

## Grafting of metallocene copolymer to higher polarity with acrylic acid

IGOR NOVÁK<sup>1)</sup>, JURAJ PAVLINEC<sup>1)</sup>, IVAN CHODÁK<sup>1)</sup>, ANGELA KLEINOVÁ<sup>1)</sup>,  
JOZEF PREŤO<sup>2)</sup>, VLADIMÍR VANKO<sup>2)</sup>

<sup>1)</sup> Polymer Institute Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

<sup>2)</sup> VIPO a.s., Gen. Svobodu 1069/4, 958 01 Partizánske, Slovakia

**Abstract:** *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 grafting efficiency of grafting in melt is high and varies 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 (Yalvac et al. 2005, Patel et al. 2010). Nevertheless efforts to adjusting the hot-melt adhesives (HMA) application parameters, especially regarding increased adhesion to polar surfaces, focus either to basic polyolefin chains polarity increase, or polar polymers addition to the adhesive compositions. The reason is that more polar compositions owing to the higher surface energy lead to adhesives with higher adhesive peel and shear strength. An increase of HMA polarity has been frequently achieved by addition of polar components to an adhesive polymer composition. An easy way of modification of polyolefin macromolecules by free radical grafting is treating the polymer powder, foils or fabrics by means of polymerizing vinyl monomer along with free radical initiator. Such approach to initiate polymer grafting is used mainly for surface modification of powders, foils and fibres.

The method how to increase the polarity of MePO macromolecules by free radical grafting is treating of the polymer powder, foils or fabrics by means of polymerizing vinyl monomer along with 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 carbon atom and RXP is insufficiently reactive in the transfer reactions compared to polymerizing chain grow rate of unbound homo-polymer formed during grafting process. It is generally accepted that this is the reason causing the low grafting effectiveness. More favorable conditions with higher grafting efficiency exist for metallocene ethylene-polypropylene copolymer (e.g. Licocene) containing hydrogen on tertiary carbon more reactive in transfer reactions (Novák et al. 2013).

The initiation of the graft polymer chains grow 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). 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 fibers.

In this contribution paper we report 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 oxygen-ozone mixture. The formed graft copolymer was used as an additive to formulate hot-melt adhesive with increased applicability in adhesive properties.

## EXPERIMENTAL

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

RXP powder was treated in the flow of O<sub>2</sub> + O<sub>3</sub> gas produced at room temperature in an atmospheric plasma generator, power = 300 W (Masaryk University, Czech Republic), input O<sub>2</sub> flow 5L/min. After 3 hours of polymer activation concentration of peroxides determined by 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 follow 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 20mm diameter. Press plates temperature was 110°C and moulding time 3 minutes, specific plates pressure 3 N/mm<sup>2</sup>.

The concentration of peroxide groups bonded to RXP was determined by volumetric analytical method based on iodine oxidation. The procedure was modified for non-aqueous systems. The saturated KI acetic anhydride solution was used as reagent and the released iodine was determined by titration. The total peroxide oxygen content in RXP sample after 3 hours 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<sup>-1</sup>) 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. Deionized 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 (Novák et al. 2013).

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.

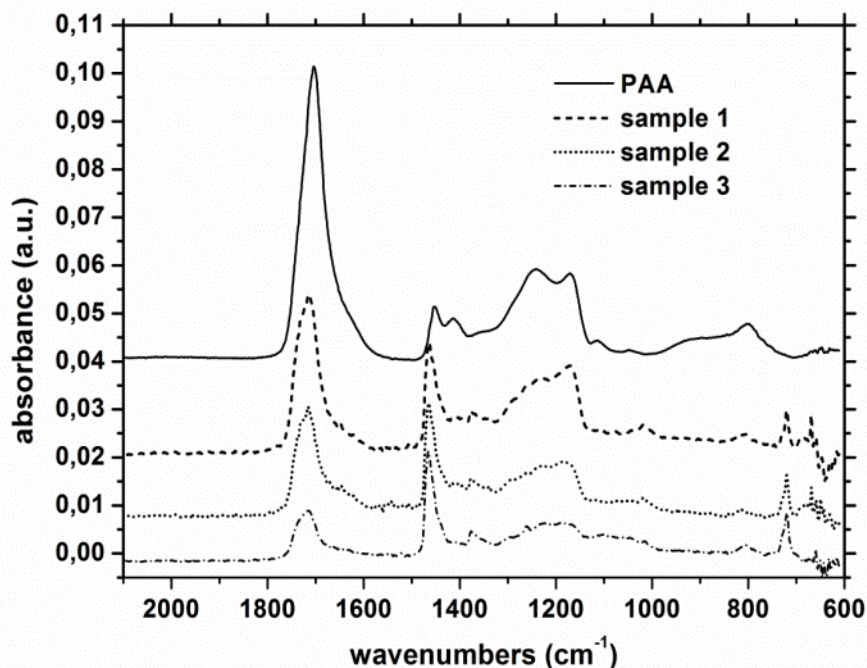
## RESULTS AND DISCUSSION

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 (region of 2800 - 3000  $\text{cm}^{-1}$ ), typical for PE. The bands for C-O and COC (1715 and 1170  $\text{cm}^{-1}$ , respectively) indicate the presence of PAA chains. The ratio of the FTIR absorbance intensities for acid carbonyl compounds at 1715  $\text{cm}^{-1}$  and the reference band at 1464  $\text{cm}^{-1}$  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.

