Macromol. Symp. ***2001,*** *164, 357-367*

Polypropylene/Polyperoxide Interaction in the Melt Phase

V. Datsyuk[1], L. Haussler[1], U. Wagenknecht[1], S. Voronov[2], V. Tokarev[2], O. Bednarska[2]

[1] Institute of Polymer Research Dresden, Hohe Str., 6, 01069 Dresden, Germany

[2] Lviv Polytechnic State University, St. Bandery Str. 12, 79013 Lviv, Ukraine

SUMMARY: This paper deals with the effect of polyperoxide on the properties and characteristics of PP. Interaction of PP with polyperoxide was carried out by their mixing in melt phase applying co-rotating twin screw machine. The analysis of melting/crystallisation processes was performed using DSC. Influence of polyperoxide concentration and mixing condition (temperature, residence time) on PP properties was investigated via determination of PP molecular weight. Mechanism of the PP degradation and decomposition of peroxide groups was judged by thermogravimetric analysis, FT-IR-, and NMR- spectroscopy. It was observed that decomposition of peroxide groups brings about degradation of polypropylene. However, simultaneously some part of short chains of PP are grafted onto macrochain of the polyperoxide decomposed.

Keywords: Polypropylene, polyperoxide, melt phase, mixing.

1. Introduction

Peroxides have a wide application for synthesis of polypropylene (PP) with reactive functionality by different methods particularly by reactive extrusion [1, 2]. These polymers include materials such as PP with grafted maleic anhydride, fumarate and maleate, acrylic and methacrylic acids as well as their esters [3-7]. The most widespread method for introducing functionality into PP substrates by reactive extrusion involves free radical-induced graft polymerisation of aforementioned functional monomers. The process is generally based on combining PP with a free radical initiator (most commonly of peroxide type although other initiators have been used as well) and a monomer or macromonomer as conveyed through the extruder.

The initiators usually applied in the synthesis of PP graft copolymers by reactive extrusion are dialkyl mono- or diperoxides, e.g. dicumyl peroxide or α,α′-di(*tert*-butylperoxy) diisopropyl benzene. The decomposition mechanism of dialkylperoxides is well established as involving initial O-O bond homolysis generating the corresponding alkoxy radicals [1].

One of the problems in PP functionalization is that the monomer during graft polymerisation forms both grafted polymer and homopolymer chains [8]. This process is hardly controlled because a large number of independent factors ought to be optimized in order to maximize

CCC 1022-1360/00/$ 17.50+.50/0

grafting yield. These include temperature, pressure, residence time, the nature and amounts of monomers, initiators, and coagents.

Reactions in the melt phase of PP are often accompanied by these side reactions [9]: crosslinking of PP substrate; radical-induced chain scission of PP macromolecules; shear induced degradation of PP substrate; homopolymerisation of the functional monomer added. Relationships between these side reactions depend on the process conditions and on the substrate particularity.

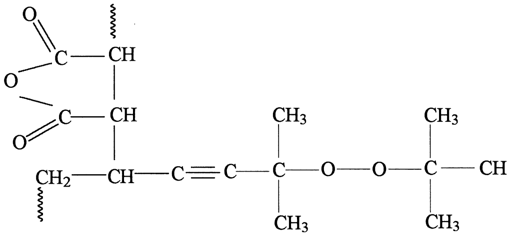
The most often cited side reaction is degradation caused by the initially formed radical undergoing ß-scission of macrochain [10]. It is important to select the proper initiator because different types of the initiators have diverse effects on the degradation degree of PP [11]. A variety of factors is needed to be considered while selecting an initiator for the grafting experiment: the initiator half-life; reactivity and specificity of initiator-derived radicals with respect to polypropylene, monomer, initiator, and other components present in the melt; the initiator concentration used; initiator solubility and so on.

The aim of the present work was the investigation of the interaction of PP with a new type of peroxides, precisely heterofunctional polymeric peroxides [12]. This type of oliperoxides contains besides peroxide groups other functionalities, owing to which they are suspected to be prospective compounds for functionalization of diverse polymer substrate. It was expected that reactive mixing of PP with polyperoxide would permit to obtain functionalized products.

