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Peroxide-Containing Compatibilizer for Polypropylene Blends with Other Polymers

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Summary: An approach to synthesize interfacial active peroxide graft copolymers, so called precompatibilizers, which are suitable for the universal compatibilization of one special polymer with a number of other polymers, has been presented. As example, this approach is illustrated by the reactive fusion of a random peroxide copolymer (VO) with polypropylene (PP) resulting in a VOgPP precompatibilizer. A mathematical model of the process of the VOgPP synthesis and the conduction of a full-factorial experiment have allowed both the optimization of the synthesis conditions and the prediction of its proceeding.

During blending PP with other polymers VOgPP localizes across the blend interphases and initiates radical processes leading to the *in situ* formation of final compatibilizer macromolecules, which are efficient just for the blends where they are formed. The universality of the precompatibilizer concept is demonstrated in PP blends of the thermoplastic/thermoplastic type (with polystyrene and polyethylene) and of the thermoplastic/thermoset type (with unsaturated polyester resin).

Keywords: compatibilization; peroxide graft copolymer; polymer blends; simulations; synthesis

Introduction

The creation of polymer blends allows to combine the properties of individual polymers providing the possibility of essential widening of an assortment of new valuable polymer materials. A general problem for the creation of new blends is the thermodynamically immiscibility of the majority of polymer combinations leading to phase separation and worse blend characteristics if the compatibility between the separated phases is poor. Today, this problem is overcome by the creation of compatibilizing systems, decreasing the interfacial tension and increasing the adhesion between the blend components [1]. The utilization of diblock, triblock, and graft copolymers as compatibilizers is efficient from this point of view [2], but their

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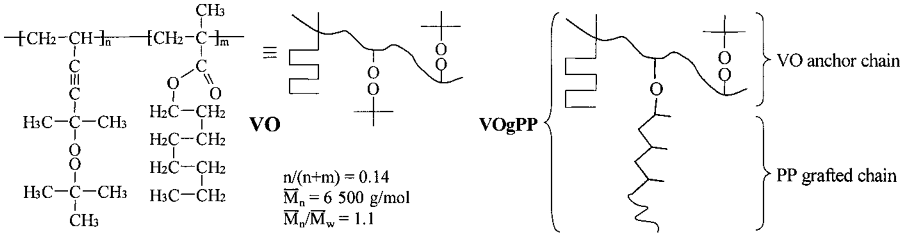
separate synthesis is rather expensive. Reactive blending of polymers, where the compatibilizing systems are formed *in situ* by the reaction of both blend components with each other, is considered to be more promising [2,3]. However, still the main problem of the contemporary methods remains, their non-universality and the necessity of the elaboration of expensive compatibilizing systems for almost every set of polymers to be blended.

Since a universal property of almost all polymers blended today is their ability to participate in free radical reactions of chain transfer and recombination, a more universal concept for the *in situ* compatibilization is the formation of compatibilizing structures by radical processes. The utilization of low molecular weight substances as radical sources is accompanied with a number of drawbacks such as their volatility at blending temperatures, their lack of interfacial activity, and, consequently, their effects on the bulk properties of the blended polymers. Thus, in our opinion, the most promising route for a universal *in situ* creation of compatibilizing systems is the elaboration and application of interfacial active peroxide-containing high molecular weight precompatibilizers, capable to locate across the interphases in different blends and generating there free radicals which results finally in the formation of the compatibilizer molecules efficient just for the blends where they are formed.

Experimental

The peroxide random copolymer VO on the basis of 2-tert-butylperoxy-2-methyl-5-hexene-3-yne (VEP) and octyl methacrylate, which was synthesized using a known technique [4], has been utilized for the synthesis of the interfacial active peroxide-containing precompatibilizer VOgPP (Scheme 1). Due to VO interactions with PP in the melt (a process that is studied in this work) at the expense of partial decomposition of peroxide groups, an alloy is formed containing $\approx$35 %wt VOgPP, which has been utilized directly for the compatibilization of blends of PP with other polymers.

PP (Aldrich 428183, fraction extractable with heptane) has been utilized for the elaboration of the VOgPP synthesis. The same PP was used for the preparation of blends with polystyrene (PS, PS143E, BASF AG, Germany) and unsaturated polyester resin (UPR, PN-15, Armoplast Co., Ukraine). PP Novolen 1106 H (Targor, France) was used for the preparation of blends with polyethylene (PE, Hostalen GC 7260, Elenac GmbH, Germany).