The way how to increase 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 higher monomer concentration (Table 1). An effort to increase the degree of RXP grafting is directed to solvent free reaction. 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 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. PC of SFE for initial RXP reached the value 2.3  $\text{mJ/m}^2$  and after grafting with AA 14.1% PC of SFE increased to 3.6  $\text{mJ/m}^2$  and/or 3.9  $\text{mJ/m}^2$  (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 is temperature resistance higher: with AA 14.1% is PAFT = 77 °C and with AA 26.8% is PAFT = 78 °C. The values of temperature resistance in shear for unmodified RXP and RXP grafted are similar and no differences were observed.



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

**Table 1.** Table 1 presents batch components concentration and grafting efficiency for RESINEX PE RXP 1502 grafting in molten state. Polymer activated 3 hours with ozone-oxygen mixture. The oxidative gas was formed during oxygen flow through atmospheric plasma generator, power = 300W, gas flow = 5L/min, room temperature. Reaction proceeds in the kneading chamber 30 ml, 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 its polar components of RXP-g-AA films.

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

1. YALVAC S., KARJALA T., O'BRYAN E. Adhesives & Sealants Industry, 2005, vol. 12, p. 34.
2. PATEL J. B., EODICE A. K., LOW Y G. Low application temperature hot melt adhesive. PCT/US 2010/043804 (2010).
3. LAZÁR M., RADO R., PAVLINEC J., 1961. Grafting of methyl methacrylate to polypropylene and polyethylene. Journal of Polymer Science, vol. 53(158), p. 163-171.
4. BUCHENSKA J., 2002: Polypropylene fibers grafted with poly(acrylic acid). Journal of Applied Polymer Science, vol. 83(11), p. 2295-2299.
5. KAUFMAN M. S. Radical-Mediated Modification of Polyolefins, Thesis, Queen's Univ. Kingston, Ontario, Canada, May 2008, p. 1.
6. NOVÁK, I., POPELKA A., LUYT, A. S. et al., 2013: Adhesive properties of polyester treated by cold plasma in oxygen and nitrogen atmospheres. Surface and Coatings Technology, vol. 235, p. 407-416.
7. NOVÁK, I., POLLÁK, V., CHODÁK, I., 2006: Study of Surface Properties of Polyolefins Modified by Corona Discharge Plasma. Plasma Processes and Polymers, vol. 3(4-5), p. 355-364.
8. ZAKI A.J.J.I., 2015: Grafting of polyethylene films with N-vinyl imidazole and acrylic acid for potential use in wastewater treatment. Revue Roumaine de Chimie, vol. 60(9), p. 867-873.
9. WANG H., BROWN H. R., 2004: UV grafting of methacrylic acid and acrylic acid on high-density polyethylene in different solvents and the wettability of grafted high-density polyethylene. II. Wettability. Journal of Polymer Science Part A: Polymer Chemistry, vol. 42(2), p. 263-270.
10. STEFFENS G.C.H., NOTHDURFT L., BUSE G., THISSEN H., HÖCKER H., KLEE D. 2002, vol. 23, p. 3523.
11. LAZÁR M., PAVLINEC J., MAŇÁSEK Z., MIČKO M., BEREK D., 1963: Ozonation of Atactic Polypropylene. Rubber Chemistry and Technology, vol. 36(2), p. 527-531.
12. RICHAUD, E.; FARCAS, F.; FAYOLLE, B.; AUDOUIN, L.; VERDU, J.,: 2006: Hydroperoxide titration by DSC in thermally oxidized polypropylene. Polymer Testing, vol. 25(6), p. 829-838.

**Streszczenie:** *Poprawa polarności poprzez szczepienie kopolimeru metalocenowego etylenu i oktenu kwasem akrylowym. Poliolefiny metalocenowe (MePO) szczepiono w stanie stopionym w celu zwiększenia ich swobodnej energii powierzchniowej i właściwości adhezyjnych. Zastosowano modyfikację MePO ozonem do zainicjowania tworzenia nadtlenków na powierzchni polimeru, a następnie stopiony polimer szczepiono kwasem akrylowym. Wydajność szczepienia polimeru w stanie stopionym była wysoka i wahała się między 0,77 a 0,97.*

Corresponding author:

Ing. Igor Novák, PhD.  
Polymer Institute Slovak Academy of Sciences  
Dúbravská cesta 9  
845 41 Bratislava  
Slovakia  
igor.novak@savba.sk

ORCID ID:

Novak Igor                      0000-0002-0568-7847