CHEMISTRY & CHEMICAL TECHNOLOGY

Vol. 1, No. 1, 2007 **Chemistry**

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HETEROFUNCTIONAL OLIGOPEROXIDES ON THE INTERFACE

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Received: April 4, 2007

Abstract. It is shown that the attachment of macromolecules of the functional oligoperoxides to the planar polymeric surfaces or to the surface of a dispersed phase results in the localization of the peroxide groups on the interface. Designing of interphase layers with a well-defined structure and nature with the use of the peroxydized interphases and grafting reaction "to" and "from" the surface is carried out. The compatibilizing polymeric layers in polymeric blends and the grafting surface layers with special properties are formed.

Keywords: interface, interphase layers, modification of surface, co-graft polymerization, oligoperoxide.

1. Introduction

Modern polymer materials – filled polymers, water polymer dispersions and polymer blends are typical colloidal systems with a highly developed interface. The properties of polymer composite materials on their basis are to a large extent determined by the structure and properties of the interfacial layers. Definitely, the progress of such polymer composites in chemistry and technology is dependent on the possibilities of designing interfacial layers. Moreover, in connection with the intensive development of nanotechnologies, there are ever increasing investigations pertaining to the modification of polymer surfaces with the aim of imparting special properties, since their interaction with the surrounding medium takes place solely via the surface. The surface modification of polymers is usually achieved through purposeful grafting of the surface polymer layer of a definite nature and structure, whereby the surface is rendered electrically conductible, imparted with catalytic or healing properties, antithrombogenicity, bactericidal, charges or other qualities [1]. The next steps of the surface modification of polymers is creation of a polymer pattern/network or tethering a definite combination of macrochains known as "smart" coatings to the surface. The surface modification therefore greatly widens their applicability. Such modification is commonly achieved [2,3] via the preliminary activation of the polymer surface by plasma, UV-, g-irradiation, and chemical means – oxidation and ozonization followed by the formation of surface polymer layers via graft polymerization of monomers or polymer macromolecules. An alternative means of activation is the formation of grafted polymer layer via graft polymerization to the polymer surface of macromolecules of heterofunctional oligoperoxides (HFO) [4].

The design of polymer nanolayers on interfaces is of high importance for obtaining polymer blends. The problems encountered during their synthesis are due to the fact that the majority of polymers are immiscible [5]. A number of ways to improve the polymer compatibility are known [5, 6, 7, 8, 9], having in common the localization at the interfacial boundaries of polymer macromolecules – compatibilizers containing fragments partially compatible with polymer blend components in their structures. Reactive blending of components whereby macromolecules of the compatibilizer are formed in situ during blending [10] is particularly promising. It has been shown [11] that these processes intensely occur upon the localization of curing agents and peroxides at the polymer blend interfacial boundaries. Conventional peroxides are however often ineffective upon polymer blending due to their volatility and occurrence of radical processes not only at the interfacial boundary but also in the bulk of polymer melt. To overcome these difficulties it is reasonable to introduce radical generating sites into the polymer structure and place their macromolecules at the interfacial boundary [12].

It was noted [13] that polymer compatibilization in the melt has much in common with the stabilization of polymer colloidal particles in an aqueous phase (lattices) using polymer surface active substances (so called polymer surfactants). These substances are capable of being localized at the interface of polymer dispersions, reducing the surface tension. We have shown that the use of polymer surfactants with peroxide groups for this purpose enables to activate the surface of latex particles and control the colloidal stability of polymer water dispersions [20,21,22], as well as create lattices with "core-shell" particle morphology. Such lattices have found application for creation of latex film-formers, as impart strength modifiers, and also as precursors for obtaining polymer hollow microspheres.

At the same time in the last decade investigations on the synthesis of heterofunctional polyperoxides, study of their properties and application for the interface modification and the creation of modified and composite polymer materials have gained an increasing development [14,15,16,17,18,19]. The attachment of the macromolecules of heterofunctional polyperoxides onto planar polymer surfaces or the surface of a dispersed phase leads to the localization of peroxide groups on the interfacial boundary. New opportunities therefore arise for the design of interfaces with predetermined structure and nature and impartation of special properties to planar polymer surfaces, the creation of polymer materials on the basis of polymer blends, as well as synthesis of polymer dispersions with "core-shell" particle morphology. The application of heterofunctional polyperoxides for these purposes consists of the following stages: (i) tailored synthesis of heterofunctional polyperoxide, (ii) its attachment to the dispersed phase surface or planar surface with the objective to peroxidize them, (iii) the formation of compatibilizing polymer layer, or grafted surface layers with special properties.

It is well-known that the general property of carbon-chain polymers (polyethylene, polystyrene, poly(methyl methacrylate) and others) is their ability to participate in free-radical reactions, especially in chain transfer and recombination reactions. Besides, a major property of oligoperoxides is their thermal decomposition leading to formation of free radicals and macroradicals allowing grafting of oligoperoxide macromolecules onto polymer surfaces, tethering thereby a controllable amount of peroxide groups. Macromolecules of heterofunctional oligoperoxides can thus play the role of polymer surface activators. Depending on the polymer surface nature and kind of heterophase system their structure should meet the following requirements: i. They should generate radicals which are active in chain transfer reactions – methyl $\cdot CH_3$, *tert*-butoxyl $\cdot O\text{-}C(CH_3)_3$; or phenyl, $\cdot C_6H_5$.

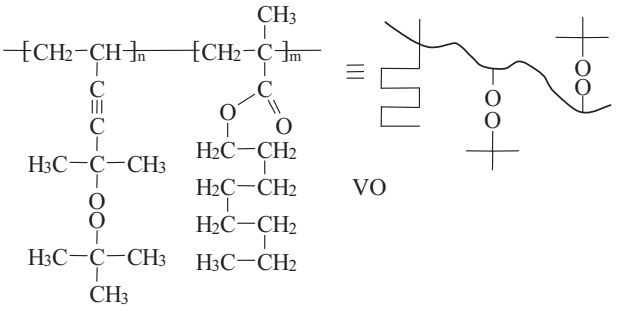
ii. Oligoperoxide macromolecules should include comonomer links capable of providing physical intermolecular interaction and their suitable conformation on the surface for further "peroxide fragment/polymer surface" chemical interaction.

Heterofunctional oligomers (HFO) are mainly prepared via the copolymerization of peroxide monomers with other functional monomers [14,15]. Peroxide monomer 2-*tert*-butylperoxy-2-methyl-5-hexen-3-yne (PM, VEP) has found the greatest application.

The possibiliies of activation (peroxidation) of the polymeric planar and the dispersion surface using oligoperoxides and obtaining the surfaces with special properties as well as the polymer blends on their basis are considered in this paper.

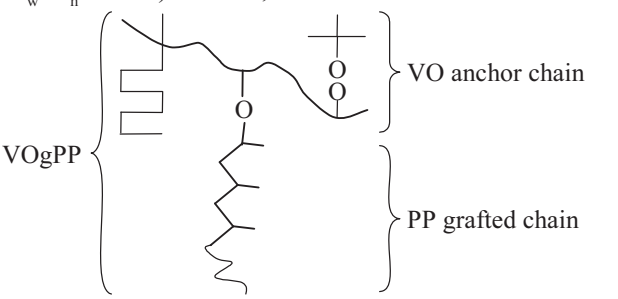
2. Experimental

The *synthesis of interface-active peroxide-containing precompatibilizer VOgPP* (Scheme 2) for the compatibilization of polypropylene blends with other carbon-chain polymers was presented earlier [43,44].



