Radical Processes for the Creation of Compatibilizing Layers in Polyolefin Blends

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SUMMARY: The method of polyolefin/polyolefin reactive blending utilizing peroxide-containing interface-active graft-copolymer is considered. The strategy of method and short description of its realization steps have been shown using an example of polypropylene/polyethylene blend. A case of real blend preparation using the method proposed is demonstrated.

Introduction

The problems of blending of thermodynamically immiscible polymers are the subject of nowadays active studies. These polymer blends possess a set of properties that cannot be realized in individual homopolymers and copolymers. The main problem at polymer blend creation is the thermodynamical immiscibility of the majority of blended polymers. Useful properties of polymer blends can be achieved providing the miscibility improvement for individual pairs of polymers only at the expense of their compatibilization [1]. Compatibilization is a process consisting in the localization of additional components at the interphase leading to the decrease in interfacial tension. The most perspective way of compatibilizing system creation is the reactive blending of polymers [1,2]. The general contemporary method used for the *in situ* compatibilizer creation is the utilization of polymer-analogous transformations. This method demands an elaboration of compatibilizing system for every pair of blended polymers and requires frequently the preliminary processing of these polymers. An alternative route is the application of radical processes. This route can be more universal because of ability of the majority of carbon-chain polymers to participate the reactions of chain transfer and recombination. This method realization is described in a number of works [3-5] for the case of utilization of low molecular weight peroxides as radical generators. Disadvantage of low molecular weight peroxide utilization is that they cause the proceeding of radical processes in all the bulk of blended materials, and these processes are mostly harmful. Besides, almost all of these peroxides are volatile at the processing

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temperatures that leads to the necessity of their quantity increase and, from the other hand, to solve the problems of their removing from the blending zone. In order to solve this problem, we propose the method of polymer blend obtaining utilizing peroxide-containing high molecular weight interface-active compounds.

The method proposed for the obtaining of compatibilized polymer blends consists of the following main stages:

- Synthesis of anchor peroxide-containing copolymer.
- Preparation of grafted peroxide-containing copolymer which structure include grafted tails of the first component of polymer blend providing interfacial activity and fragments of peroxide initiator of radical processes. The compound obtained at this stage may be referred as "half-universal compatibilizer" since it allows to obtain different blends of one polymer (which tails are grafted) with other carbon-chain polymer materials.
- Localization of graft-copolymer obtained across the interphases of polymer blend during its preparation and grafting of polymer material of the second component of polymer blend initiated from interphase with *in situ* formation of final compatibilizer.

The realization of similar type reactions utilizing polyperoxides at interphases [6] have allowed already to obtain dispersion-filled polymers possessing enhanced properties [7], reinforced polymers, water emulsions of "core-shell" morphology [8].

Materials and Methods

Peroxide-containing statistical anchor copolymers (VEP-OMA and VEP-HA) have been synthesized via radical copolymerization of 2-*tert*-butylperoxy-2-methyl-5-hexene-3-yne (VEP) with octyl methacrylate (OMA) or hexyl acrylate (HA) at polymerization initiation by 2,2'-azobisisobutyronitrile (AIBN). Polymerization was performed in the medium of cyclohexanone at 70^0C. VEP has been synthesized at Organic Chemistry Department of National University "Lvivska Polytechnica" [9] with purity of 98%. OMA was obtained via transesterification of methacrylic acid with *n*-octyl alcohol using a well-known technique [10] with purity of 99.3%. All the monomers (including HA, Aldrich 408905) were washed with 5% Na_2CO_3 solution and distilled in order to remove the inhibitors before polymerization. AIBN (Aldrich 441090) 98% was utilized as received.

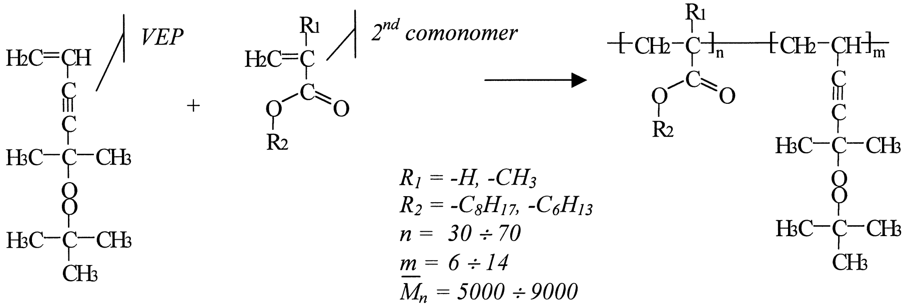
Specimens for AFM-study performance were prepared as follows. Solution of anchor copolymer (VEP-OMA, $\overline{M}_n$ 6500) in acetone ($1 \cdot 10^{-3}$ g/l) was applied to polypropylene plaques (Montell Profax) and dried. One-half of specimens was heated in oven at 70^0C for 24 hours, the rest of plaques (control specimens) were left at room temperature. Then, all the specimens were placed into the Soxhlet apparatus and extracted by acetone during 24 hours. Dried specimens were tested using an Atomic Scale Tribometer ST, (Center Suisse d'Electronique et Microtechnique, Neuchatel, Switzerland) under the ambient conditions without additional treatment in Pulse Force Mode.

