment, are lowered at the utilization of the proposed method of surface peroxidation; and the sources of free radicals are placed uniformly over the surfaces that relieve the problem of their different reactivity at further modification.

## Materials and methods

Heterofunctional copolymer VEP-OMA based on 2-tert-butylperoxy-2-methyl-5-hexene-3-yne and octyl methacrylate has been utilized for the surface peroxidation. Its structure can be presented with the following scheme:



Scheme 2. Structure of VEP-OMA polyperoxide.

This copolymer synthesis has been reported earlier [5]. Similar synthesis technique has been applied for preparation of other copolymers of VEP with higher (meth)acrylates (lauryl methacrylate (LAMA); hexyl acrylate (HAT); butyl acrylate (BA)) utilized in work for comparison purposes.

Viscosity averaged molecular weight ($M_v$) of copolymers was measured after determination of the constants for Mark–Houwink equation [6] via the fractionating of copolymer samples and determination of fraction molecular weights by gel permeating chromatography using a HP 5890 CasChromat equipped with HP 7694 detector (Hewlett Packard, Japan). Characteristic viscosities of the copolymer samples were determined using an Ubbelohde viscometer.

Conversion of peroxide groups from copolymer composition at the heating in bulk was measured via chromatographic analysis of decomposition products using a gas-liquid chromatograph Selmichrom-1 (Selmi, Ukraine).

Polypropylene (PP, Montel Profax) and thermoplastic polyolefin (TPO, Solvay) as substrates of 20×20×3 $mm^3$ size were chosen for the studies. For the ellipsometric studies, the model substrates of polypropylene (Aldrich) and polystyrene (Aldrich) attached covalently to silicon wafers (Wacker-Chemitronics) of 10×10×1 $mm^3$ size were utilized in accordance with known technique [6].

Peroxidation of polymer substrates was performed as follows. Substrates were washed in Soxhlet apparatus with propanone for 4 hours in order to remove the impurities and technological additives from their surface. Then, substrates were dried under vacuum till constant weight. Application of peroxide copolymer solution of certain concentration was performed using a spincoating technique [6]. Peroxide-containing copolymer solution in heptane (0.08 ml) or toluene (model substrates) was applied to the substrate surface and substrate was kept at 2000 rpm for 1 min. Control substrates were treated with respective solvent. Then, substrates were thermostatted in hermetic box under argon atmosphere or in vacuum oven (model substrates) at defined temperature for certain time (temperature range at the performance of experiments was of $80 \div 130\ ^0C$). After the thermoprocessing, substrates were placed into Soxhlet apparatus and extracted with propanone for 4 hours and dried under vacuum till constant weight.

The changes of free surface energy components were determined using a known technique [7] measuring the contact angles for two liquids.

Null-ellipsometry studies and ellipsometric mapping were performed on model substrates of hydroxyl terminated polystyrene, PS-COOH ($M_n$ ca. 16 000), grafted to silicon wafers (Wacker-Chemitronics) using a High-Speed In-Situ-44-Wave Lengths Ellipsometer (Woollam Co.) under ambient conditions. Surface area of single measurement covered by laser spot was of $0.1\times0.2$ cm$^2$. PP refractive index (1.490) was taken from ellipsometer software data. Cross-linked VO refractive index (1.482) was determined for separately obtained silicon wafers with correspondingly heated VO layers of approximately 60÷120 nm performing the measurements using the same ellipsometer and solution of equation system using an ellipsometer software. After every experiment stage samples were placed onto ellipsometer working table with accuracy of ±0.01 cm. Measurements were performed in the middle part of the samples (in order to avoid the edge effects of PP and VO application) in 100 positions for total area of $0.9\times0.9$ cm$^2$ with step of 0.1 cm in the direction of both abscissa and ordinate axes. The results obtained for ellipsometric mapping were transferred to matrix form and processed using a Microcal Origin 5.0 software.