Scheme 1. The structure of the random anchor peroxide-containing polymer VO

It consists of two stages, the first of them is the synthesis of the random copolymer of 2-*tert*-butylperoxy-2-methyl-5-hexene-3-yne (VEP) and octyl methacrylate (OMA). (VO, Scheme 1), and the second one is the VOgPP preparation, performed in a DACA Micro-Compounder (volume 4.5 cm^3) (DACA Instruments) in accordance with the parameters optimized by means of a full-factorial second order orthogonal design: temperature 448K, VO concentration in PP (Aldrich 428183, M_n ca. 5400 g/mol, M_w/M_n = 3.63) 18 wt%, reaction time: 12 min.



Scheme 2. The structure of the precompatibilizer VOgPP

The VO had a M_n of ca. 6500 g/mol with M_w/M_n = 1.1 and contains 14 mole % of VEP units. VOgPP has been utilized as its 35wt% blend with PP. The active oxygen content in VOgPP was of 0.7 mmole/g.

Ellipsometric mapping. Specimens for ellipsometric mapping were prepared as follows. Highly polished silicon wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath with dichloromethane (three times, each 5 min), placed in cleaning solution (NH_4OH : H_2O_2 : H_2O = 1 : 1 : 1 (by volume)) at 333 K for 1 h, and then washed several times with Millipore water (18 MΩ×cm). Dried with a nitrogen stream the silicon

substrates were placed into an argon-filled glove box and immersed into 3-glycidoxypropyl trimethoxysilane (GPS, Aldrich) solution (1 wt%) in dry toluene for 16 h. The modified substrates were rinsed several times with dry toluene and ethanol in an ultrasonic bath to remove unattached GPS. Maleic anhydride terminated polypropylene (PP-MA, M_n ca. 9100 g/mol, M_w/M_n = 2.64) was spincoated from 1 wt% toluene solution onto the surface of the GPS modified silicon substrates. Then substrates were placed to a vacuum oven at 443K for 24 h to graft the PP chains covalently. Unattached PP-MA was removed by soxhlet extraction with toluene for 5 h. The grafted PP layer was mapped after substrates were dried using a high-speed in-situ-44-wave length ellipsometer (Woollam Co.). VO was spincoated from 1 wt% toluene solution onto the surface of PP-MA modified silicon substrates. The thickness of these VO films before grafting was 35±4 nm. Then substrates were placed to the vacuum oven at 403 K for 24 h and unattached VO was removed by the soxhlet extraction with toluene for 5 h. An ellipsometric map was built for the VO layer grafted to the PP layer.

Blends of polypropylene/polystyrene (PP/PS; 30/70; PP amorphous, Aldrich 428183; PS 143 E (BASF AG) and *polypropylene/polyethylene* (PP/PE; 10/90; PP Novolen 1106 H (Targor); PE Hostalen GC 7260 (Elenac GmbH) were obtained as follows. The precompatibilizer was premixed at ambient conditions with granules of PP and the second component used for blend preparation. Reactive blending was performed by means of DACA Micro-Compounder at 463K for 10 min. Blends prepared were extruded as strands into a container with water.

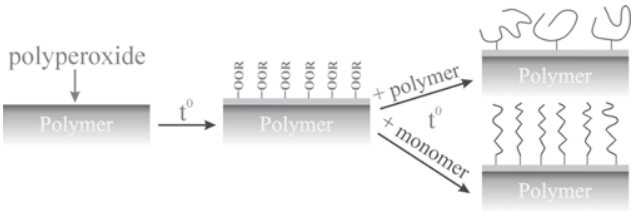
Blends of polypropylene with unsaturated polyester resin dissolved in styrene (uncured and cured compositions) (PP/UPR-styrene; composition of 3/97 to 20/80; PP amorphous, Aldrich 428183; UPR PN-15 (Ukraine); styrene, Aldrich) have been prepared as follows. Polypropylene without any precompatibilizer or with VOgPP is added to UPR melt heated to 463K in a steel mixing chamber (Universal Laboratory AID type MPW-309 (Mechanika Precyzyjna); Steel turbine blade; internal chamber diameter : blade diameter = 3 : 1. Mixing is performed at 2000 rpm during 15 min at 463K. After that styrene heated to 323K is added to the mixing chamber (with heating turned off) in order to achieve a UPR/styrene ratio of 60/40 (wt). At this time, PP particles become solidified and the UPR phase dissolves gradually in styrene with simultaneous cooling to 293K during 20 min. The obtained liquid composition may be stored for necessary time at ambient conditions (see Results and Discussion). For composition curing, benzoyl peroxide (40 wt %. blend in dibutyl phthalate, Aldrich) in the quantity of 5 wt % and 2,4-dimethylaniline (Aldrich) in the quantity of 0.15 wt % both upon the total quantity of UPR and styrene are added to the composition before its casting to mold. After casting composition curing proceeds at room temperature during 24 hours with obtaining of solid specimens sized as 0.5×1.0×8.0 cm^3.

Scanning electron micrographs were obtained from cryofractured surfaces by means of a scanning electron microscope DSM982 Gemini or a scanning electron microscope LEO VP435 at 10 kV.

3. Results and discussion

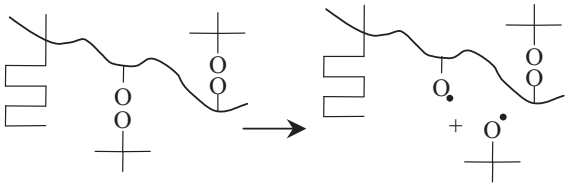
3.1. Peroxidization of polymer surfaces by oligoperoxides and formation of graft layers with special properties

Peroxidation of polymer surfaces with the aid of oligoperoxides consists of their grafting onto the surface by a free-radical mechanism [25,26]. Synthesis of polymer layers grafted to peroxidized surface enables the impartation of special properties. These processes can be represented by the following scheme:

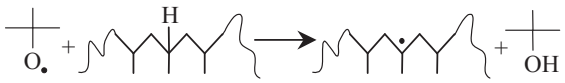


Grafting to the polymer surface in this case includes these series of reactions:

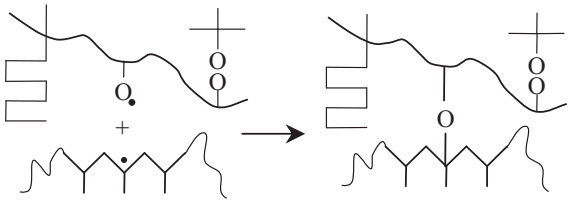
a) Decomposition of the peroxide groups of oligoperoxide:



b) Hydrogen abstraction from the polymer surface macromolecule:



c) Recombination of macroradicals at the polymer surface:



Grafting of surface nanolayer of the oligoperoxide occurs during partial (not exceeding 50 %) decomposition of peroxide groups. The control decomposition of peroxide bonds provides the possibility of grafting the macromolecules of special polymers (dextran, heparin) or the initiation of the polymerization of functional monomers (acrylic acid, vinyl acetate, acrylonitril) from the surface. A widespread application for the peroxidization of polymer surface has found a heterofunctional cooligomer VEP-OMA derived from 2-*tert*-butylperoxy-2-methyl-5-hexen-3-yne and octylmetacrylate (VO) [25,26,27].

The formation of the structure and property of the oligoperoxide nanolayer grafted to the polymer surface, as well as the surface coverage depend on the type of a peroxide group, their conversion and the height of the precoated oligoperoxide nanolayer. Curve 1 on Fig. 1 reflects the concentration dependence of ellipsometrical thickness of the coated layer of oligoperoxide on model polymer substrates. The use of a spincoating technique allowed to form oligoperoxide layers with the height in the range 7–200 nm. Homopolymers and copolymers of higher esters of the (meth)acrylic series are known to exhibit anisotropy [28,29,30], caused by self-assembly orientation of macromolecules and the interaction of the macromolecular backbones and the interaction of side chains.