Scheme 1. Structure of the peroxide containing random copolymer VO (left) and of its fusion product with PP, the precompatibilizer VOgPP (right)

The melt blending of PP/PS and PP/PE was performed using a DACA Micro-Compounder (volume 4.5 cm^3, DACA-Instruments, USA) at 190 °C for 10 min at 100 rpm. Prepared blends were extruded as strands into water. Micrographs were obtained from cryocuts by means of a scanning electron microscope LEO VP435 (Zeiss, Germany) at 10 kV.

The thermoplastic/thermoset blends (PP/UPR) were prepared at 190 °C by mixing PP and UPR for 15 min. Then styrene preheated to 50 °C was added to the mixing chamber (with heating turned off) reaching an UPR/styrene ratio of 60/40 by weight. The mixture cooled down to 20 °C within 20 min under stirring. 5 %wt benzoyl peroxide (40 %wt blend in dibutyl phthalate, Aldrich) and 0.15 %wt 2,4-dimethylaniline (Aldrich), both upon the total quantity of UPR and styrene; were added to the blend before molding. Then, blends were cured at ambient temperature during 24 hours in form of specimens sized 0.5×1.0×8.0 cm^3. Charpy unnotched impact strength of cured PP/UPR-styrene samples was measured using a pendulum striker TiraTest 2000 (TIRA, Germany). Results were averaged over 12 measurements.

Results and Discussion

Elaboration of the synthesis conditions for the peroxide precompatibilizer

We have established earlier the ability of VO to bind with PP using ellipsometry and atomic force microscopy, and also to form crosslinked products [5]. During the performance of fusion of VO with PP, the formation of several fractions of polymer materials possessing different molecular weight (MW) was observed. Corresponding results were obtained by a consequent soxhlet extraction with hexane and heptane of obtained specimens (Figure 1).

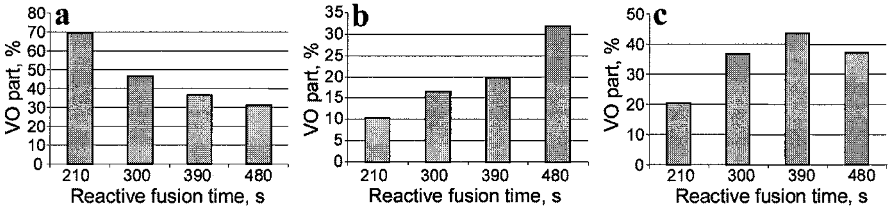


Figure 1. Dependence of VO part (determined by quantitative IR-spectroscopy) after the interaction with PP on the time of fusion at 190 °C (initial VO content: 2.5 %wt) in: **a** - hexane fraction (lower MW); **b:** heptane fraction (higher MW); **c:** heptane gel-fraction (highest MW).

One can see from Figure 1 that VO transforms steadily to higher molecular weight compounds at the proceeding of free radical processes in its melt with PP. It is worth to note, that if recombination proceeds between the macroradicals of VO and PP (which was at the solubility limit in heptane) then the resulting product will be part of the gel-fraction insoluble in the solvents utilized. The latter fraction includes also the crosslinked products.

The target process of the interaction studied is a recombination of VO and PP macroradicals with the formation of VOgPP. This part of the work is devoted to the optimization of this process. A mathematical model of the grafting has been built on the basis of the detailed scheme of possible reactions proceeding during the fusion interaction of VO and PP. The final integral equation of the current VO concentration can be presented as follows:

$$[\mathrm{VO}] = \frac{[\mathrm{VO}]_0}{e^{k_{C1}\cdot\tau}(1+k_{C2})-k_{C2}}, \qquad (1)$$

with [VO] and $[\mathrm{VO}]_0$ are the current and initial VO concentration, respectively; and k_{C1} and k_{C2} are process effective constants.

