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Prediction of Interfacial Interactions between Polymer Layers

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Summary: Results of a study on polymer surface modification using heterofunctional polyperoxides are presented. A prognostic model of the polymer surface modifier efficiency was developed on the basis of obtained data. It was shown that implementation of demands to the macromolecule composition during development of new peroxide-containing modifiers in combination with sufficient peroxide group reactivity increased efficiency of the polymer surface modification.

Keywords: nanolayers; polymer surface; polyperoxides; surface modification

Introduction

Achieving surface activation is a common problem for the various approaches to modification of polymeric materials surfaces. In the case of polyolefin surfaces, activation takes place via formation of reactive centers of a radical nature – free radicals or peroxide/hydroperoxide groups. The research data concerning the activation of polyolefine surfaces due to the grafting of functional polyperoxides are represented in [1-4]. The macromolecular structure of polyperoxide modifiers is presented in Scheme 1. Such modifiers include peroxide groups with different macromolecular structures resulting in different thermal stability and reactivity.

Covalent grafting of polyperoxide macromolecules to a polyolefin surface takes place due to the radical processes initiated by thermolysis of the peroxide groups. Interphase covalent bonds are formed due to the reaction of chain transfer to the polymeric surface macromolecules, followed by recombination between surface macroradicals and functional peroxide macromolecules. A more detailed description of the mechanism that results in the grafting of polyperoxides onto polymer surfaces is given in [2]. Using a series of chemical and physico-chemical methods, it has been shown [3,4] that polyperoxide layer grafting to a surface is accompanied by modifier macromolecules interaction resulting in simultaneous polyperoxide layer crosslinking. The grafted polyperoxide layer will contain peroxide groups if the conversion of the peroxide groups is incomplete. These groups can be used for further surface modification by functional polymers using the methods known as "grafting from" and "grafting to." As polyolefin surfaces have low reactivity, main efforts were directed to its activation. But a number of problems occurred during extending obtained experience towards other polymer surfaces and other types of peroxide groups. Thus it becomes necessary to consider a concept of polyperoxide layer physical interaction with the polymer surface and its compatibility. The aim of this work is design of simplified prognostic model for structure prediction of functional polyperoxide macromolecule able to form reactive layer against polymer surface nature.

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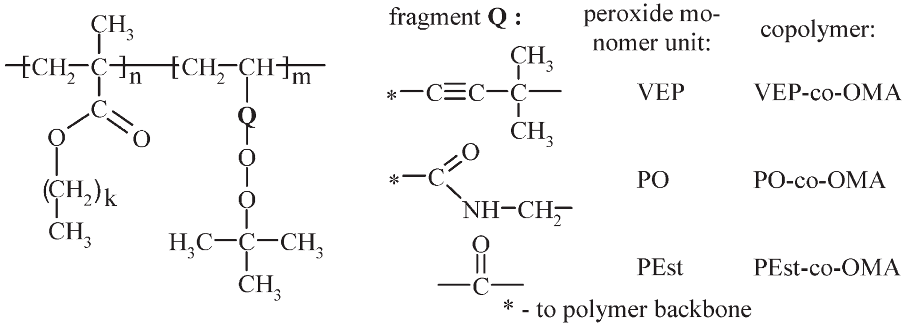

Scheme 1.
Macromolecular structure of functional polyperoxides.

Experimental Part

Polymer Surfaces

The polyolefine substrates (polypropylene (PP) Hostalen 0180 D, polyethylene (PE) Hostalen GC 7260, polyethylene terephthalate (PET), polyphenyloxide, polymethylmethacrylate, nylon-6,6 and copolymer of polyethylene with polypropylene (TPO) Solvay 880-1) measuring $20 \times 20\,mm^2$ were extracted in a Soxhlet apparatus with their respective solvents for 3 hr to remove impurities and technological additives from the surfaces and then dried to constant weight in a vacuum. After the extraction, mean values of a water contact angle on each purified substrate surface corresponded to the reference data [5].

As polymer surface modifiers, the synthesized [6-8] peroxide-containing copolymers – poly(2-tert-butylperoxy-2-methyl-5-hexene-3-yne-co-octyl methacrylate) (VEP-co-OMA, incorporating 6.5, 13.8 or 19.9 mol % of VEP units); poly{N-[(tert-butylperoxy)-methyl]acrylamide-co-octyl methacrylate} (PO-co-OMA, incorporating 6.3 or 12.1 mol % of PO units) and poly(tert-butylperoxy-methacrylate-co-octyl methacrylate) (PEst-co-OMA, incorporating 7.2 or 20.1 mol % of PEst units) were utilized.