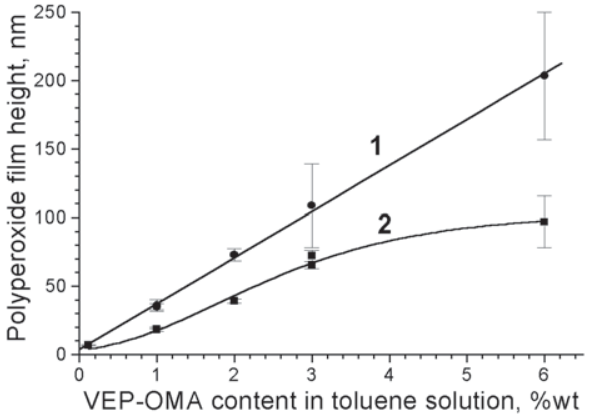
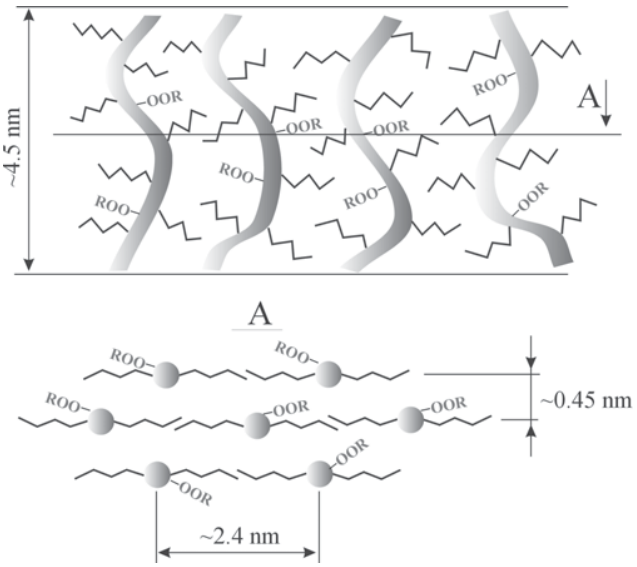


Fig. 1. Concentration dependence of the height of coated (**1**) and grafted (**2**) oligoperoxide layer

Based on the literature data [28,29,30] and our experimental results the oligoperoxide layer on the surface of a polymer substrate can be schematically represented by the following scheme:



As a result of such orientation the oligoperoxide deposited on a polymer surface has a layer-like structure. Such structure is liable to the intermolecular interaction and the formation of assembled crosslinked networks. Realization of this structure in the case of VEP-OMA oligomer can be confirmed by the calculations using the ellipsometric investigation data and the gravimetric determination of the coated layer weight: upon spincoating from a 4% solution in toluene $(3.0\pm0.2)\times10^5$ g/cm^2 of oligoperoxide is deposited on the surface. This corresponds to 2.58×10^{15} molecules/cm^2 with the formation of VEP-OMA layer of height 130 nm (Fig. 1, curve 1). Counter calculations with the aid of known parameters of the molecular distribution [30,31], layer height of 130 nm, taking into account the most probable distance between chain ends of 4.5 nm (estimated from literature data [29]) have shown that the weight of oligoperoxide deposited on the surface amounts to $(2.7\pm0.1)\times10^5$ g/cm^2. A satisfactory coincidence of theoretical and experimental data verifies the layer-like structure of the oligoperoxide on the surface.

Comb-like polymers with side aliphatic chains exhibit an adsorption activity with respect to polymer (polyolefine) surfaces [32]. In the case of VEP-OMA, the adsorption of oligoperoxide molecules onto polyolefine surfaces is verified by the dependence of cosine of the contact angle of wetting by VEP-OMA solution in diiodomethane on its concentration in the solution (Fig. 2).

The physical interaction of the first layers of VEP-OMA macromolecules with a polymer surface facilitates their covalent grafting to the latter during thermal treatment. Heating of the polymer substrate with the coated oligoperoxide leads to the decomposition of peroxide

bonds. Curves of the thermolysis of peroxide groups are presented on Fig. 3a. The thermolysis of peroxide bonds envisages the crosslinking of the oligoperoxide layer. This is confirmed by the change in the oligoperoxide molecular weight with an increasing conversion of peroxide groups. (Fig. 3b). Formation of crosslinked three-dimensional network occurs when the peroxide group conversion exceeds 30 % and is sparingly dependent on the thermolysis temperature.

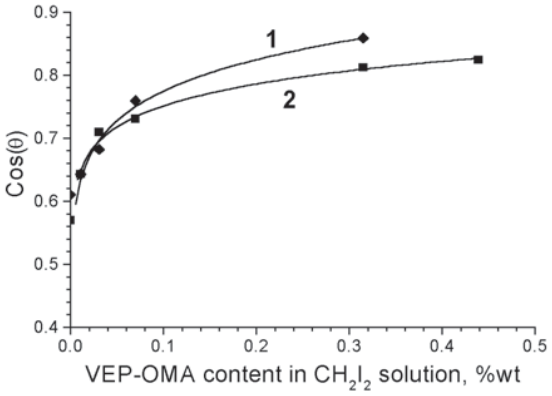


Fig. 2. Cosine of the contact angle of wetting polyolefine surface (TPO, Solvay) (1) and PP (2)

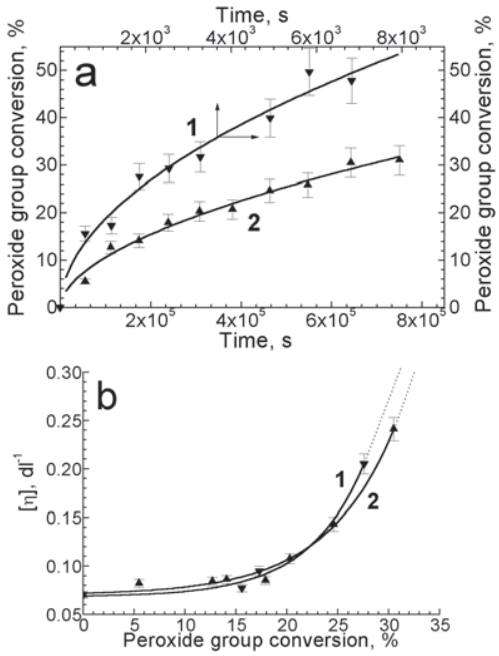
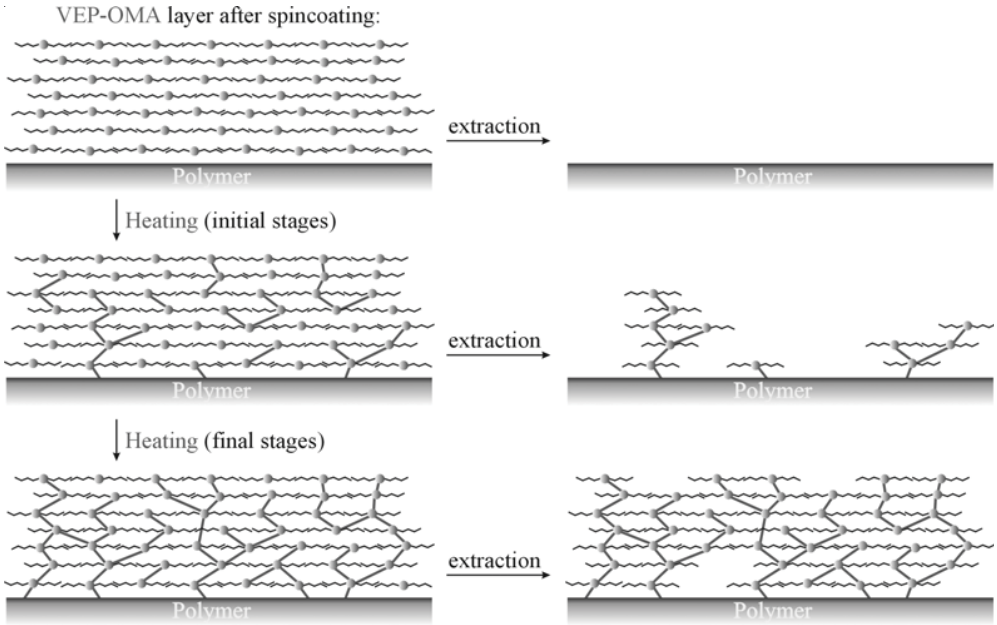