Integral equations describing the formation of the target product VOgPP, C_{TP}, and the formation of non-target products of VO interaction (including the crosslinked products), C_{NP}, are:

$$C_{TP} = S_{TP}\cdot\frac{100}{\rho}\cdot[\mathrm{VO}]_0\cdot\left(1-\frac{1}{e^{k_{C1}\cdot\tau}(1+k_{C2})-k_{C2}}\right), \qquad (2)$$

$$C_{NP} = S_{NP}\cdot\frac{100}{\rho}\cdot[\mathrm{VO}]_0\cdot\left(1-\frac{1}{e^{k_{C1}\cdot\tau}(1+k_{C2})-k_{C2}}\right), \qquad (3)$$

where S_{TP} and S_{NP} are coefficients of the formation of target and non-target products, respectively;

and ρ is the reaction mass density. Values of constants and coefficients of the equations shown have been listed in Table 1.

Table 1. Values of the equation (**1**) constants and coefficients S_{TP} and S_{NP} from equations (**2**) and (**3**) obtained by optimization of experimental data in dependence on the conditions of proceeding the reactive fusion of VO and PP.

Temperature K	$[VO]_0$ mol/dm^3	$k_{C1}\times10^4$ s^{-1}	k_{C2}	S_{TP} g/mol	S_{NP} g/mol
443	0.0325	3.3±0.7	7.5±0.6	4370±70	1320±80
453	0.0185	5.6±0.3	5.1±0.2	4640±120	1000±60
	0.0250	5.9±0.6	4.8±0.5	4610±40	1100±40
	0.0325	5.7±0.4	5.0±0.4	4500±70	1220±70
463	0.0325	9.6±0.3	3.1±0.4	3880±90	1780±70

The model built and its parameters optimized using the experimental data allow to find an optimal temperature of target VOgPP formation (Figure 2) and to predict the proceeding of the process of precompatibilizer formation during reactive fusion of VO with PP (Figure 3).

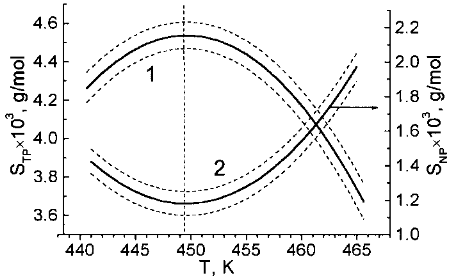


Figure 2. S_{TP} (**1**) and S_{NP} (**2**) coefficients vs. process proceeding temperature.

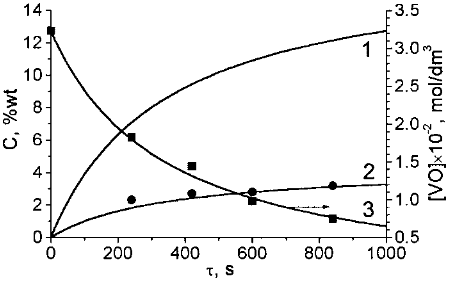


Figure 3. Predicted curves of VOgPP accumulation (**1**), non-productive VO interaction (**2**), and VO consumption (**3**). Points are experimental. T = 449 K, $[VO]_0$=0.0325 mol/dm^3.

One can see from Figure 2 that the optimal temperature for yielding the maximum quantity of the target precompatibilizer VOgPP and minimum of byproducts of VO and PP interactions is 449 K. At this temperature a control experiment has been performed for the estimation of obtained model adequacy. Figure 3 represents the results of that experiment. It can be seen that calculated curves describe the experimental data satisfactorily. About 80 % VO is consumed for the formation of target VOgPP at optimal temperature. At this, grafting is performed statistically on the residue of one peroxide group of VO and, because of the dominant β-decomposition of PP radicals under the fusion conditions, by the end of polypropylene chain.

Full-factorial experiment performance

A study in accordance with a full-factorial orthogonal second-order design with three variable parameters (VO concentration, time, temperature) has been performed for the optimization of the reactive fusion of VO and PP. Graphic representation (Figure 4) of the responses allowed to obtain optimal values for the fusion conditions.