2. Experimental

2.1. Material

Polypropylene PPN 1106 (M_w = 431000; M_N = 17200) from TARGOR (Germany) was used. Polyperoxide (Pper) is the copolymer of maleic anhydride and 5- *tert*-butylperoxy-5-methyl-1-hexen-3-yne (mol. ratio 1:1) with Mn ≈ 22000 and content of $[O]_{act.}$ = 5.6 wt %, synthesized at the Organic Chemistry Department of Lviv Polytechnic State University [13].



2.2. Methods

Degradation of the PP was investigated under various conditions such as: temperature (200 °C, 220 °C, 240 °C); residence time (5 min, 10 min, and 15 min) and concentration of Pper (0.5, 1.0, 2.5, 5.0 wt %). Samples were processed in a DACA microcompounder, a co-rotating twin screw machine, cycling 4 g of the polymer blend for several minutes in a circle.

Melting and crystallisation analysis of various PP samples was carried out using differential scanning calorimeter DSC 7, Perkin Elmer (Poris-Software, version 3.51) at two heating and one cooling in the range from –40 °C to 160 °C and heating and cooling rates of 20 K/min.

Thermogravimetric analysis (TGA 7, Perkin Elmer, Poris-Software, version 3.51, heating range 50-700 °C under N_2, heating rate of 10 K/min) was performed for determining the changes in the PP structure.

Molecular weight of PP samples indicating the level of their degradation was measured by high temperature GPC analyses (high temperature size exclusion chromatograph PL-GPC 210 [Polymer Laboratories]) in 1,2,4- trichlorobenzene at 135 °C and PP as standard.

FT-IR-spectra of the samples (films with the thickness of 100 μm) were obtained with IFS66V/S – instrument, at 170 °C.

Solid state ^{13}C NMR- spectra were obtained with an AMX300 spectrometer, at Larmor frequencies of 300 MHz and 75 MHz for protons and ^{13}C respectively. Data were acquired under cross polarization from ^{1}H to ^{13}C with the excitation pulse duration of 5 μs and contact time of 1 ms and 5 kHz sample rotation frequency.

3. Results and discussion

Evident from the structure of the polymeric initiator (polyperoxide) used is the fact that it is a polyfunctional compound. Pper is an excellent candidate for free radical grafting in the melt phase processing for several reasons.

Pper contains peroxide groups, therefore has initiating properties similar to other dialkyl peroxides (see Table 1). The mechanism of its decomposition is similar to that described elsewhere [12].

Table 1.

Comparison of the properties of the Pper to some dialkyl peroxides

Peroxide	Radical formed		$t_{1/2}$ (min) at		
	Primary	Secondary	100 °C	150 °C	200 °C
Dicumylperoxide (DCP)	Cumyloxy	Methyl	890	9.2	0.25
α,α′- di(*tert.*-butylperoxy)diizopropylbenzene (DIPB)	*tert.*-butoxy alkoxy	Methyl Alkyl	1500	13	0.31
Poly(5-(*tert.*-butylperoxy)-5-methyl-1-hexene-3-yne-co-maleic anhydride (polyperoxide)	*tert.*-butoxy macrooxy	Methyl	3200	72.63	0.72

Pper has the polymerized maleic acid anhydride links within a long polymer chain, therefore it could serve as a functional compound in various grafting processes. In the case of polyolefine filled with mineral or polymer fillers, it could be exploited for design of interfacial layers [14, 15] and for formation of compatibilizing layers chemically bonded simultaneously to both the filler surface and polymer matrix [16, 17].

3.1. Effect of Pper on the melt viscosity of PP

Figure 1 shows an example of the mixing torque data obtained during melt degradation of PP in the presence of Pper and without it. Comparison of there data showed a strong decreasing of torque in the case of using of the polyperoxide that is in consequence of PP degradation via reaction with radicals of Pper.