A solution of peroxide-containing copolymer was applied to the polymer plate surface using a spin-coating technique [9] as follows: the plate was fixed in the apparatus and rotated at the speed of 1200–2000 rpm, then 0.1ml of a 4%-solution of peroxide-containing polymer in its respective solvent was applied to its surface with continued rotation for 1 minute. The reference plates were treated with the solvent. The samples were held in a vacuum exsiccator under 20 mm Hg of pressure for 1 hour to remove the solvent. Prepared samples were placed into a temperature-controlled cell with argon atmosphere and heated for the time necessary to achieve a certain conversion of peroxide groups. The treatment temperature for peroxide modifiers with PEst fragments is 70–80 °C, with PO fragments, - 90-110°C, and with VEP fragments, - 100–130°C. After heating, the non-grafted polyperoxide was extracted from the surface using a Soxhlet apparatus. Surface coverage (degree of surface modification) was evaluated by the Cassie equation using contact angle measurements data. Contact angles were measured with the aid of a DataPhysics OCA20 instrument [10,11]. The validity of this method was checked by comparison of experimental results with the results obtained by null-ellipsometry and AFM-microscopy [see supplemental material].

Results and Discussion

The dependencies of polypropylene surface modification (peroxidation) degree by VEP-co-OMA and PO-co-OMA copolymers on peroxide groups conversion is represented in Figure 1. One can see that

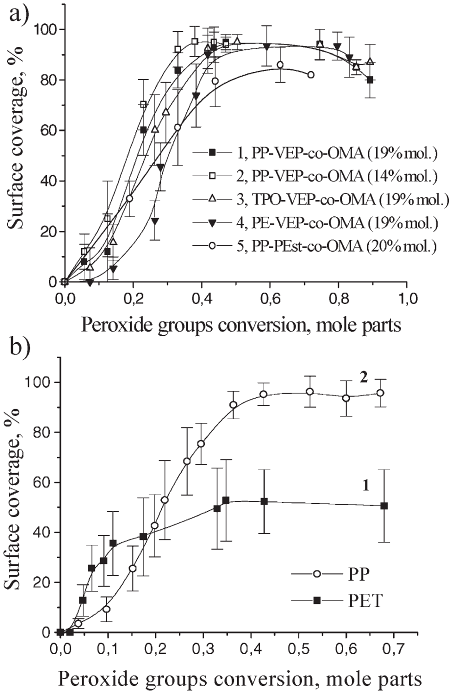

Figure 1.
The dependence of the polymer surface* coverage on peroxide groups conversion: a) modification of surfaces with VEP-co-OMA at 110°C (1-4), PEst-co-OMA at 80°C (5); b) the dependence of the surface coverage on modification with VEP-co-OMA (19.9% mol. VEP units) substrates (PET (1), PP (2), T = 100 °C) on conversion.
* polymer surfaces: PP; TPO; PE.

the high surface coverage (90–95%) is achieved at different temperatures and contents of peroxide groups in the copolymers at conversion values of 20–60%. Practically all carbon-chain polymers are able to take part in chain transfer and recombination reactions. The grafting mechanism does not essentially limit the nature of surface macromolecules. At the same time the effective surface peroxidation by the copolymers VEP-co-OMA or PO-co-OMA is determined by the surface nature. The characteristic curve of the dependence of PET surface coverage on the VEP-co-OMA peroxide group conversion is represented in Figure 1b in comparison with the curve obtained on the PP surface. In the case of the PET surface, coverage does not exceed 40–50%. The same dependence is observed for copolymers VEP-co-OMA and PO-co-OMA and the modification of polyphenyloxide, polymethylmethacrylate and nylon-6,6 surfaces.

The initial segment of curve 1 (Figure 1b) confirms polyperoxide grafting. Simultaneously, a process takes place which decreases the efficiency of surface modification. It has been experimentally established that modifier layer diffusion into the substrate bulk is such a process. We may assert that partial compatibility of modifier and surface macromolecules takes place. The term "partial compatibility" was used by other authors [12] to mean the thermodynamic compatibility of the polymeric blend with a low amount of one of the components.