Fig. 3. Dependence of VEP-OMA peroxide group conversion on the heating time (a). Dependence of the intrinsic viscosity of VEP-OMA solution in hexane on the conversion of peroxide group (b).
VEP-OMA was heated in bulk at 417K (1) and 382K (2)

Crosslinking of VEP-OMA layer takes place simultaneously with its grafting to the surface. The graft layer thus formed is not extractable from the substrate surface in Soxhlette device. Series of ellipsometric mappings obtained after the extraction of the samples at different heating durations are shown. Curve 2 on Fig. 1 demonstrates the graft crosslinked layer thickness in comparison with the thickness of the coated layer (curve 1, Fig. 1). The graft layer thickness upon 50 % conversion of peroxide group equals 40-50 % of the coated layer thickness.

The experimental data obtained allow to distinguish the following stages of a peroxide layer grafted to the surface:



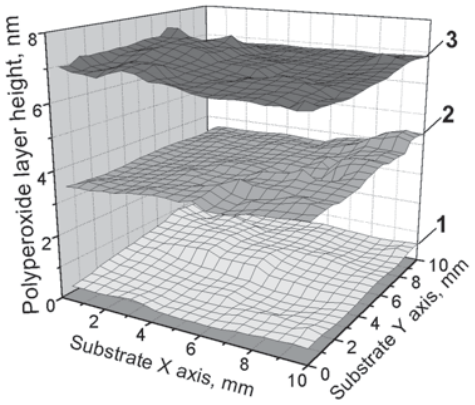


Fig. 4. Dynamics of change in the layer thickness of polyperoxide grafted to model PS layer with the heating time. Coating was performed by spin-coating technique from 0.12 % (wt.) solution in toluene; grafting at 403K for: (**1**) 5; (**2**) 10; and (**3**) 20 hours

At the first step crosslinking of the oligoperoxide takes place in the bulk with simultaneous grafting of the crosslinked macromolecules of the first layer oligoperoxide to the polymer surface. As a result crosslinked molecule groups are formed which either includes molecules grafted to the surface or not. Besides, non-crosslinked oligoperoxide molecules also remain in the oligoperoxide layer. The extraction of this layer by a solvent at this stage leads to the formation of a zone of "island" graft at the surface. For such surface the contact angle of wetting will be determined as a function of the contact angles of both oligoperoxide and PP surface.

The next step involves the growth of the crosslinked groups and the formation of new ones. This step develops into the end phase, when the amount of crosslinked groups becomes enough for binding together, thus, leading to full surface coverage by the peroxide-containing layer. At this step the extraction by a solvent does not lead to the creation of open zones of the substrate surface, but only to the washing-out of crosslinked groups non grafted to the surface. In this case the contact angle of wetting is determined only by the free surface energy of crosslinked VEP-OMA. At this step these are mainly the groups formed at the pre-surface layer and their dewetting explains why the graft layer has a lower height than the initial layer. It is evident that further heating leads to full crosslinking, but such layer loses its functionality due to a complete dissociation of the peroxide bonds.

The comparative analysis of the ellipsometric mappings and changes in the contact angle of wetting have shown that at 50 % conversion of peroxide groups full surface coverage occurs at the height of coated layer equaling 130 nm. It is interesting to note that this is provided by approximately 240 layers of oligoperoxide macromolecules assembled layer by layer. The modification of the peroxidized surface was later performed by "grafting from" (acrylic acid, acrylonitrile, vinyl acetate) and "grafting to" techniques (heparin, dextran, dextran sulfate).

3.2. Formation of graft layers with hemocompatible properties on peroxidized polymer surfaces

Graft polymerization to the peroxidized surface of 2–hydroxyethyl methacrylate (HEM), acryl amide (Aam) and vinyl acetate (VA) was carried out in aqueous solutions, and polymer layers of different nature were thus grafted to the polymer surface. The formation of poly(vinyl alcohol) polymer layers was performed by hydrolysis of poly(vinyl acetate) chains grafted to the surface. The analysis of the contact angle of wetting and the free surface energy parameters has shown the possibility of controlling the hydrophilic properties of the modified polymer surface. The results of these investigations are given in Table 1.

Table 1

Surface characteristics of polymer surfaces of various chemical natures

Nature of surface	Contact angle of surface, *		Free surface energy, mN/m		
	Water	Methylene iodide	λ_S^d	λ_S^h	λ_S
PP (polypropylene)	91	54.1	31.2	0.2	31.3
PP+VEP-OMA	101.5	55.3	30.8	1.6	32.4
PP+VEP-OMA+HEM*	63.7	48	26.1	14.1	40.2
PP+VEP-OMA+Aam	34.5	54.4	19.0	41.5	60.5
PP+VEP-OMA+VA	49.3	50.2	23.0	29.1	52.2
PP+VEP-OMA +VA+Hydrolysis	61	46.3	27.3	18.7	46.0

* Grafting was carried out in the aqueous solution of monomers (1%) under argon at 393K, 62 hours

It can be seen that the application of monomers differing in nature permits to control the polymer surface properties. Grafting poly(acryl amide) chains to the surface yields the maximal surface hydrophilicity. It is known [33] that in order to create hemocompatible surfaces it is necessary, first and foremost, to lower or completely avoid the adsorption of fibrinogen to the surface. This is achieved in two ways: the creation of surfaces on which plasma blood proteins are either not adsorbed at all (so called "pure surfaces") or are adsorbed, mainly albumin ("albumin protection ") [34]. This avoids the adsorption of fibrinogen. The adsorption capability of plasma blood proteins on the modified surface was estimatedaccording to the adsorption activity coefficient values of albumin and fibrinogen determined with the aid of Shiskovskiy's equation [35] (Table 2). Evident is the fact that VEP-OMA oligoperoxide peroxidation of PP surface by itself leads to a significant decrease of the adsorption activity of fibrinogen (A_F) and an increase in the according to the adsorption activity of albumin (A_A). Their ration rises from 0.06 to 2.29. The enhancement of albumin adsorption on the polymer surface can be explained by the modification of the surface by octylmethacrylate fragments. This conforms well to known data [36]. Furthermore, the formation of polymer layers at the interfacial boundary (polymer "brushes" and gels) is considered the most promising way of creating hemocompatible surfaces [37,38].The results of the adsorption activity of plasma blood proteins on polymer layers of different nature formed on the peroxidized surface have shown that the formation of such layers at the interface predominantly leads to a decrease in the adsorption activity of fibrinogen and increase of the adsorption activity of albumin (Table 2).

