

The grafting of metallocene copolymer to higher polarity with acrylic acid

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Abstract: *The grafting of metallocene ethylene-octene copolymer to higher polarity with acrylic acid. Metallocene polyolefins (MePO) were grafted in melt due to increasing their surface free energy and adhesive properties. MePO modification with ozone was used to initiate the creation of peroxides on the surface of the polymer with subsequently grafting of acrylic acid in polymer melt. The efficiency of grafting in melt is high, ranging between 0.77 and 0.97.*

Keywords: metallocene polyolefin, ethylene-octene copolymer, acrylic acid grafting

INTRODUCTION

Metallocene polyolefins (MePO) represent a sort of polymers with some special properties, i.e. mechanical properties, melting temperature, etc. MePO contain non-polar chains which can interact well with non-polar surfaces (1, 2). Nevertheless, efforts to adjust the hot-melt adhesives (HMA) application parameters, especially regarding increased adhesion to polar surfaces, focus either on basic polyolefin chains polarity increase or on polar polymers addition to the adhesive compositions. The reason is that, owing to their higher surface energy, more polar compositions lead to adhesives with higher adhesive peel and shear strength. An increase of HMA polarity has been frequently achieved by adding polar components to an adhesive polymer composition. An easy way of modifying polyolefin macromolecules by free radical grafting is treating the polymer powder, foils or fabrics by means of polymerizing vinyl monomer along with a free radical initiator (3–7). Such an approach to initiate polymer grafting is used mainly for surface modification of powders, foils and fibres.

The method of increasing the polarity of MePO macromolecules by free radical grafting is to treat the polymer powder, foils or fabrics with a polymerizing vinyl monomer along with a free radical initiator. Nevertheless, grafting initiation due to the transfer of the free valence from the polymerizing monomer to the modified polymer represents ineffective process. The ethylene groups in main chain of metallocene copolymer – ethylene-octene copolymer Resinex PE RXP 1502 (RXP) – are tightly bound to the carbon atom and RXP is insufficiently reactive in transfer reactions compared to polymerizing chain growth rate of an unbound homo-polymer formed during grafting process. It is generally accepted that this is the reason causing the low grafting effectiveness. More favourable conditions with higher grafting efficiency exist for metallocene ethylene-polypropylene copolymer (e.g. Licocene) containing hydrogen on tertiary carbon more reactive in transfer reactions (6).

The initiation of the graft polymer chains growth on the polymer is the most important reaction for effective binding of polymer branches to the main chain of polymer. The free radical decomposition of hydro peroxide and peroxide groups accumulated on polyolefin molecules is the very effective technique to initiate MePO grafting in high yield. The approach to peroxides accumulation on MePO chain is based on macromolecules oxidation initiated by peroxides, e.g. benzoyl peroxide (BP) (7–9). Oxidation initiated by ozone during polymer treatment in ozone-oxygen mixture considerably accelerates peroxide creation. The polymer oxidation activated with ozone goes over the use of radiation sources applied as

initiators in polymer oxidation and this method of polymer initiation with subsequently used grafting is applied for modification of powders, foils and fibres (10–12).

In this contribution paper, we are reporting on the experiments consisting in the modification of MePO with the aim to increase of polarity of the polymer. Acrylic acid (AA) was grafted on polymer activated with an oxygen-ozone mixture. The formed graft copolymer was used as an additive to formulate hot-melt adhesive with increased applicability in adhesive properties.

EXPERIMENT

In this work, the metallocene ethylene-octene random copolymer Resinex PE RXP 1502 (melting temperature = 70°C, density = 0.874 g.cm⁻³, tensile stress at yield = 1.76 MPa) was used for HMA preparation in virgin form as the basic component as well as the adhesive additive after modification by grafting. An acrylic acid (AA, Aldrich, Netherlands) monomer, 99% purity, was stabilized with 180–200 ppm of methyl hydroquinone).

RXP powder was treated in the flow of O₂ + O₃ gas produced at a room temperature in an atmospheric plasma generator, power = 300 W (Masaryk University, Czech Republic), input O₂ flow = 5L/min. After 3 hours of polymer activation, the concentration of peroxides determined by the volumetric analytical method based on iodine oxidation was $(9.1 \pm 0.7) \cdot 10^{-3}$ (mol/kg).

The modification of the activated RXP powder proceeded in Brabender Plasticorder mixer in 30 mL chamber at 110°C for 30 minutes. Blades revolutions started at 15 rpm, and after 5 minutes they were increased to 30 rpm and followed the step-by-step monomer addition.

The samples for analytical procedures were prepared from RXP grafted product by compression-moulding to disks 1mm thick with 20 mm diameter. Press plates temperature was 110°C and moulding time 3 minutes, specific plates pressure 3 N/mm².