The polymeric surface-modifier layer system meets the described condition, since the amount of modifier accumulated on the polymeric surface is negligible. Thus, obtained results allow use to form speculations concerning how the structure of the polyperoxide modifier ensures its covalent grafting to the polymeric surface: (i) the structure of the modifier macromolecules must include reactive groups capable of forming macroradicals on the polymeric surface; (ii) the structure of the modifier macromolecules must ensure interfacial interaction at the level of physical forces, which is sufficient to form a thermostable film and guarantee the effective proceeding of chain transfer to the surface macromolecules.

Moreover, under the described conditions, a modifier polymer must be thermodynamically incompatible with a substrate polymer in order to prevent modifier penetration into the substrate bulk.

For the polymeric surface-modifier layer system, the first condition is realized by the introduction of peroxide groups into the copolymer. The reactivity of peroxide groups is substantially determined by their nature and predicted by the thermolysis rate. The presence of tert-butoxyl groups in the structure of peroxide fragments is also important. It is known that tert-butoxyl radicals are effective in the reactions of chain transfer, including transfers to polypropylene and polyethylene molecules [13,14].

For prognostic evaluation of the interfacial interaction between the polymer surface and the modifier macromolecules (according to 2nd condition), the affinity criteria (L_{12}) can be used. Such criteria can be calculated according to a Young equation. Thereto it is necessary to combine the Young equation with a Girifalco-Hud equation, as was shown by Van Krevelen [11]:

$$L_{12} = 2\Phi \cdot \left(\frac{\gamma_1}{\gamma_2}\right)^{1/2} \text{ where } \Phi \cong \frac{4(V_1 \cdot V_2)^{1/3}}{\left(V_1^{1/3} + V_2^{1/3}\right)^2} \qquad (1)$$

and γ_i is the free surface energy; V_i is the macromolecule molar volume. Index 1 relates to the surface, index 2 to the modifier.

The physical matter of the described criteria is determined as the ratio between the reverse work of adhesion (determined by the Dupré ratio) and the modifier free surface energy. Moreover, these criteria are equal to the hypothetical contact angle between the modifier and the polymeric surface cosine value, shifted on 1. Thus we may assert that cohesion interacting forces between macromolecules dominate and interfacial interacting forces are insignificant at the value L_{12} close to 0. This can be seen in the balance between adhesive and cohesive forces at $L_{12} = 1$ and the domination of the adhesive interaction between the modifier and surface macromolecules at $L_{12} > 1$.

For the prognostic scheme, unknown in the literature, γ_i and V_i values can be experimentally obtained, but it is more interesting to obtain these values by calculations. The calculation algorithm according to the additive scheme is represented in [15,16]. The values of L_{12} for the interaction of polyperoxides with polymeric surfaces (Scheme 1) have been calculated using table values γ_1 and V_1 for polymeric surfaces and calculated values γ_2 and V_2 for polyperoxide structures. Calculated characteristic dependencies of L_{12} are represented in Figure 2.

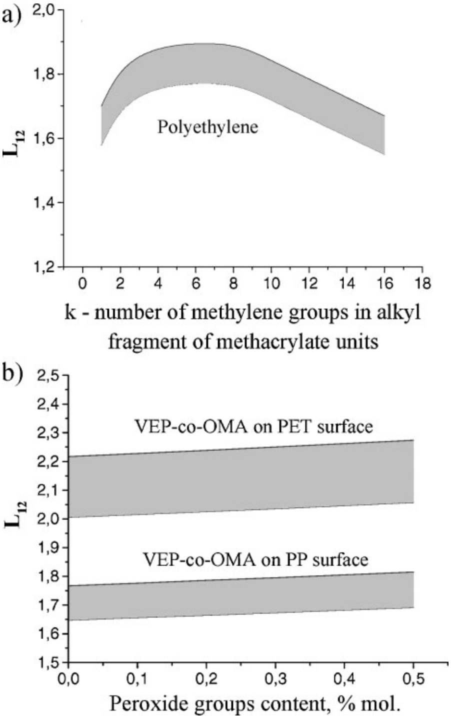

Figure 2.
a) The dependence of affinity criteria to PP surface (L_{12}) on the alkyl fragment length in homopolymers of higher methacrylic esters; b) the dependence of affinity to PP and PET surfaces criteria L_{12} for VEP-co-OMA ($k = 7$) on the remaining peroxide groups content.