## Experiment and discussion

Structure formation and properties of heterofunctional polyperoxide nanolayer at polymer surface as well as a completeness of surface coating have to be dependent upon a type of peroxide group used in polyperoxide, their conversion and a height of applied nanolayer. Curve 1 in Figure 1 shows a dependency of ellipsometric height of polyperoxide layer applied to model substrates upon its concentration in solution utilized for spincoating. Application of this technique allows the formation of polyperoxide layer of 7 to 200 nm height. In accordance with literature data [8, 9] obtained using a low angle X-ray scattering, homopolymers and copolymers of higher esters of (meth)acrylic series display anisotropy in their bulk caused by the orientation of macromolecules skeleton chains and interaction of side branches. A determination of constants for Mark–Houwink equation [10] was performed in this work (Table 1) in comparison with mentioned literature data for higher (meth)acrylate homopolymers. Good accordance of $\alpha$ constant between these data allows to conclude that incorporation of peroxide links into higher (meth)acrylate polymers does not affect essentially the conformation state of their macromolecules. This, in turn, allows to suppose that the copolymers synthesized retain their anisotropy in bulk.

Schematically a polyperoxide layer at the substrate surface is represented in Scheme 3.

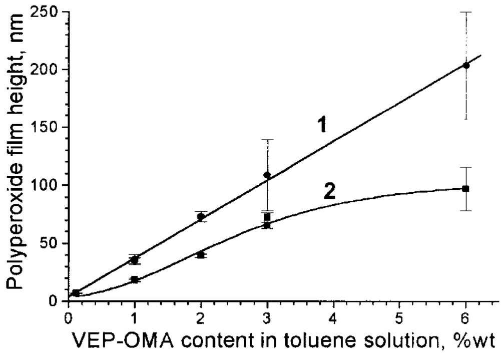
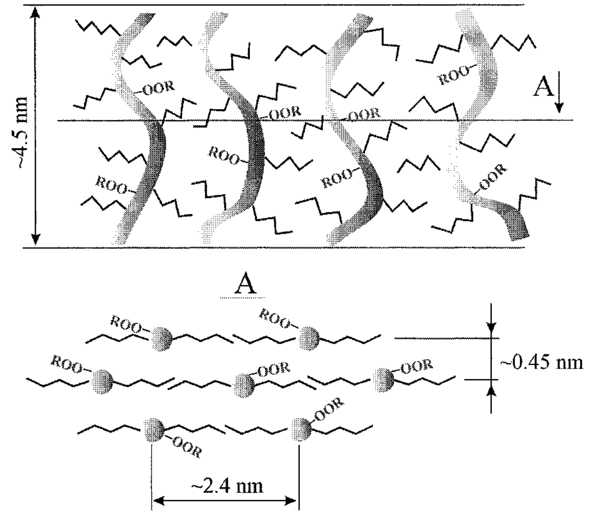


Figure 1. Dependence of the height of polyperoxide layer applied (**1**) and grafted (**2**) upon its concentration in toluene solution for spincoating.

Table 1. Characteristics of peroxide-containing copolymers and literature data for homopolymers [7,11] of higher (meth)acrylates. Measurements were performed at 20 $^0$C.

| (Co)polymer | VEP links | Solvent | $K \cdot 10^4$ | $\alpha$ | $M_v$ | [η] |
|---|---|---|---|---|---|---|
| | %mol | | | | kg/mol | dl/g |
| VEP-OMA | 15.3 | butanone | 1.76±0.05 | 0.71±0.03 | 6.2 | 0.0818±0.001 |
| VEP-LAMA | 15.2 | butyl acetate | 3.31±0.07 | 0.65±0.04 | 12 | 0.0127±0.0005 |
| VEP-HAT | 15.0 | butanone | 1.05±0.02 | 0.83±0.03 | 9 | 0.182±0.002 |
| VEP-BA | 15.1 | butanone | 0.84±0.07 | 0.85±0.05 | 11 | 0.291±0.001 |
| PolyOMA | 0 | butanone | 0.447 | 0.69 | – | – |
| PolyLAMA | 0 | butyl acetate | 0.846 | 0.64 | – | – |
| PolyHAT | 0 | butanone | 0.212 | 0.78 | – | – |
| PolyBA | 0 | butanone | 0.156 | 0.81 | – | – |

A layer structure as indicated in Scheme 3 is of course not rigorously conclusive from our investigations. It is, however, quite probable also in view of literature data [8, 9] that at least a short range order is present which resembles the arrangement from Scheme 3 over some distance. The free surface and interface with the substrate can induce order over larger scale and the layer structure therefore is easier to achieve in thinner films. Coming from the opposite direction, using the parameters of molecule placement shown above and the layer height measured, and accounting for the most probable distance between chain end of 4.5 nm (estimated in accordance with [11]), a weight applied to the surface should be of $(2.7 \pm 0.1) \times 10^{-5}$ g/cm$^2$. Satisfactory coinciding of these results confirms the layered structure of polyperoxide over the surface.