Table 2

An adsorption activity of plasma blood proteins of fibrinogen and albumin at the surfaces differing in chemical nature

Nature of surface	Adsorption activity, m^2/mmol		A_A/A_F
	Albumin (A_A)	Fibrinogen (A_F)	
PP	9	145	0.06
PP+VEP-OMA	16	7	2.29
PP+VEP-OMA+HEM	~0	~0	–
PP+VEP-OMA+Aam	23	94	0.24
PP+VEP-OMA+VA	74	61	1.21

Such change of surface properties according to the literature data [33,34,37,38] envisages their hemocompatibilty. The surface modification by poly(acryl amide) enhances the ratio of adsorption activities to 0.24. The surface modification by vinyl acetate is more promising since this ratio increases to 1.21. The formation of polymer layers generally leads to a 1.5…2.5 times decrease in the adsorption activity of fibrinogen with the simultaneous magnification of the adsorption activity of albumin by 2.5–8 times, i.e. "albumin protection" mechanism is realized. The result of the surface modification by HEM ought to be considered separately. In this case there is a sharp decrease in the adsorption activity of both albumin and fibrinogen. Such drop in the adsorption activity leads to the hemocompatibilty of the modified surface by a "pure surfaces" mechanism [34].

The results obtained were confirmed by Scanning Electron Microscopy (SEM) It has been established that the thrombus-formation process at peroxidized PP surface modified by graft layer of poly(2-hydroxyethyl methacrylate) (HEM) occurs with low intensity compared to the untreated PP surface.

It is known that the immobilization of dextran sulfate and heparin onto polymer surfaces impart hydrophilicity, bio- and hemocompatibilty to them [38]. We have carried out the modification of PP surface by polysaccharides applying the "grafting to" technique. Ellipsometric mapping of the polymer surface modified by heparin and dextran sulfate (Fig. 5) has proved the immobilization of polysaccharides.

The results of ellipsometric investigations have indicated the capability of polysaccharide towards a chain transfer reaction which leads to their grafting reactions to the peroxidized polymer surface. Fig. 5 shows that the height of graft polysaccharide layers is a function of their nature. The results obtained permit to propose the following scheme of polysaccharide immobilization to the peroxidized surface.

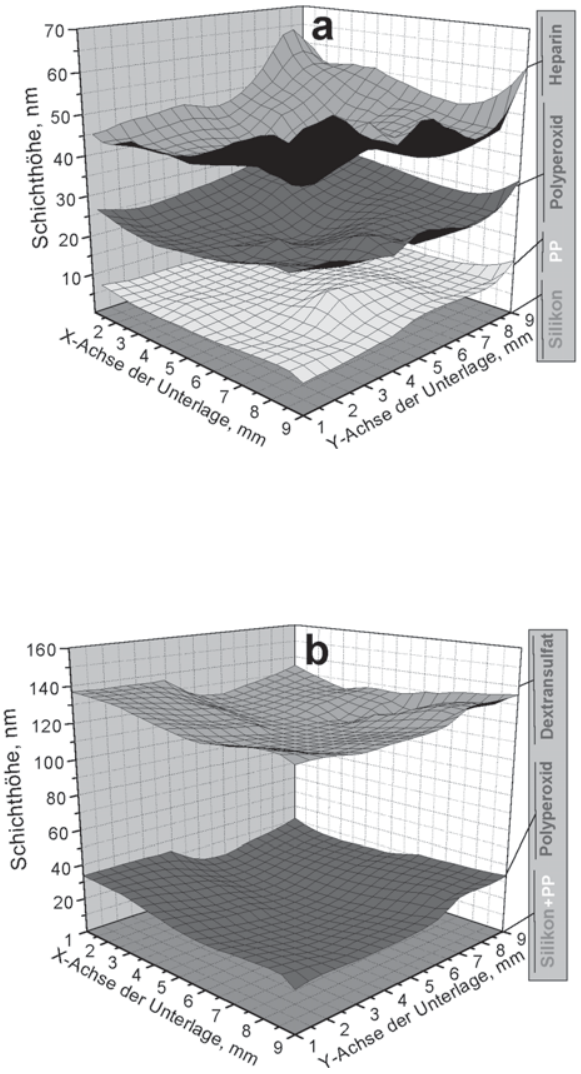
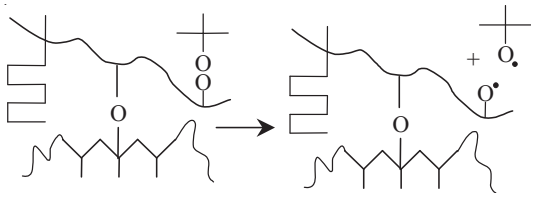
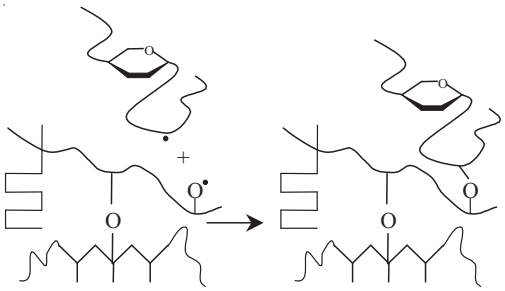


Fig. 5. Ellipsometric mapping of peroxidized PP surface modified by heparin (a), and dextran sulfate (b)

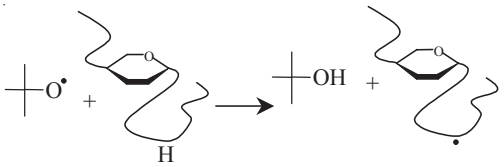
a) Decomposition of the surface peroxide bonds:



b) Hydrogen atom abstraction from polysaccharide molecule:



c) Recombination of polymer surface macroradical with polysaccharide macroradical:



The scheme proposed has also been confirmed by AFM data [26].

3.3. Formation of antibacterial coatings on peroxidized polymer surfaces

The method of creating antibacterial surfaces utilizing covalent grafting of bactericides to polymer surfaces is very promising. The suppression of the bacterial growth is achieved by grafting to it, for example, poly(4-vinyl-N-hexylpyridinium chloride (VGPC) [39]. The investigation results of antibacterial properties of modified PP surfaces are presented in Table 3. The best results were obtained for PP-VEP-OMA-VGPC samples, for which clearly distinguished growth suppression zones of *S.aureus* bacteria were observed.

Table 3

Antibacterial properties of polymer surfaces

Surface nature	Number of colonies grown per cm².	Relative number of colonies grown (%)	Growth suppression zone of a test microorganism
PP	145	100	-
PP-VEP-OMA*	169	116	-
PP-VEP-OMA-4-VP	123	84	-
PP-VEP-OMA-4-VGPC	15	10	+
PP-VEP-OMA-2-HEM	185	127	-
PP-VEP-OMA-dextran	97	66	-

The number of colonies grown on this surface is only 10 % of the number of colonies grown on the surface of unmodified PP. The growth suppression of a test microorganism was not observed for the other surfaces examined. PP-VEP-OMA-VGPC sample results from the polymeranalogous transformations of PP-VEP-OMA-VP in which poly(N-vinyl-2-pyridine) chains grafted to the surface were quarternized by n-hexyl chloride. Polymeranalogous transformations performed on PP surface yielded a covalently immobilized modifying layer of similar nature as described in the previous work [39]. The results obtained almost completely coincide with the data of this work, confirming the prospect of the proposed technique for creating antibacterial coatings on polymer surfaces.