The curve in Figure 2a shows the described criteria dependence on the alkyl fragment length (k-number of methylene groups) in methacrylate units and the curve in Figure 2b – the dependence of the L_{12} criteria on the ditertiary peroxide groups content in the copolymer at $k = 7$. Obtained calculations allow us to conclude that almost all investigated structures realize considerable interfacial interaction due to the alkyl radicals. This fact is in agreement with the results described in [15]. The optimal dependence on alkyl radical length also agrees with the optimum for $k = 6$-8. Such agreement allows us to attribute the experimentally obtained dependence of the

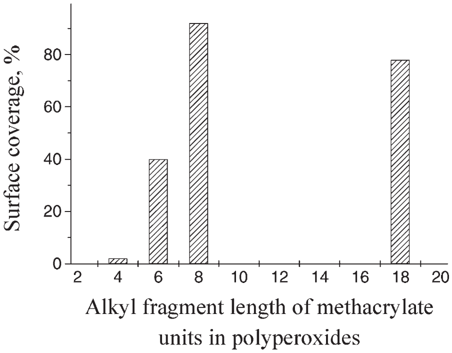

Figure 3.
Experimental dependence of the PP modified surface coverage on the length of alkyl fragments in copolymer of VEP with alkyl-methacrylate.

polyperoxides grafting efficiency to the polymeric surface (Figure 3) and the efficiency of interfacial interacting forces formation, as well as to confirm the importance of these forces during grafted polyperoxide layer formation.

The value of the L_{12} criteria is higher for PET than for PP (Figure 2b). Therefore, the efficiency of surface modification should not be less. But this fact contradicts the data given in Figure 1b. This can be explained by the partial compatibility of the polymers caused by the increase of interfacial forces, and this fact should be taken into consideration. In our case it is convenient to create the prognostic model of partial compatibility using the scheme proposed by Askadskii [16] which was proved for a number of polymeric blends:

$$\mu_1 = \frac{\delta_1^2}{\delta_2^2} < 1.374 \cdot \Phi \cdot \left(\Phi - \sqrt{\Phi^2 - 1 + \frac{\gamma_{12}}{\gamma_2}}\right) \quad (2)$$

$$\mu_2 = \frac{\delta_2^2}{\delta_1^2} < 1.374 \cdot \Phi \cdot \left(\Phi - \sqrt{\Phi^2 - 1 + \frac{\gamma_{12}}{\gamma_1}}\right) \quad (3)$$

where $\gamma_{12} = \gamma_1 + \gamma_2 - 2 \cdot \Phi \cdot (\gamma_1 \cdot \gamma_2)^{1/2}$

Correspondingly, the execution of equation (2) means that an insignificant amount of polymer 1 dissolves in polymer 2. This means that substrate material may dissolve in the modifier layer. Analogously, the execution of equation (3) means that an insignificant amount of polymer 2 may dissolve in polymer 1. This means that macromolecules of the modifier layer may penetrate into the substrate bulk. According to given criteria, thermodynamically complete mixing may be possible during the simultaneous implementation of both conditions.

The calculations of criteria μ_1 and μ_2 for polyperoxides (Scheme 1) are given in Table 1.

The comparison of data from Table 1 and experimental results including those presented in Figure 1 allows us to conclude that the effective grafting of a polyperoxide layer onto the polymeric surface is observed in the case when equation (3) is not true. Equation (2) appears not to have considerable influence on the efficiency of the peroxide-containing modifier grafting.

Table 1.
Solutions of equations (3) and (2) for μ_1 and μ_2 criteria.

Peroxide group nature	Ditertriary (VEP)		Primary-tertriary (PO)		Peresteric (PEst)	
Surface nature	μ_1	μ_2	μ_1	μ_2	μ_1	M_2
Poly(propylene)	+	−	+	−	+	−
Polyethylene	+/−	−	+	−	+	−
Poly(ethylene terephthalate)	+/−	+	+/−	+	+/−	+
Nylon-6.6	−	+	−	+	−	+
Poly(methylmethacrylate)	+/−	+				

For μ_1: "+" - thermodynamically driven penetration of polymer substrate into the modifier coating; "−" - substrate molecules penetration in modifier coating is not possible; "+/−" - depends on the modifier structure.For μ_2: "+" - thermodynamically driven penetration of molecules into the polymer substrate; "−"- modifier molecules penetration in polymer substrate is not possible; "+/−" - depends on the modifier structure.