Scheme 3. Bulk copolymer layer of higher esters of (meth)acrylic series in accordance with literature data [8, 9].

Comb-like polymers with side aliphatic chains display adsorption activity to the polyolefin surfaces [12]. Thermal treatment of substrate with applied polyperoxide leads to the thermolysis of peroxide groups. The curves of peroxide group thermolysis obtained for polyperoxide decomposition in its bulk, are shown in Figure 2a. Peroxide group thermolysis leads to the crosslinking of polyperoxide layer that is witnessed by the change of polyperoxide molecular weight upon a conversion of peroxide groups shown in Figure 2b. Complete crosslinking to 3D network takes place at peroxide group conversion exceeding 30 % and it is weakly dependent upon a thermolysis temperature.

Layer grafting to the surface proceeds along with it crosslinking. The latter results in that the layer grafted cannot be soxhlet extracted from the substrate surface. A series of ellipsometric mappings obtained after extraction of the specimens heated for different times has been shown in Figure 3. Besides, curve 2 in Figure 1 demonstrates a height of grafted crosslinked layer in comparison with the height of applied layer (curve 1, Figure 1). Height of grafted layer at 50 % conversion of peroxide groups is of 50÷80 % in respect to the applied layer.

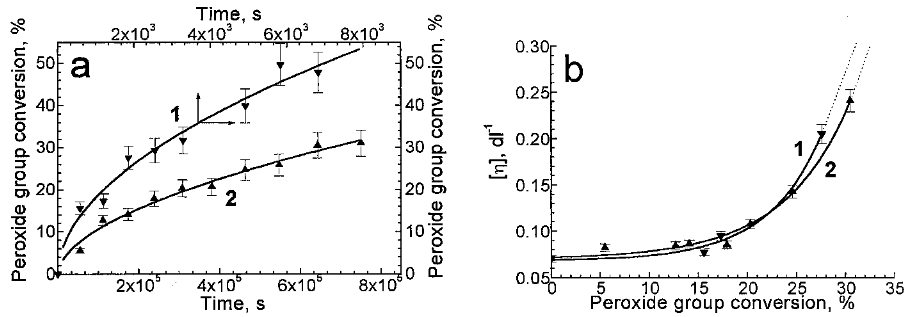


Figure 2. (**a**) Dependence of VEP-OMA peroxide group conversion upon a heating time in bulk. (**b**) Dependence of intrinsic viscosity of VEP-OMA solution in hexane upon a conversion of peroxide groups. Dotted lines point to the formation of crosslinked polyperoxide insoluble in organic solvents after ~30 % peroxide group conversion. VEP-OMA heating was performed in bulk at (**1**) 144 °C and (**2**) 109 °C.

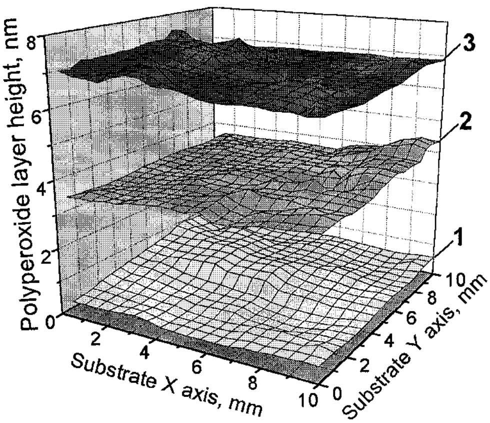


Figure 3. Dynamics of height changes of polyperoxide layer grafted to model layer of polystyrene upon a time of its thermoprocessing. Layer was spincoated from 0.12 %wt solution in toluene; grafting was performed at 130 °C for: (**1**) 5 hours; (**2**) 10 hours; and (**3**) 20 hours.

Experimental data presented above allow to suppose that polyperoxide grafting to polymer surface proceeds with simultaneous cross-linking in bulk. This bulk cross-linking has a higher rate than the grafting to the surface. At the initial stages, when grafting is not significant, the extraction of polyperoxide layer with solvent (acetone) cleans completely almost the substrate (polypropylene) surface and distribution of measured water contact angles corresponds to one for virgin PP (Curve 1, Figure 4). With further accumulation of grafted sites, distribution of contact angles shifts (Curves 2, 3) to the one of peroxide-containing copolymer (Curve 5). Average height of the grafted layer at this stage is of 8÷45 nm -- much higher than polyperoxide macromolecule sizes. This witnesses that not single VEP-OMA molecules but their cross-linked ensembles are grafted to the surface. The process is finished by the complete practically coating of the surface by cross-linked layer (Curve 4, Figure 4) grafted covalently to the polymer surface. Joint analysis of ellipsometric mapping and contact angle changes has shown that at 50 % of peroxide group conversion, complete coating takes place for the case of applied layer height of 130 nm (under conditions of the spincoating described, it relates to the utilization of 4 % VEP-OMA solution). It may be of interest that it is provided by about 240 layers of polyperoxide macromolecules.