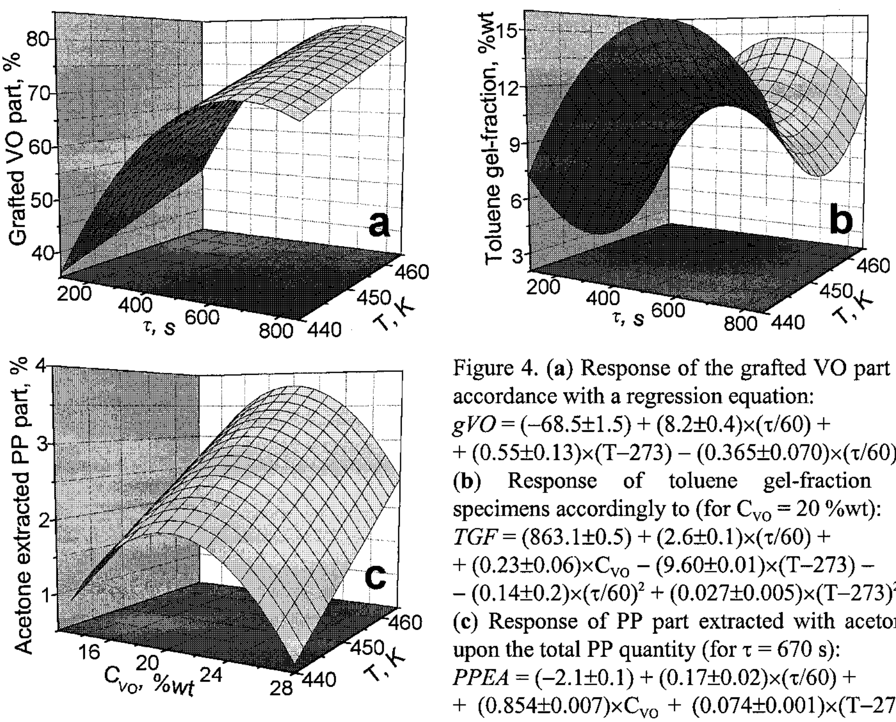


Figure 4. (**a**) Response of the grafted VO part in accordance with a regression equation:
$gVO = (-68.5\pm1.5) + (8.2\pm0.4)\times(\tau/60) + (0.55\pm0.13)\times(T-273) - (0.365\pm0.070)\times(\tau/60)^2$
(**b**) Response of toluene gel-fraction in specimens accordingly to (for $C_{VO} = 20$ %wt):
$TGF = (863.1\pm0.5) + (2.6\pm0.1)\times(\tau/60) + (0.23\pm0.06)\times C_{VO} - (9.60\pm0.01)\times(T-273) - (0.14\pm0.2)\times(\tau/60)^2 + (0.027\pm0.005)\times(T-273)^2$
(**c**) Response of PP part extracted with acetone upon the total PP quantity (for $\tau = 670$ s):
$PPEA = (-2.1\pm0.1) + (0.17\pm0.02)\times(\tau/60) + (0.854\pm0.007)\times C_{VO} + (0.074\pm0.001)\times(T-273) - (0.021\pm0.003)\times C_{VO}^2$

A value of τ = 670±160 s for the time of fusion has been determined on the basis of grafted VO part response (Figure 4a) by differentiation of its regression equation. The optimal process temperature is T = 450±8 K determined from the toluene gel fraction (TGF) response (Figure 4b) based on minimizing the crosslinked product quantity. This agrees well with the temperature mentioned above (449±5 K), which was optimized independently from the coefficients of the target and non-target product formation.

At last, an optimal value of 20±3 %wt VO has been determined from the response of the amount of PP extractable with acetone (PPEA, Figure 4c). According to the activation parameters of the VEP peroxide group decomposition [6] 51 % of the peroxide groups decompose during 670 s at 449 K. This provides an active proceeding of PP radical β-decomposition and its grafting by one end. The latter fact is important to form the desired structure (Figure 5). This structure facilitates the diffusion of VOgPP in PP blends and its location across the blend interphases due to the PP fragments miscible with the PP-phase and the VO fragments incompatible with PP. The quantity of peroxide groups remained is satisfactory for the further VOgPP utilization for the creation of compatibilizing systems in PP blends with other polymers.

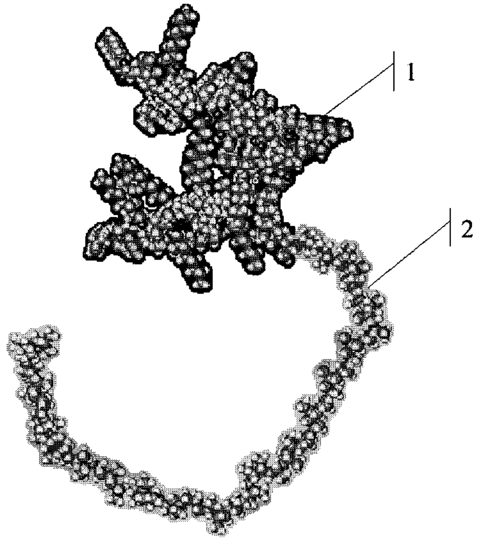


Figure 5. Model of a VOgPP molecule (9143 g/mol), optimized with HyperChem™ software using a MM+ method. **1** – anchor VO fragment; **2** – grafted PP fragment.