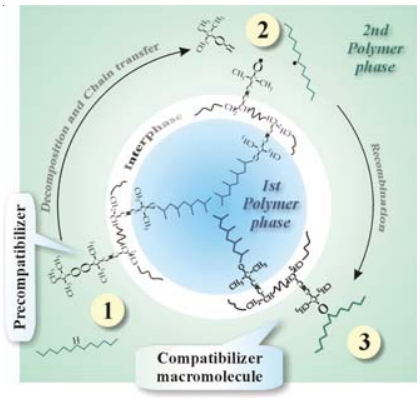


Fig. 6. Formation of the compatibilizer macromolecule

3.4. Formation of oligomer compatibilizing layers on the interface of disperse polymer blends

The basis of well-known polymer blend compatibilization reactions is predominantly a condensation mechanism of interaction [40]. Besides, a free-radical mechanism with the aid of low-molecular-weight peroxides has been employed in a number of works [41]. The synthesis of interfacial oligomer peroxides – precompatibilizers enable the development of a new approach towards the mixing of polymer blends [43,44]. As the basis for creating precompatibilizers a statistical cooligomer VEP-OMA was used (Fig. 6). Grafting of PP chains to VEP-OMA cooligomer leads to the formation of a precompatibilizer with the structure VogPP (sheme 2).

In this case compatibilization includes the localization of the precompatibilizer at the interface of polymer blends, generation of free radicals and *in situ* formation of the end compatibilizer molecules. It is noteworthy that as a result of grafting the macromolecule fragments of the polymer being blended to the precompatibilizer molecule a highly effective end compatibilizer is created which is ideally formed just for the given system (Fig. 6).

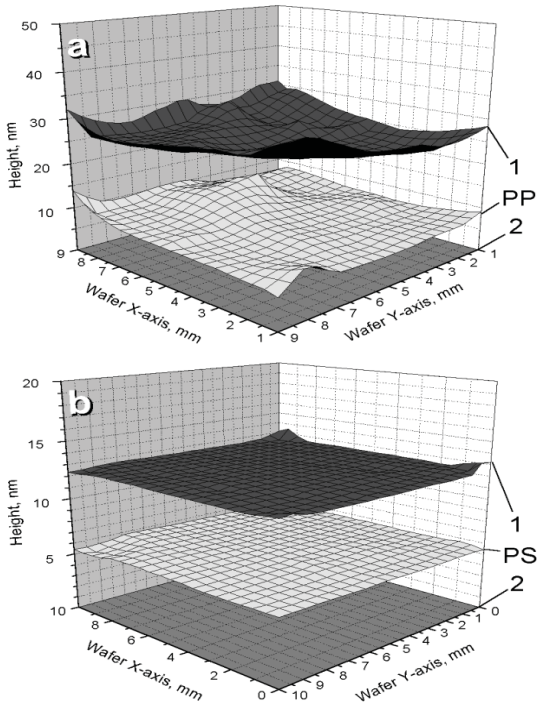
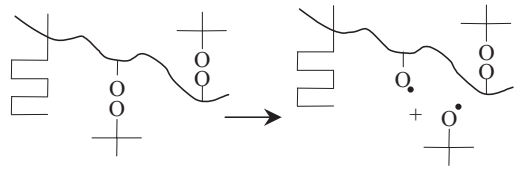


Fig. 7. Ellipsometric mapping of VEP-OMA layer grafted to PP (a) and PS (b) layers

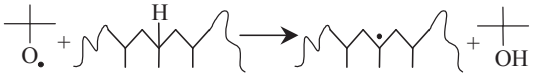
The following prerequisites must be fulfilled during such compatibilization scheme, namely: they should be maximally localized at the interface; peroxide group reactivity must be sufficient enough to graft the macromolecules of the blend components at the conditions of localization at the interface. Fig. 7 shows the ellipsometric mapping of VEP-OMA layer grafted to PP and PS layers, which were in turn grafted to silicon wafer modified by 3-glycydyloxypropyltrimethoxysilane. Non-grafted oligoperoxide molecules were removed from the surface on completing the process.

The presented views confirm the capability of oligoperoxide molecules to be effectively grafted to relatively low-reactive polymer surfaces. By PP example, the principal scheme of grafting could be described by a combination of the following elementary reactions:

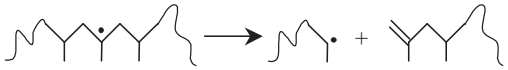
a) VEP-OMA peroxide bond decomposition:



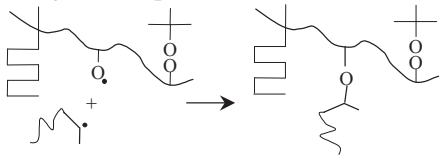
b) Proton abstraction from PP macromolecule:



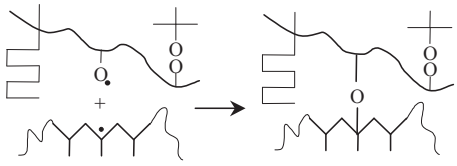
b') β-decomposition:



c) Recombination with PP macroradicals, which underwent β-decomposition:



c') or with those, which did not decompose:



The process described was used for obtaining a precompatibilizer, VEP-OMA-g-PP. For this purpose, side chains of PP were grafted to VEP-OMA utilizing the decomposition of half of the initial peroxide bonds [44]. The resulting precompatibilizer exhibit an interfacial activity similar to surfactant molecules for water systems, in which one part of the molecule is hydrophilic, while the other part – hydrophobic. In this case PP chains are completely compatible with PP phase, while the anchor VEP-OMA chain is not. SEM microphotographs of sample cryofractures of PP/PS polymer blends (30/70) with varying precompatibilizer content are shown in Fig. 8, whereby, a – without any precompatibilizer; b – 0.3 % (wt) and c – 0.9 % (wt).

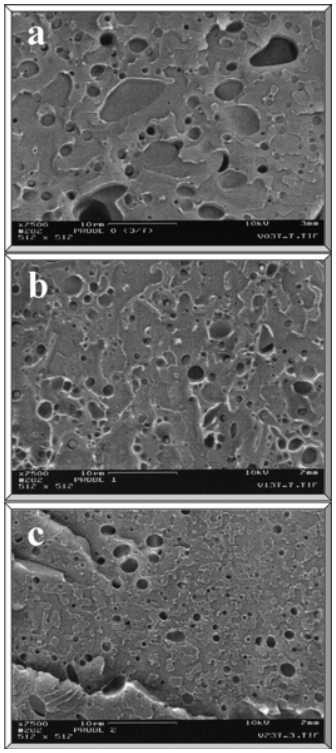


Fig. 8. SEM micrographs of cryofractures

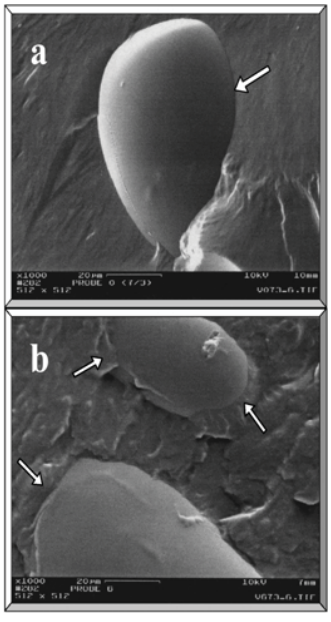
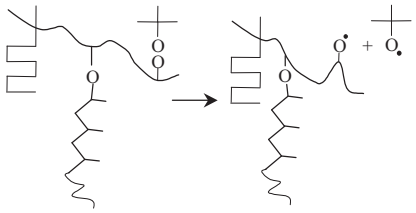


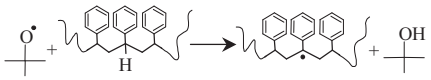
Fig. 9. SEM micrographs of cryofractures