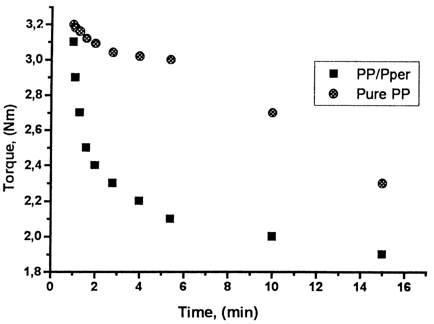


Figure 1. Profile of torque vs. mixing time indicating degradation process of PP in the presence of polyperoxide and without it
Conditions:
200 °C, 100 rpm, Pper concentration – 1 wt %.

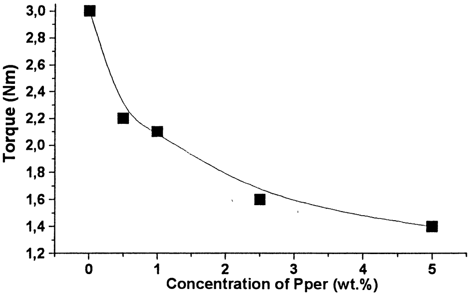


Figure. 2. Torque after 5 min of mixing as a function of Pper concentration in PP blends.
Conditions: 200 °C, 100 rpm.

Figures 2 shows the torque values, measured after 5 min of mixing, as a function of Pper concentration in the samples. It is clearly seen that the torque depends on Pper contents which strongly affects the degradation process.

3.2. Effect of Pper on the phase transition temperatures of PP

Data on DSC tests (cooling) are presented in Figure 3. The DSC curves obtained for pure PP and PP after degradation in the presence of Pper show shift of the crystallization temperature (T_c) in comparison to PPN-1106. The most shift is observed for PP with 1% of Pper and it change are decreased in the row 2,5% Pper < 5% Pper < pure PP. It is explained by increasing of the grafted PP segments to Pper chains at the increasing of Pper amount.

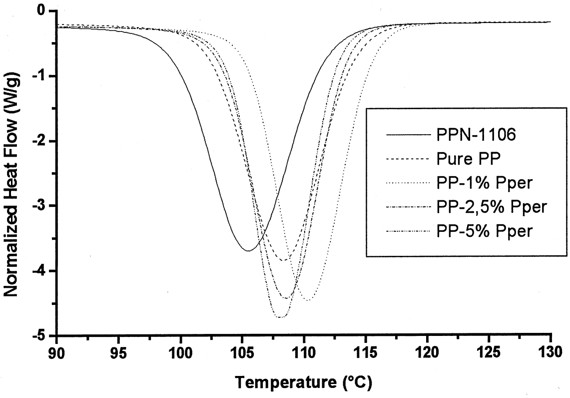


Figure 3. DSC traces of PP samples after melt mixing with Pper

3.3. Effect of Pper on Molecular Weight of PP

The major apparent effects of Pper on altering PP characteristics revealed by GPC analysis are disappearance of the high molecular weight tail and corresponding narrowing of the molecular weight distribution (MWD). Thus, measurement of the weight-average molecular weight (M_w) and the MWD will be considered as a direct evidence that PP degradation occurred under influence of Pper. M_w of pure PP and PP after 5 min of degradation in the presence of various Pper concentrations are shown in Figure 4. Decrease of M_w indicates that the basic reaction, occurring during the melt mixing of PP with Pper, is the degradation of polypropylene macromolecules.

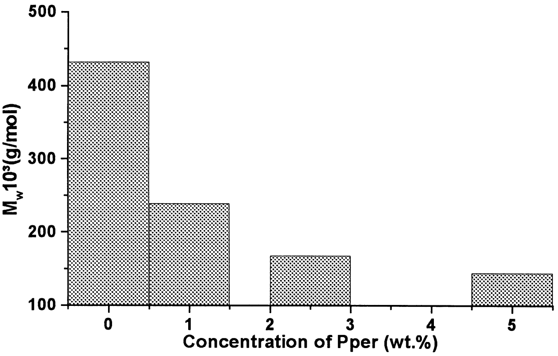


Figure 4. Effect of Pper concentration on M_w of PP. (T=200°C; residence time 5 min)