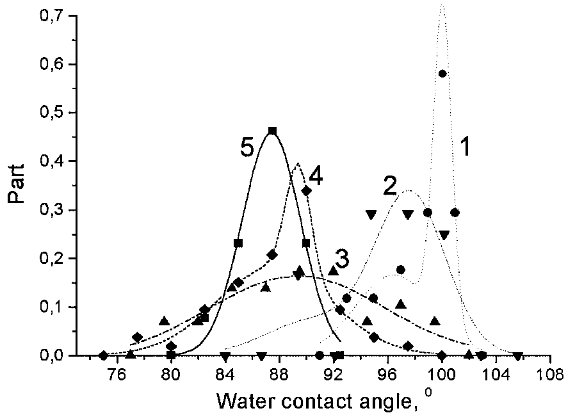


Figure 4. Distribution of water contact angles for the surfaces of different level of modification. **1** -- virgin PP surface, VEP-OMA layer grafted to PP surface (ellipsometric height): **2** -- 8÷10 nm; **3** -- 40÷45 nm; **4** -- 82÷90 nm; **5** -- model surface of cross-linked VEP-OMA.

As a result of further investigations performed, the modification of peroxidized polymer surfaces has been conducted successfully applying both "grafting to" (heparin, dextran, dextran sulfate) and "grafting from" (acrylic acid, acrylonitrile, vinyl acetate) techniques.

## Conclusions

Surface grafted 3D network is formed in the result of heterofunctional polyperoxide grafting to polyolefin surface at the expense of free radical process proceeding. Since grafting is conducted with incomplete thermolysis of peroxide groups from polyperoxide structure, the network incorporates peroxide groups that may be used for the further surface modification. Formation of grafted 3D network is dependent upon a conversion of peroxide groups and a height of applied polyperoxide layer.

[1] US Patent 6,210,516 (2001), NeoMecs Inc., invs.: R. S. Nohr, J. G. MacDonald.

[2] US Patent 5,972,176 (1999), 3M Innovative Properties Company, invs.: S. M. Kirk, C. S. Lyons, R. L. Walter.

[3] US Patent 6,203,850 (2001), NeoMecs Inc., inv.: H. Nomura.

[4] US Patent 6,023,025 (2000), Nissin Electric Co., Ltd., invs.: T. Nakahigashi, A. Doi.

[5] S. A. Voronov, V. Ya. Samaryk, S. M. Varvarenko, N. H. Nosova, Yu. V. Roiter, *Dopovidi NAN Ukrayiny (Reports of National Academy of Sciences of Ukraine)* **2002**, *6*, 147.

[6] S. Minko, S. Patil, V. Datsyuk, F. Simon, K.-J. Echhorn, M. Motornov, D. Usov, I. Tokarev, M. Stamm, *Langmuir* **2002**, *18*, 289.

[7] D. W. Van Krevelen, *"Properties of polymers correlations with chemical structure"*, Khimiya, Moscow, 1976, p. 413, in Russian; transl. from: D. W. Van Krevelen, *"Properties of polymers correlations with chemical structure"*, Elsevier, Amsterdam, London, New York, 1972.

[8] N. A. Plate, V. P. Shybaev, *Vysokomol. soedinen.* **1971**, *13A(3)*, 410.

[9] N. A. Plate, V. P. Shybaev, V. P. Talroze, *Vysokomol. soedinen.* **1977**, *18B(5)*, 110.

[10] *"Compendium of Chemical Terminology. The Gold Book"*, 2nd ed., A. D. McNaught, A. Wilkinson, Eds., Blackwell Science, Oxford 1997.

[11] Yu. S. Lipatov, A. E. Nesterov, T. M. Gritsenko, *"Polymer chemistry hand-book"*, Naukova dumka, Kiev, 1971, in Russian.

[12] L. Leger, E. Raphael, H. Hervet, *Adv. Polym. Sci* **1999**, *138*, 185.