Application of peroxide precompatibilizer in blends

The VOgPP quantity necessary for the compatibilization of PP blends with other polymers can be calculated on the basis of the surface area of the dispersed PP phase in the blends and the area occupied by the anchor fragment of VOgPP molecule accounting for the Van der Waals radii (Figure 5, region dark circumscribed). The precompatibilizer synthesized under optimal conditions (an alloy of 35 %wt VOgPP in PP) has been applied for the compatibilization of both blend types: thermoplastic/thermoplastic and thermoplastic/thermoset blends.

In blends of PP with unsaturated polyester resin (UPR dissolved in styrene, see experimental part) the compatibilization with VOgPP resulted in dispersions with high stability (more than the observed 6 months). Noteworthy, the non-compatibilized composition was unstable and separated at once (one day as maximum) after preparation; which is in accordance with patent literature [7]. 2 months stability for such compositions is considered as applicable term.

Besides, an improvement of flexibility and impact strength of the specimens cured from the compatibilized compositions has been established. The maximal impact strength has been observed for the specimens obtained at a ratio of VOgPP to PP dispersed phase of 7 %wt, independent on the PP content in the blend (3 to 10 %wt) (Figure 6).

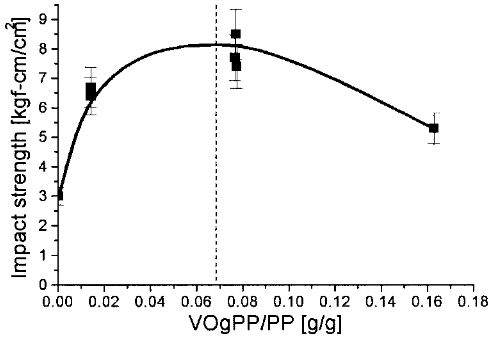


Figure 6. Impact strength of cured specimens obtained from PP/UPR compositions vs. VOgPP/PP ratio.

In addition, the precompatibilizer VOgPP has been successfully utilized for the compatibilization of thermoplastic/thermoplastic PP/PE and PP/PS blends (Figure 7), as reported earlier [6, 8].

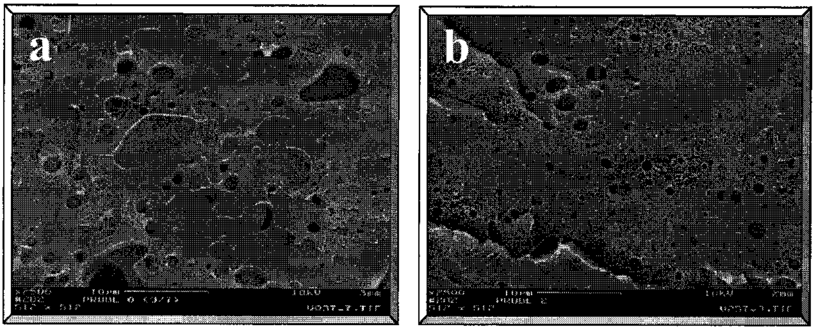


Figure 7. SEM-micrographs of cryofractured surfaces of PP/PS (30/70) blends (**a**) without VOgPP and (**b**) with 0.9 %wt VOgPP.

Conclusions

An approach has been elaborated for the synthesis of precompatibilizers universal for the compatibilization of polymer blends. In this approach a fragment of one polymer to be blended has to be grafted to an anchor copolymer. Fragments of the second blend copolymer will graft to the precompatibilizer during blending, forming the final compatibilizing structures.

Methods for the mathematical description and optimization of the synthesis conditions have been presented using as example the creation of an interfacial active precompatibilizer based on peroxide copolymer and polypropylene. These methods may be applied for the modeling of precompatibilizer formation for other polymer blends, which do not include polypropylene.

The universality of the precompatibilizer synthesized has been shown for the compatibilization of polypropylene with other thermoplastics and also with an UPR thermoset.

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