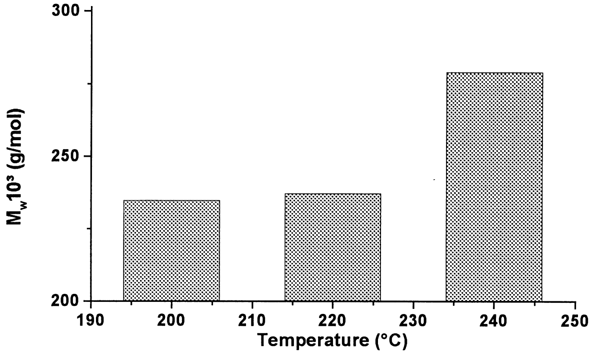


Figure 5. Effect of temperature on M_w of PP mixed in melt with 1 % Pper and at the residence time 5 min

Dependence of M_w on the mixing temperature (Figure 5) demonstrates the sharp increase of the M_w for samples prepared at 240 °C. Two possible reasons should be considered for explanation of this fact namely non effective decomposition of peroxide groups of Pper and the formation of graft copolymers. Efficiency of Pper in the cleavage reactions of PP could be reduced at higher temperatures due to rapid decomposition of peroxide groups and fragmentation of the alkoxy radicals formed. On the other hand, efficiency of grafting reactions proceeding as the interaction of PP macrochain splinters with macroradicals formed from Pper increases with increasing temperature. Both these processes should lead to M_w enhancement; however, on comparing the results of GPC and TGA it could be assumed that the major reason for increase of the sample molecular weight is grafting of PP to Pper macrochain.

Increase of the melt mixing residence time instigates a decrease in M_w (Figure 6). Similar dependency was found when studying viscosity of the melts (Figure 1) most appreciable lowering of M_w value occurs in the first 5 min of processing.

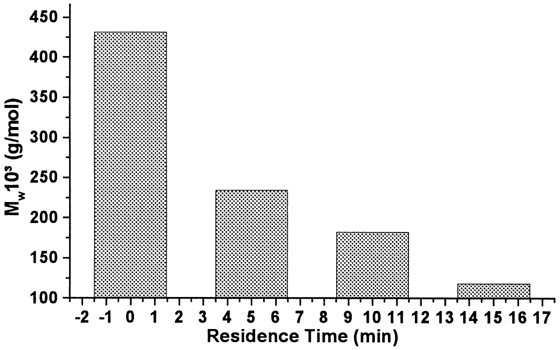


Figure 6. Effect of the mixing residence time on M_w of PP at 200°C and Pper contain =1 wt.%

Plots of the number-average molecular weights (M_n) of PP samples (original and after melt mixing in the presence of Pper) versus Pper concentration and residence time (Figure 7) show maxima.

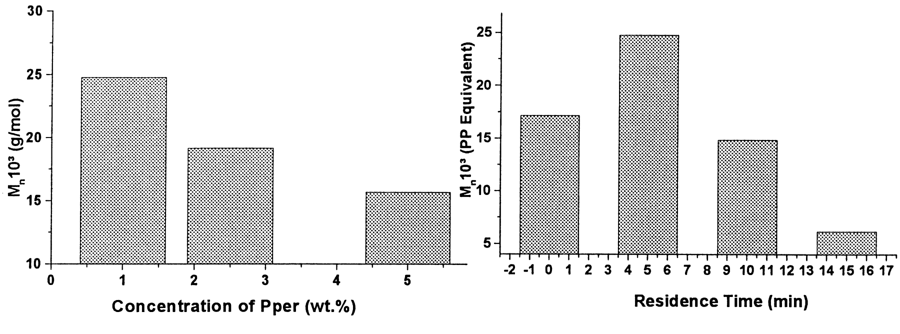


Figure 7. Effect of the reaction condition on M_n of PP

Non adequate responses of M_w and M_n on altering the reaction conditions (Compare Figures 4 and 6 with 7) is presumably connected with their distinguished sensitivity to the content of low molecular and high molecular fraction. The longer macrochains the higher their probability to be cloven, what is the reason for disappearance of this fraction observed by

GPC for samples of PP mixed in the melt with Pper. M_w, being more sensitive to the content of high molecular fraction than M_n, replies more appreciably to alteration of the conditions of PP melt mixing (See Table 2). Indeed, increasing the Pper concentration or residence time, both facilitating degradation of PP, brings about lowering of M_w (Table 2, Figures 4 and 6) while elevation of the process temperature raises the M_w (Figure 5) due to intensive formation of graft polymers.