Polypropylene (PP) (amorphous PP, $\overline{M}_n$=5400, $\overline{M}_w$=19600, Aldrich 428183) grafting to VEP-OMA was performed as follows: VEP-OMA $\overline{M}_n$ 6500 in concentration of 12 to 28 %wt. was preliminary fused with PP at 150^0C during 2 min. Then, the grafting reaction was conducted in the temperature range from 165 to 195^0C during 1.5 to 15 min. Specimens were washed from ungrafted VEP-OMA by acetone in the Soxhlet apparatus during 36 hours. Content of grafted VEP-OMA in specimens was analyzed by IR-spectroscopy using a Specord M80 spectrophotometer checking the band of carbonyl group at 1732 cm^{-1}. Before utilization, virgin PP was purified from the fraction (ca. 6.5 %wt.) soluble in acetone by extraction in the Soxhlet apparatus during 36 hours.

Polymer blends polypropylene/polyethylene (PP/PE=10/90) with addition of 0 to 1 %wt. of polypropylene grafted VEP-OMA have been prepared using a DACA twin-screw microcompounder (DACA-Instruments, USA). All the materials were charged to microcompounder and preliminary blended at 155^0C for 2 min. Then, temperature was raised during 1.5 min to 190^0C and the reaction blending was performed at screw rotation rate of 100 rpm. Torque (N·m) and load on nozzle (N) were checked during blending. After 8 min blending, blends were extruded to water. Obtained samples were rinsed to liquid nitrogen and broken with cooled pliers. Scanning electronic microscope LEO VP415 (Zeiss) was used for micrographs obtaining.

Results and Discussion

The first step of the creation of compatibilizing system for the blends of immiscible polymers is a synthesis of anchor peroxide-containing copolymer that is shown schematically below:



R_1 = -H, $-CH_3$
R_2 = $-C_8H_{17}$, $-C_6H_{13}$
$n = 30 \div 70$
$m = 6 \div 14$
$\overline{M}_n = 5000 \div 9000$

Quantity of peroxide links in copolymer is dependent upon the conditions of synthesis conduction and listed in Table 1 together with general characteristics of copolymers obtained.

Table 1. Synthesis conditions and obtained anchor copolymer characteristics.

No	R_1	R_2	Monomer mixture, mole/l		Anchor copolymer characteristics		
					Peroxide link content, mole part	Copolymer obtained at 40% 2nd monomer conversion	
			VEP	2nd monomer		Intrinsic viscosity (acetone), dl/g	$\overline{M}_n$
1[a)]	$-CH_3$	$-C_8H_{17}$	0.16	2.00	0.13	0.054±0.005	6800±300
2[a)]			0.32	2.00	0.24	0.052±0.006	6500±400
3[b)]			0.16	2.00	0.15	0.047±0.008	5400±500
4[a)]	-H	$-C_6H_{13}$	0.30	2.00	0.27	–	–
5[a)]			0.23	2.00	0.21	–	–
6[a)]			0.16	2.00	0.13	–	–

[a)] *- AIBN concentration 0.142 mole/l.*
[b)] *- AIBN concentration 0.070 mole/l.*

Thermal stability of peroxide groups in aliphatic medium was studied for the obtained class of peroxide-containing copolymers with the purpose of their predictable utilization in compatibilization reactions. In particular, semilogarithmic anamorphoses of kinetic curves of VEP-OMA peroxide group thermolysis in heptane are shown for the cases different temperatures in Fig. 1. Good enough linearization of kinetic curves in semilogarithmic co-ordinates allows to estimate the quantity of decomposed peroxide groups using the first order kinetic equation ($C = C_0 \cdot \exp(-k_d/T)$), and to calculate the values of constants using a standard procedure for the first kinetic order reactions. Linearization of the constants obtained in

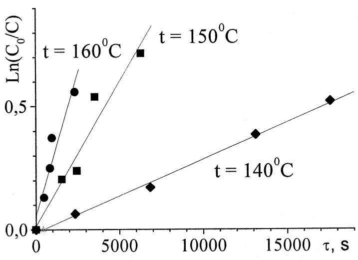


Fig. 1. Copolymer peroxide group decomposition.