The decrease of the dispersed phase (PP) particle size and the formation of particles with the right shape with increasing precompatibilizer content prove that compatibilization of the system occurs. It is evident that the compatibilization of the system upon blending takes place via the immigration of the VEP-OMA-g-PP anchor chain to the particle surface with the localization of peroxide groups at the interface. PP side chain thus remains in the bulk of dispersed phase. This leads to the initiation of radical processes at the PP/PS interface in accordance with the following scheme:

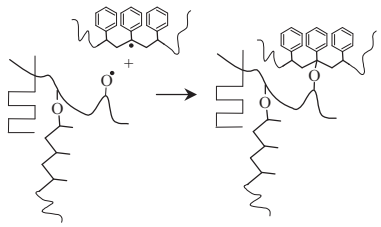
a) Peroxide bond decomposition of VEP-OMA:



b) Hydrogen atom abstraction from polystyrene macromolecule:



c) Recombination with polystyrene macroradical and formation of macromolecule of the end compatibilizer:



A highly effective end compatibilizer is thus formed, whose end chain has the same chemical nature, from one side of the component – polypropylene, while from the other side the other polymer blend component – polystyrene. SEM micrographs of the polypropylene/polystyrene (70/30) blend sample cryofractures are given on Fig. 9, where (a) – without any compatibilizer and (b) – in the presence of 1.5% (wt) compatibilizer. Arrows indicate the characteristic zones with and without the compatibilizer, confirming in the latter case the occurrence of compatibilization. Thus, with the aid of peroxide-containing precompatibilizer of radical processes at the interfacial boundary the localization leads to the formation of grafted polymer molecules with fragments compatible with both phases, i.e. the compatibilization of polymer blends. The values obtained point out that the use of interfacial-active peroxide cooligomers for reactive blending of immiscible polymers is a universal technique for the compatibilization of polymer blends.

3.5. Polypropylene/unsaturated polyester resin polymer blend preparation

The creation of thermoplastic/thermoset polymer blends is of great interest [5,6,7,8,9,10]. In order to check the possibility of the compatibilization of thermoplastic/thermoset polymer blends, the blend of polypropylene with the unsaturated polyester resin (UPR) has been studied. The task was solved in two stages. At the first stage, the dispersion of polyolefin in prepolymer, which was a non-cured solution of UPR in styrene (UPR-Styrene), was obtained. In the second stage the UPR-styrene was cured resulting in a homogeneous UPR/styrene matrix resin with a dispersed PP phase.

Table 4

Initial formulas and properties of obtained PP/UPR-Styrene compositions compatibilized with VOgPP

#	Component content in compositions, %wt				Composition properties	
	PP	UPR	Styrene	VOgPP	Stability, days	Charpy unnotched impact strength, kJ/m^2
1	0	60.0	40.0	0	–[a]	5.8±0.7
2	3.0	58.2	38.8	0	1	2.9±0.3
3	20.0	48.0	32.0	0	–[b]	–[c]
4	4.8	57.0	38.0	0.2	52	6.3±0.8
5	9.6	54.0	36.0	0.4	35	6.6±0.7
6	3.9	57.1	38.0	1.0	>180	8.3±0.8
7	6.2	55.3	36.8	1.6	>180	7.3±0.8
8	3.0	57.0	38.0	2.0	>180	5.2±0.6
9	9.4	52.9	35.3	2.4	>180	7.5±0.6

[a] composition does not contain a polyolefin dispersed phase (homogeneous);
[b] stratification occurs at the discharge from a mixing chamber; at lower PP content stratification onset time increases steadily to about 1 day.
[c] cured samples could not be prepared because of the composition stratification.

At the first stage conclusion about the compatibilizing efficiency of the precompatibilizer can be made by evaluating the stability of the polyolefin dispersion in the UPR/styrene solution. One can see from the data in Table 4 that dispersions obtained without any precompatibilizer

are unstable: at high polypropylene content, stratification begins at once after the discharge from a mixing chamber, and at a polypropylene content near to 3 wt% stratification begins approximately after 24 hours. The incorporation of a small quantity of VOgPP to the blend during polypropylene dispersing in the UPR melt increases the dispersion stability drastically: at 0.2ч0.4 wt% VOgPP content, the stability increases in dependence on the dispersed phase content to 35ч52 days. During the observation period of 6 months at addition of 1 to 4 wt% of the precompatibilizer stratification did not take place at all.

After composition curing, the compatibilization effect has been revealed by the dependence of the sample mechanical properties on the precompatibilizer content. If no precompatibilizer is present already small amounts of added PP drastically reduce the impact strength. However, the addition of 0.2÷2.4 wt%. VOgPP leads to an increase in impact strength up to 45 % (this increase was dependent also upon a weight part of PP phase).

The analysis of Table 4 data shows that a maximum increase has been achieved if 5 to 10 wt% of pure VOgPP related to the dispersed phase quantity are utilized (Fig.10, these data account for the purity of VOgPP (~35 %wt) with the rest quantity of PP from additive combined with the quantity of PP phase). A further increase in the precompatibilizer quantity leads to a decrease in impact strength of samples.

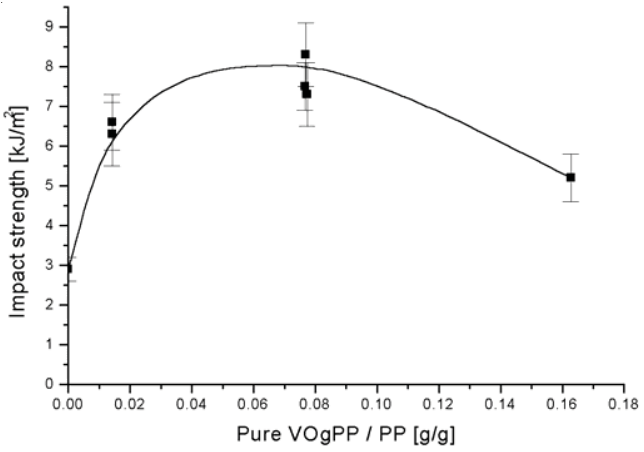


Fig. 10. Dependence of impact strength of cured blends PP/UPR-Styrene upon a weight ratio VOgPP/PP accounting the purity of VOgPP (~35 %wt)

Thus, the approach proposed allows the compatibilization of polymer blends both of thermoplastic/thermoplastic and thermoplastic/thermoset types with the same peroxide precompatibilizer.

4. Conclusions

The method of polyolefin surface activation via covalent grafting of polyperoxide nanolayer by a free radical mechanism has been presented. The features of such nanolayer formation under the thermoprocessing conditions, i.e.: the formation of 3D crosslinked network in a polyperoxide bulk; and its grafting with complete coating of the polyolefin surface, - is considered. The method provides an availability of uniformly placed peroxide groups of one type over the olefin 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.

The utilization of interface active high molecular peroxides is a universal and effective approach to the compatibilization of immiscible polymer blends, of the thermoplastic/thermoplastic as well as of the thermoplastic/thermoset blend type. The radical processes localized to the interface lead to the formation of compatibilizer molecules with thefragments of both polymers to be compatibilized. The resulting partial compatibility to both blend phases causes the high efficiency of the *in situ* formed compatibilizer. Since the majority of carbon-chain polymers is able to participate in free radical processes additional treatments of virgin materials are not necessary. The method described allows to create flexible schemes of the universal compatibilization of different polymer blend systems.