Table 2.

Molecular Weight Distribution data

Sample	Mn [g/mol]	Mw [g/mol]	MWD
PPN-1106	17200	431800	25.10
PP (without Pper, 200°C, 5 min)		426000	
PP (without Pper, 200°C, 15 min)		241400	
PP-Pper (1% Pper, 200°C, 5 min)	24800	234900	9.47
PP-Pper (2,5% Pper, 200°C, 5 min)	19200	167500	8.72
PP-Pper (5% Pper, 200°C, 5 min)	15700	144000	9.17
PP-Pper (1% Pper, 200°C, 10 min)	14700	163000	11.09
PP-Pper (1% Pper, 200°C, 15 min)	6200	118300	19.08
PP-Pper (1% Pper, 220°C, 5 min)	29200	237100	8.12
PP-Pper (1% Pper, 240°C, 5 min)	24800	278900	11.25

3.4. Investigation of the structure of PP by spectroscopy methods

3.4.1. Fourier Transform Infra-Red Spectroscopy

FTIR spectra for homopolymer of PP and PP after melt mixing with Pper are given in Figure 8. Absorbance peak belonging to maleic anhydride moieties at 1783 cm^{-1} [$\nu_{(C=O)}$] is easy recognized in the spectrum of PP sample after mixing with Pper, while it is not observed in the case of original PP.

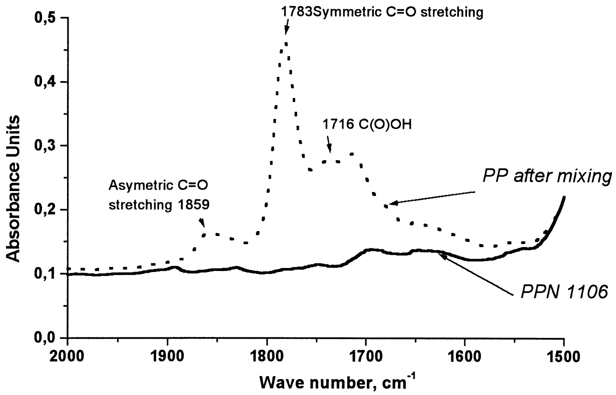


Figure 8. FT-IR Spectra (in the range between 2000 and 1500 cm^{-1}) of PP samples. Mixing of PP with Pper (2,5 wt.%) was carried out at the 200°C and residence time 5 min.

Based on these results it can be concluded that under conditions of melt mixing no appreciable decarboxylation of maleic anhydride moieties occurs and that the macroradicals derived from PP macromolecules besides scission reactions are intensively involved in the grafting reactions.

3.4.2. NMR – Spectroscopy in solid state

Solid state CP/MAS ^{13}C NMR spectra for original PP and PP after mixing with Pper in the melt phase (200 °C, 5 min, 100 rpm, 1 wt % Pper) acquired with a AMX 300 spectrometer are presented in Figure 9.

Both spectra of original PP (Spectrum 1) and that treated with Pper sample (Spectrum 2) are quite similar, but in 10-fold zoomed by vertical spectrum of the latter (Spectrum 3) there are clearly visible three additional peaks in the range of 80...110 ppm, which could be attributed to the chemical shifts of ^{13}C in >C=C<, >C=O, and –C–O–C– groups. Vinylic groups appear owing to scission reactions of PP macrochains which, as have been shown above, intensively proceed under the action of Pper.