ln k → 1/T co-ordinates allowed to describe the dependence of constants upon temperature using the Arrenius equation:

$$k = A_0 e^{-\frac{E_A}{RT}}$$

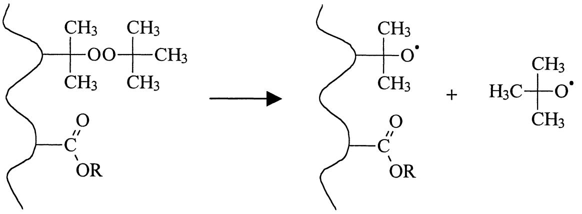
$$A_0 = (6.9\pm0.3)\cdot10^{14}\ s^{-1}$$

$$E_A = 153\pm7\ kJ/mol$$

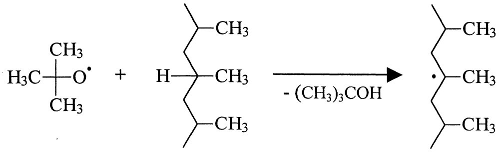
It is noteworthy that thermolysis activation energy E_A coincides well with corresponding value obtained for the case of monomer VEP [11]. Then, one can conclude that VEP copolymerization with the higher esters of acrylic type does not effect on the thermal stability of VEP peroxide group. The activation parameters obtained were applied for the prediction of peroxide group decomposition at the temperatures of radical grafting of PP side chains to anchor copolymer.

PP fusing with statistical copolymers of VEP and higher esters of acrylic and methacrylic acids (octyl methacrylate and hexyl acrylate, $\overline{M}_n$ from 5000 to 9000 c.u.) at wide enough studied range of temperatures (140÷220^{0}C) and concentration (1÷30 %wt. of copolymer) does not lead to phase splitting and the blends obtained cooling to the room temperature results in the formation of transparent films. These properties are utilized for polypropylene modification with copolymers obtained. Peroxide group presence in copolymer molecule allows to perform the reaction of intermolecular grafting between copolymer and polypropylene macromolecules as follows:

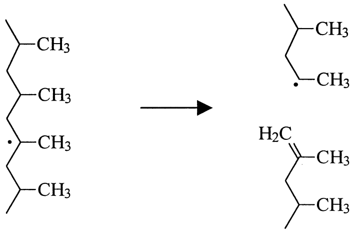
- thermal decomposition of peroxide group in copolymer:



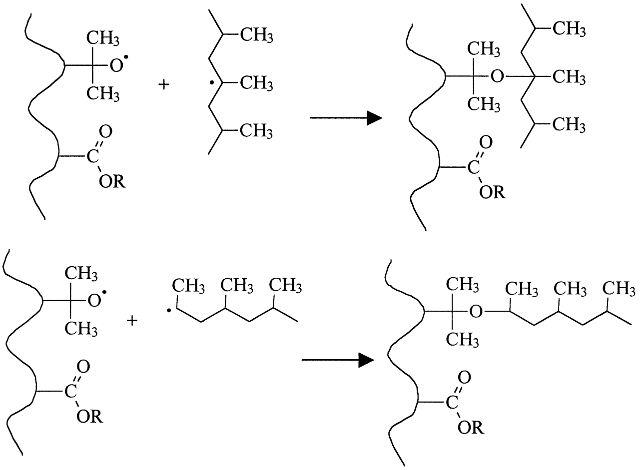
- proton deposition from PP macromolecule:



- polypropylene macroradical β-decomposition:



- and two main types of VEP-OMA and PP macroradical recombination:



This scheme is also valid for the case when peroxide-containing copolymer is applied to the surface of polypropylene (not blended) as thin layer. The results of AFM study of the specimens prepared confirm this interaction. The AFM-images shown in Fig. 3 illustrate these results for the case of characteristical specimens.

For example, specimen that was heated at 70^0C (see *Materials and Methods*) after the anchor peroxide-containing copolymer application to PP surface is shown as images 2 in Fig. 2. AFM testing shows that after heating, the island-like spots possessing much higher adhesion than PP appeared at PP surface (some of them are highlighted in the images). AFM-image of control specimen (that was not heated) is given in Fig. 2 (images 1) for comparison. Island-like spots are not observed at its surface. Thus, it can be asserted that island-like spots at PP surface are the zones were radical grafting of peroxide-containing copolymer to PP took place.