References

[1] Hoffman A.: Macromolecular Symposia, 1996, **101,** 443.
[2] Uyama Y., Kato K. and Ikada Y.: Advances in Polymer Science, 1998, **137,** 1.
[3] Kato K., Uchida E., Uyama Y. and Ikada Y.: Prog. Polym. Sci., 2003, **28,** 209.
[4] Nosova N., Roiter Yu., Samaryk V., Varvarenko S., Stetsyshyn Yu., Minko S., Stamm M. and Voronov S.: Macromolecular Symposia, 2004, **210,** 339.
[5] Pol D. and Nyumen S. (eds.): Polymer blend (in 2 vol.). Moskwa, Mir, 1981.
[6] Menson J. and Sperling L.: Polymer blends and composites (translated by Godovskiy Y.), Moskwa, Chimya, 1979.
[7] Wool R.P.: Polymer Interphaces. Structure and Strength. Munich-Vienna-New York: Hanser Publishers, 1995.
[8] Plochocki A.P. and Dagli S.S., Andrews R.D.: Polym. Eng. Sci., 1990, **30** (12), 741.
[9] Askadskiy A.A.: Uspekhi chimii, 1999, **64 (**4), 349.
[10] Kim J.-K., Kim S. and Park C.-E.: Polymer, 1997, **38** (9), 2155.

[11] Xanthos M.: Recent Adv., Polym. Eng. Sci., 1988, **28** (21). - P. 1392-1400.
[12] Boutevin B., Pietrasanta Y. and Robin J.-J.: Macromol. Chem., Macromol. Symp., 1992, **57**,371.
[13] Piirma I.: Polymeric Surfactants. NY-Basel-Hong Kong: Marcel Dekker, Inc., 1992.
[14] Voronov S., Tokarev V. and Petrovska G.: Ukraine Ministry of Education, State University "Lvivska Polytechnica". Lviv: State University "Lvivska Polytechnica", 1994.
[15] Voronov S., Tokarev V., Oduola K. and Lastukhin Yu.: J. Appl. Polym. Sci., 2000, **76** (8), 1217.
[16] Voronov S., Tokarev V., Datsyuk V., Seredyuk V., Bednarska O., Oduola K., Adler H., Puschke C., Pich A. and Wagenknecht U.: J. Appl. Polym. Sci., 2000, **76** (8), 1228.
[17] Minko S., Gafiychuk G., Sidorenko A. and Voronov S.: Macromolecules, 1999, **32** (14), 4525.
[18] Minko S., Sidorenko A., Stamm M., Gafiychuk G., Senkovsky V. and Voronov S.: Macromolecules, 1999, **32** (14), 4532.
[19] Sidorenko A., Minko S., Gafiychuk G. and Voronov S.: Macromolecules, 1999, **32** (14), 4539.
[20] Voronov S., Tokarev V., Datsyuk V. and Kozar M.: Progr. Colloid Polym. Sci., 1996, **101**, 189.
[21] Datsyuk V.V., Tokarev V.S., Voronov S.A., Trosenko S.E. and Pich A.Z.: Dopovidi NAN Ukrainy, 1998, **6,** 145.
[22] Voronov S.A., Tokarev V.S., Datsyuk V.V., Adler H.J., Puschke G. and Pich A.: Dopovidi NAN Ukrainy, 1999, **2,** 145.
[23] Varvearenko S.M., Roiter Y.V. and Nosova N.G.: Vysnik NU "Lvivska polytechnica", Chimiya, technologija ta ix zactosuvannja, 1999, **361**, 69.
[24] Nosova N.G.: Synthesis and investigation of copolymers of 2-tert-butylperoxy-2-methyl-5-hexen-3-yne with higher esters of (meth)acrylic series. PhD Dissertation, Lviv, 2002.
[25] Samaryk V.Y., Roiter Yu.V., Nosova N.G., Stetsyshyn Yu.B., Varvarenko S.M. and Voronov S.: Dopovidi NAN Ukrainy, 2004, **4**, 136.
[26] Voronov S., Tokarev V., Samaryk V., Stetsyshyn Yu., Roiter Yu., Varvarenko S. and Nosova N.: Technomer 2003, 2003, **F.18,** MT2(1)-MT2(11).
[27] Voronov S.A., Samaryk V.Ya., Varverenko S.M., Nosova N.G. and Roiter Yu.V.: Ukrainian Patent 46481A, MPC C 08 J 007/12. Means of polymer surface modification, 15.05.2002.
[28] Plate N.A. and Shibaev V.P.: Vysokomol. Soedinenja, 1971, **13(A)**, 410.
[29] Plate N.A., Shibaev V.P. and Tal'roze V.P.: Vysokomol. Soedinenja, 1977, **18(B),** 110.
[30] Plate N.A., Shibaev V.P. and Tal'roze V.P.: [in:] Uspekhi chimii I physiki polimerov, Slonimskiy (ed.). Moscow, Chimiya, 1973, 127.
[31] Lipatov Yu.S., Nesterov A.E., Gritsenko T.M. and Veselovskiy R.A. (eds.): Encyclopedia of polymer chemistry. Kyiv, Naukova dumka, 1971.
[32] Leger L. Raphael E. and Hervet H.: Adv. Polym. Sci., 1999, **138**, 185.
[33] Baier R.: Am. N. Y. Acad. Sci., 1977, **17**, 283.
[34] Loh I.-H., Sheu M.-S. and Fischer A. B.: [in:] Desk Reference of Functional Polymers: Syntheses and Applications. Arshady R. (ed.), Washington, American Chemical Society Books, 1997, 657.
[35] Schukin E.D., Pertsov A. V. and Amelina E. A.: Colloidal chemistry. Moscow University, 1982, 348.
[36] Kidoaki S., Nakayama Y. and Matsuda T.: Langmuir, 2001, **17,** 1080.
[37] Kato K., Sano S. and Ikada Y.: Colloids Surf. Biointerf., 1995, **4,** 221.
[38] Larm O., Larsson R. and Olsson R.: [in:] Heparin. Chemical and Biological Properties. Clinical Applications. Lane D. and Lindahl U. (eds.). London, Edward Arnold., 1989, 597.
[39] Tiller J. C., Liao C.-J., Lewis K. and Klibanov A. M.: PNAS, 2001, **98** (11), 5981.
[40] Orr C.A., Cernohous J.J., Guegan P., Hirao A., Jeon H.K. and Macosko C.W.: Polymer, 2001, **42**, 8171.
[41] Vivier T.and Xanthos M.: J. Appl. Pol. Sci., 1994, **54,** 569.
[42] Hu G.-H., Flat J.-J.and Lambla M.: [in:] Blackie Academic and Professional, Al-Malaika S. (ed.)., London, Charpman and Hall, 1997, Chap.1.
[43] Voronov S.A., Samaryk V.Y., Varvarenko S.M., Nosova N.G. and Royter Y.V.: Dopovidi NAN Ukrainy, 2001, **5,** 132.
[44] Roiter Yu., Samaryk V., Varvarenko S., Nosova N., Tarnavchyk I., Pionteck J., Pųtschke P. and Voronov S.: Macromolecular Symposia, 2004, **210**, 209.

ГЕТЕРОФУНКЦІОНАЛЬНІ ОЛІГОПЕРОКСИДИ НА МІЖФАЗІ

Анотація. *Показано, що закріплення макромолекул гетерофункціональних олігопероксидів на планарних полімерних поверхнях, або на поверхні дисперсної фази приводить до локалізації пероксидних груп на міжфазній границі. Здійснено конструювання міжфазних шарів визначеної структури і природи з застосуванням пероксидованих міжфазних поверхонь та реакцій прищеплення «до» та «від поверхні». Сформовані компатибілізуючі полімерні шари в полімерних сумішах та прищеплені поверхневі шари із спеціальними властивостями.*

Ключові слова: *міжфаза, міжфазні шари, модифікація поверхні, олігопероксид, прищеплена полімеризація.*