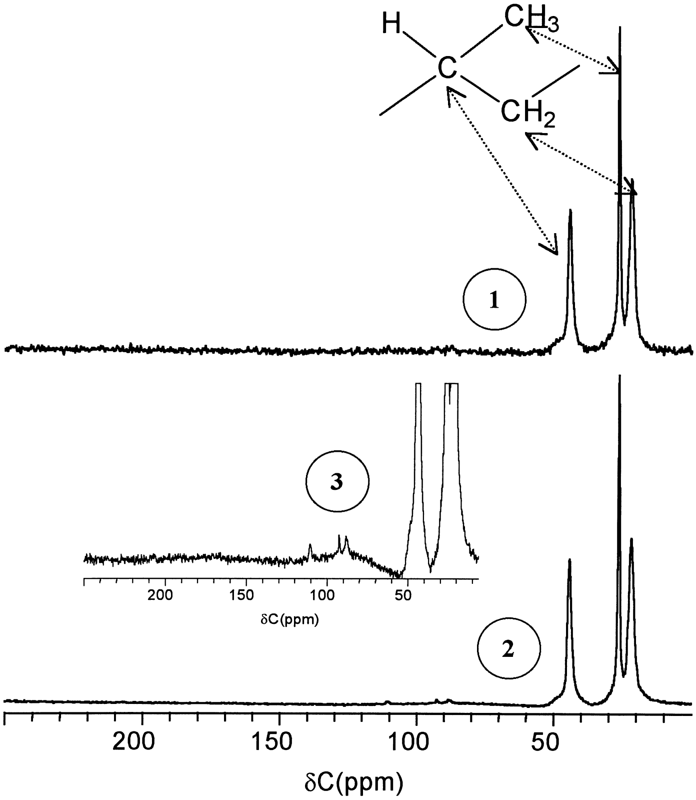


Figure 9. Solid state CP/MAS ^{13}C NMR spectra of original PP and PP after mixing with Pper in the melt phase:

1 – Original polypropylene (PPN 10/60);

2 – Polypropylene after mixing;

3 – Polypropylene after mixing (10-fold vertical zoom of the spectrum 2).

4. Conclusion

The results considered above point out that melt mixing of PP in the presence of Pper brings about degradation of PP macromolecules. However, grafting of short chains of PP onto macrochain of polyperoxide decomposed occur during this process providing thereby functionalization of polypropylene.

Reference

1. Moad G., Solomon D.H. The Chemistry of Free Radical Polymerisation. Oxford: Pergamon, 1995.
2. Hogt A.H., Meijer J., Jelenic J., In: Al-Malaika S., editor. Reactive Modifiers for Polymers, Cambridge: Cambridge University Press,1997
3. Russell K.E. J., Polym. Sci. Part A: Polym. Chem. 27 (1989) 3353-3362.
4. Wong Shing J.B., Baker W.E., Russell K.E., J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 633-642.
5. Gaylord N.G., In: Xanthos M., editor. Reactive Extrusion, Munich: Hanser, 1992.
6. Hoo V.M., Whitney R.A., Baker W.E., Polymer 41 (2000) 4367-4371.
7. Song Z., Baker W.E., J. Appl. Polym. Sci. 44 (1992) 2167-2177.
8. Bray T., Damiris S. Grace A., Moad G., O'Shea M., Rizzardo E., Van Diepen G., Macromol. Symp. 129 (1998) 109-118.
9. Moad G., Prog. Polym. Sci. 24 (1999) 81-142.
10. Dorn M., Adv. Polym. Technol. 5 (1985) 87-97.
11. Borsig E., Hrckova L., Fiedlerova A., Lazar M., Rätzch M., Hesse A., J. Macromol. Sci. – Pure Appl. Chem. A35 (1998) 1313-1326.
12. Voronov S., Tokarev V., Oduola K., Lastukhin Yu., J. Appl. Polym. Sci. 76 (2000) 1217-1227.
13. Voronov S., Tokarev V., Petrovska G. Heterofunktional Polyperoxides. Theoretical Basis of their Synthesis and Application in Compounds. State University Lvivska Polytechnika (1994), 85 p.
14. Voronov S., Tokarev V., Datsyuk V., Kozar M., Prog. Colloid. Polym. Sci. 101, (1996) 189-193.
15. Voronov S., Tokarev V., Seredyuk V., Datsyuk V., In "Eurofillers-95", Mulhouse, (1995), p. 99-102.
16. Voronov S., Tokarev V., Datsyuk V., Seredyuk V., Bednarska O., Oduola K., Adler H.Y., Puschke C., Pich A., Wagenknecht U., J. Appl. Polym. Sci. 76 (2000) 1228-1239.
17. Wagenknecht U., Tokarev V., Kretzschmar B., Voronov S., Kunststoffberater 43 (1998) 5, 27 – 30.