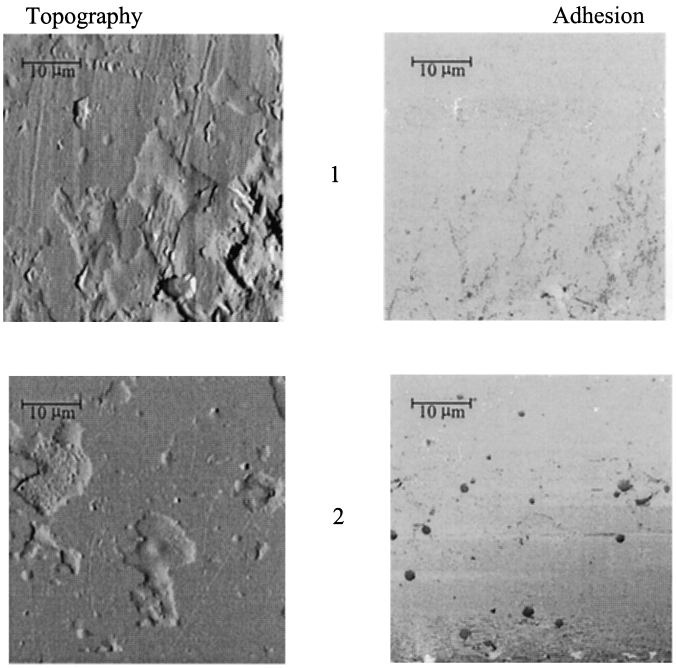
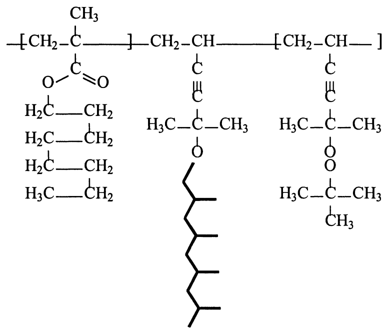


Fig. 2: AFM images obtained using a Pulse-Force Mode. 1st Images: control surface of PP substrate. 2nd Images: PP substrate surface with grafted (at 70^{0}C) anchor copolymer.

We have utilized the ability of peroxide-containing copolymers to radical grafting of polyolefin macromolecules for the creation of compatibilizing system for the blends of thermodynamically immiscible polymers and, in particular for polypropylene-polyethylene blends, which are known as immiscible [12].

Compatibilizing system for polyolefin blends is designed on the basis of grafted peroxide-containing copolymer of the following general structure:



The polymer material necessary for compatibilizer design has been prepared via radical grafting of polypropylene chains to anchor peroxide-containing copolymer under the condition of partial (in the considered case - 50%) thermolysis of peroxide groups. Grafting chemism was published earlier [13]. Studies have been performed in accordance to procedure described in *Materials and Methods*. In the present paper, we discuss the results obtained for the grafting time equal to decomposition time of half quantity of peroxide groups. Quantity of grafted copolymer under this condition was of 40 to 80% and it was dependent upon anchor copolymer initial concentration and grafting temperature. The dependence of VEP-OMA grafted upon its initial concentration for the number of temperatures is given in Fig. 3 and Table 2. Fig. 3 represents also the grafting time that is defined by the time of half-decomposition at certain temperature. The content of remained peroxide groups is also listed in Table 2.

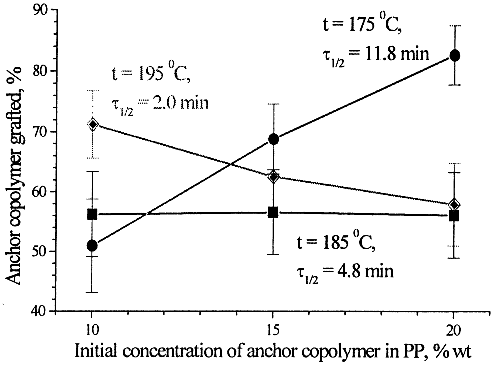


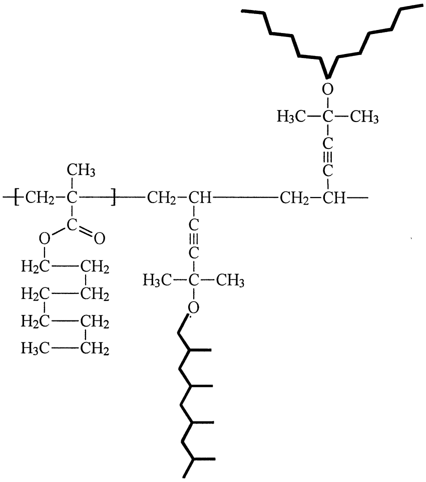
Fig. 3. Anchor copolymer - PP grafting efficiency at decomposition of 50% peroxide groups.