Thus, such a modifier is effective towards the surface if penetration of its macromolecules or macromolecule segments into the substrate is thermodynamically disadvantageous.

The reverse penetration of substrate macromolecules or their segments into the modifier phase does not decrease the grafting efficiency but probably promotes it. At the same time the above-mentioned dependencies generally relate to copolymers VEP-co-OMA and PO-co-OMA, which have relatively thermostable peroxide groups. Copolymer grafting to the polymeric surface takes place within a temperature range of 90–130 °C over 6–40 hours. We may assert that interpenetration of substrate and modifier macromolecules is thermodynamically controlled. The modification proceeds for 2–3 hours within the temperature range of 70–80°C for PEst-co-OMA modifier with the perester peroxide group nature. One can obtain high surface coverage on PET and nylon 6,6 surfaces using such modifiers in spite of the prediction of low efficiency according to the μ_2 criteria (Figure 4a). It should be noted that the low thermal stability of the perester group allows modifier grafting under conditions where the rate of polymer interpenetration is low and the process is kinetically controlled. This fact is confirmed by the curves presented in Figure 3b. A decrease of surface modification efficiency by the copolymer PEst-co-OMA is observed in the case of polyperoxide layer formation on the polymeric surface from the solution, which increases reciprocal polymer diffusion rate due to increasing interfacial interactions [11] (the same as in the given case).

At the same time, the low thermal resistance of the perester group cannot be considered an unquestionable advantage. The modifiers with perester groups are difficult to obtain, and they are unstable in time, which limits their application. The use of a primary-tertiary peroxide group (PO) in the modifier composition is more effective in order to meet requirements of the modifier structure.

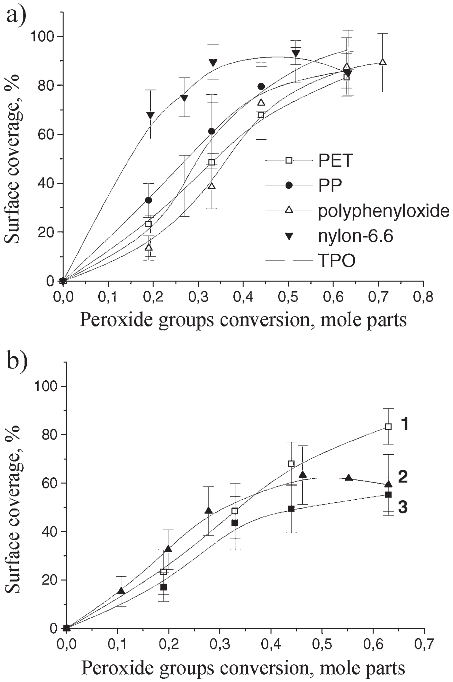

Figure 4.
Grafting of PEst-co-OMA copolymer to the polymer surfaces (peroxide groups content 20%* mol., processing temperature T = 80°C); a) modification of polymer surfaces of different nature; b) modification of PET surface via VEP-co-OMA film formation from hexane (1,2) and benzene (3).
*except curve 2 Figure 4b (peroxide groups content 6% mol.).

Conclusion

For the successful realization of polyperoxide grafting to the polymeric surface from the condensed phase via the radical mechanism, the modifier structure has to provide the possibility of interfacial interactions formation due to physical forces. It is possible to predict the formation of the described forces by prognostic estimations made on the basis of the modifier macromolecule structure and affinity criteria (L_{12}) values. The diffusion of modifier macromolecules into the substrate bulk is possible if the treatment temperature is close to the polymer softening temperature and the time of treatment is sufficiently long (the equilibrium process is controlled thermodynamically). This will essentially decrease the modification efficiency. Thus, it is necessary to develop the modifier structure in such a manner that its molecules would be thermodynamically incompatible with the polymer substrate. The prognostic estimation of thermodynamic compatibility can be made using the scheme proposed by Askadskii. Fulfillment of the conditions concerning the structure of the modifier macromolecules, as well as process optimal conditions, ensures high efficiency of polymeric surface modification.

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