The concentration of peroxide groups bonded to RXP was determined by the volumetric analytical method based on iodine oxidation. The procedure was modified for non-aqueous systems. A saturated KI acetic anhydride solution was used as the reagent and the released iodine was determined by titration. The total peroxide oxygen content in RXP sample after 3 hours of oxidation was $(9.1 \pm 0.7) \cdot 10^{-3}$ (mol/kg).

The presence of grafted PAA in RXP-g-AA was proved by FTIR analysis. The spectrometer Nicolet 8700TM in the attenuated total reflectance spectroscopy mood was used. The valence band typical for PE, pertaining to the CH deformation vibrations (region of 2800–3000 cm⁻¹) was observed.

Based on contact angle measurements the hydrophilicity changes of RXP-g-AA surfaces were evaluated. The surface energy evaluation (SEE) system with CCD camera, Advex Instruments, Czech Republic) was used for experiments and a sessile drop technique was applied. Deionised water was used as a polar testing liquid. The drops with a volume 20 µl were deposited on a RXP surface and were immediately measured. The SFE of the wood as well as the corresponding polar and dispersive components of the SFE (PC SFE and DC SFE, respectively) were evaluated by the Owens–Wendt–Rabel–Kaelble (OWRK) method modified by incorporating at least squares method [6].

The temperature resistance of the adhesive joints was evaluated by measuring the strength of the adhesive joints in peeling (shear) on the laminated paper with biaxially oriented polypropylene (BOPP) foil used in the packaging industry. The adhesive properties were evaluated by testing the adhesive joints in peel by ASTM-D-4498 (Peel Adhesion Failure Temperature, PAFT) and in shear by ASTM D-4498 (Shear Adhesion Failure Temperature, SAFT) on laminated paper with BOPP foil.

RESULTS AND DISCUSSION

The presence of grafted PAA in RXP-g-AA was proved by FTIR analysis. For all samples prepared in this study the valence bands have been observed pertaining to CH deformation vibration (the region of 2800–3000 cm^{-1}), typical for PE. The bands for C-O and COC (1715 and 1170 cm^{-1} , respectively) indicate the presence of PAA chains. The ratio of the FTIR absorbance intensities for acid carbonyl compounds at 1715 cm^{-1} and the reference band at 1464 cm^{-1} serves for the PAA concentration determination in grafted copolymer. Changes in FTIR absorbance of these bands in samples 1–3 prepared in polymer melt and with a various amounts of AA are shown in Figure 1.

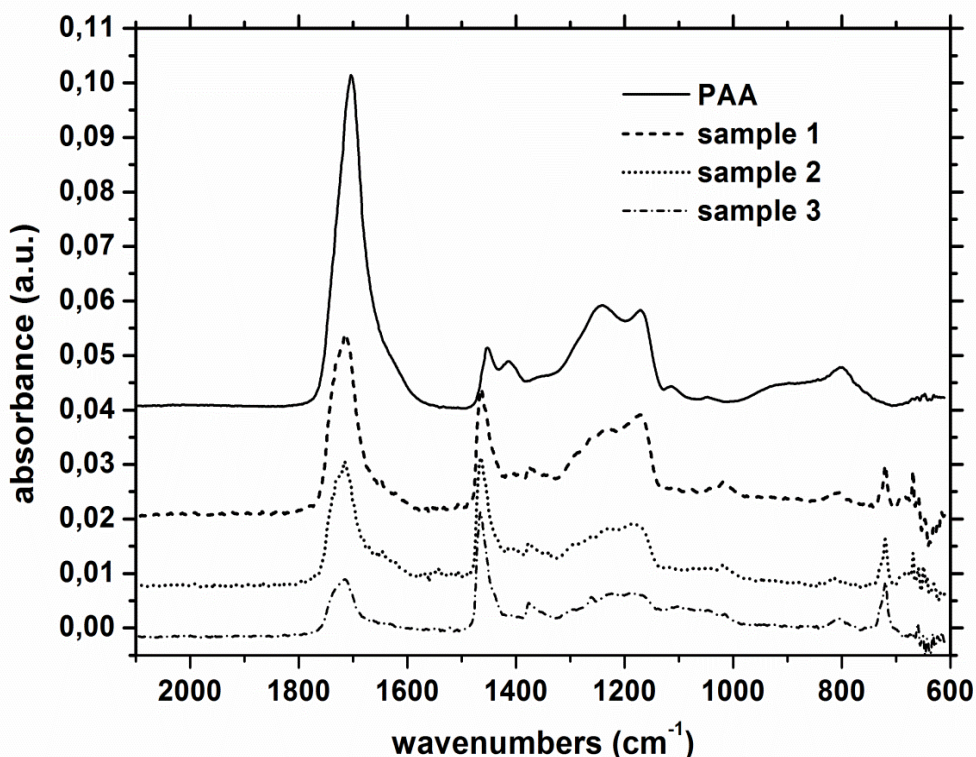


Figure 1. FTIR spectra of RXP grafted with AA in polymer melt. Sample 1 (9.2% PAA), sample 2 (18.4% PAA) and sample 3 (27.6% PAA) were prepared in a Brabender Plasticoder mixer