Table 2. Anchor copolymer-PP grafting and peroxide group content in PP/PP-g-anchor copolymer blend prepared

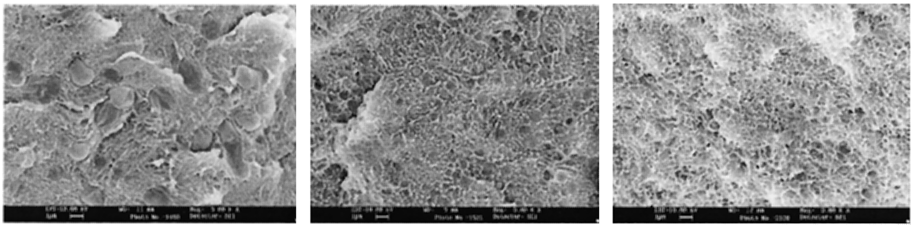
Specimen No	*Initial anchor copolymer content in blend with PP, % wt.*	*Temperature,* ^0C	*Grafting time, min*	*Grafting efficiency, %*	*Remaining peroxide link content, g-ekv/g of specimen* $\times 10^6$
1	10	175	11.8	51.0	0.99
2	10	185	4.8	56.2	1.09
3	10	195	2.0	71.2	1.35
4	15	175	11.8	68.8	2.00
5	15	185	4.8	56.6	1.68
6	15	195	2.0	62.5	1.83
7	20	175	11.8	82.6	**3.16**
8	20	185	4.8	56.1	2.27
9	20	195	2.0	57.9	2.33

These data analysis shows that the character of grafting efficiency curves is determined by grafting temperature: at high temperatures, concentration increase leads to the drop in grafting efficiency; at the lowest temperatures from the studied range, curve character is changed oppositely. Such dependence can be explained by increase of by-destruction processes at higher temperatures. Concluding the data analyzed we can say that if the grafting process will be conducted at temperature of 170÷175^{0}C, VEP-OMA initial concentration in blend of 20% during 10÷12 min, then, after the extraction of ungrafted VEP-OMA with acetone, the blend of PP-g-VEP-OMA (30÷40 %wt.) in polypropylene will be obtained.

In accordance with the method proposed, this blend can be utilized for the reactive compatibilization of polymer blends of polypropylene with thermodynamically immiscible polymers, in particular, with polyethylene. From our point of view, grafted peroxide-containing polymer is localized with its anchor fragment at blend interphase at the expense of its interface-active properties. The latter and utilization of high temperature at reaction blending allows to conduct radical grafting of the second component of blend to anchor fragment with the formation of the macromolecule with following general structure:



Such amphipathic polymer macromolecules play a role of compatibilizers in polymer blends polypropylene/polyethylene (10/90) we prepared with different initial content of polypropylene grafted peroxide-containing copolymer. One can see the changes in blend morphology in the dependence upon a concentration of grafted peroxide-containing copolymer in Fig. 4. Besides, we have observed the drop in torque values from 3.4 to 2.7 N·m with increase of grafted copolymer concentration in blend from 0 to 1 %wt.



0 %wt. of grafted copolymer 0.2 %wt. of grafted copolymer 1 %wt. of grafted copolymer

Fig. 4. Cryo cuts SEM micrographs (×5000, scale bar in micrographs corresponds to 1 μm) of the PP/PE (10/90) blends prepared with utilization of different quantities of graft-copolymer.

The morphology refinement and observed torque drop point on the possibility of polymer blend compatibilization using the compatibilizers obtained and allow us to continue the works directed on optimization of the elaborated compatibilizing systems for blends of thermodynamically immiscible polymers.

Conclusions

In comparison with existing techniques of reactive and non-reactive compatibilization of polymer blends, the method proposed possesses the following advantages.

- Reactive groups of the proposed graft polyperoxides localize and initiate radical processes mainly across the interphase; in the case of nowadays known functionalized polymers and low molecular weight volatile at processing temperatures peroxides the major part of reactive material is localized in the bulk of phases.
- Compatibilizing fragments of grafted polymer (tail) are linked to anchor fragment via one end only that facilitates significantly its conformational transformations and interaction with macromolecules of the main blend components.
- Peroxide-containing graft copolymer prepared is universal for the number of polymer blends simultaneously because the majority of carbon-chain polymers are able of participation in radical chain transfer and recombination reactions. Concerning the case studied: peroxide-containing polypropylene grafted copolymer can be utilized for the blending of polypropylene with the number of other carbon-chain polymers, that is proved to be true by our recent studies of polypropylene/polystyrene blend compatibilization, which results we prepare at present for publication.

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