The method of increasing the degree of grafting is based on increasing reactants concentration in reaction batches. Although the grafting experiments in solvent indicate low utilization AA to modification RXP, the degree of grafting increases in systems containing a higher monomer concentration (Table 1). An effort to increase the degree of RXP grafting is directed to solvent free reaction. The most important benefit of solvent free reaction conditions is substantial increase in grafting efficiency.

The water contact angle (WCA) of initial RXP (106.4°) after grafting by AA decreased (Table 2). This decrease depends on the amount of the grafted AA (RXP with AA 14.1% – WCA = 99° , RXP with AA 26.8% – WCA = 87°). The increase of hydrophilicity of the grafted RXP samples reflects the growth of PC of SFE. For initial RXP, the PC of SFE reached the value 2.3 mJ/m^2 and after grafting with AA 14.1% PC of SFE, it increased to 3.6 mJ/m^2 and/or 3.9 mJ/m^2 (AA 26.8%).

The temperature resistance in peel as well as in shear of the adhesives based on RXP polymer is summarized in Table 3. The temperature resistance in peel for unmodified RXP is

PAFT = 64°C, but for RXP-g-AA, the temperature resistance is higher: with AA 14.1% – it is PAFT = 77°C and with AA 26.8% – it is PAFT = 78°C. The values of temperature resistance in shear for unmodified RXP and RXP grafted are similar and no differences were observed.

Table 1. Table 1 presents the batch components concentration and the grafting efficiency for RESINEX PE RXP 1502 grafting in molten state. Polymer was activated 3 hours with ozone-oxygen mixture. The oxidative gas was formed during oxygen flow through an atmospheric plasma generator: power = 300W, gas flow = 5L/min, room temperature. The reaction proceeds in the kneading chamber 30 ml for 30 minutes at 110°C

Activated	sample 1	sample 2	sample 3
RXP (g)	24.7	22.2	19.7
AA (ml)	2.5	5	7.5
PAA in sample (%)	9.2	18.4	27.6 %
Grafted PAA	8.7	14.1	26.8
(% in sample)			
Grafting Efficiency	0.88	0.77	0.97

Table 2. Contact angles, surface free energies and their polar components of RXP-g-AA films

Sample	CA water (deg)	CA GL (deg)	CA DMSO (deg)	Total SFE ⁻² (mJ.m ⁻²)	PC SFE ⁻² (mJ.m ⁻²)
RXP initial	106.4 ± 2.4 ^o	101.4 ± 1.4 ^o	63.5 ± 2.7 ^o	29.2	2.3
1 AA 8.7%	105.0 ± 1.8 ^o	89.3 ± 3.4 ^o	53.2 ± 3.1 ^o	29.8	2.5
2 AA 14.1%	99.0 ± 2.0 ^o	88.7 ± 1.7 ^o	62.0 ± 1.1 ^o	30.2	3.6
3 AA 26.8%	87.0 ± 3.2 ^o	85.7 ± 2.3 ^o	66.2 ± 2.8 ^o	30.0	3.8
4 CRA 9.5%	77.0 ± 2.2 ^o	74.7 ± 3.3 ^o	48.9 ± 2.8 ^o	31.8	4.2

CA = contact angle, GL = glycerin, DMSO = dimethyl sulfoxid,
PC and DC of the SFE = polar and dispersion component of the surface free energy.

Table 3. Temperature resistance of adhesive joints using peel (PAFT) and shear (SAFT) tests for RXP-g-AA samples

Sample	PAA grafted (%)	PAFT (°C)	SAFT (°C)
1	8.7	75	90
2	14.1	77	92
3	26.8	78	95
RXP initial	0	64	93

CONCLUSION

The most effective way in RXP grafting with AA is kneading molten RXP with reaction components in a Brabender Plasticoder. The determined grafting efficiency is high and varies between 0.77 and 0.97. The water contact angle on RXP surface grafted with PAA

decreased by at least 15%, or more and the surface energy and its polar component increased 1.1–1.7 times. The temperature resistance in peel of RXP-g-PAA increased 1.3 times, and the values of temperature resistance of adhesive joints in shear are similar.

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