

## SYNTHESIS AND EVALUATION OF MODIFIED POLYETHYLENE WAX APPLIED AS DISPERSANT IN RUBBER BITUMEN COMPOSITES

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Grain rubber obtained from waste tyre has become one of the most important bitumen modifiers nowadays, but rubber precipitation from bitumen can cause problems during utilization. In our experimental work additives were synthesised as dispersant for rubber bitumen composites. Raw material was polyethylene wax (PEW) obtained from mild thermal cracking of polyethylene waste. The synthesis was a copolymerisation of olefins and maleic-anhydride. During the products evaluation the main analytical method was Fourier transform infra-red (FT-IR) spectroscopy. There were significant differences between the characteristic of raw material and synthesised products. The dispersant effect of the additives was studied in rubber-bitumen composites. All additives increased the stability of rubber-bitumen composites. From the results of the experiments it was stated that the modified polyethylene wax obtained from polyethylene waste can solve the instability problem of rubber-bitumen composites.

**Keywords:** polyethylene wax, rubber-bitumen, dispersant additive

### Introduction

The free-radical grafting of maleic anhydride (MA) onto polyolefins in presence of initiator was the topic of several researches in the last decades. These investigations resulted that the chemically modified polyolefins can be used in polymer blends and composites to improve the chemical and mechanical properties [1-4]. Several successful polyolefin grafting methods have been developed, the functionalization of polyolefins can be achieved either in a melt process or in a solution process [5-7]. In a solution process the polyolefins are dissolved in a suitable solvent at reaction temperature (100–200°C), than MA and an initiator (usually peroxide) are added into the reaction mixture. This method is relatively complex, but it is advantageous because the individual molecular structures of grafted polyolefins can be achieved easier with different feeding order of reactants. There are methods which can increase the rate of grafting by adding another co-monomer into the reaction mixture [8-9]. Ying et al. studied the grafting of MA onto polypropylene in the presence of styrene. They investigated the graft degree of MA at different rate of monomers. It was established that styrene reacts with MA to form styrene-maleic-anhydride copolymer during the grafting process and it leads to improving the graft degree of MA [10].

In most experiments the grafting of MA onto polyethylene and polypropylene have been studied and there are studies about modifying of polystyrene [11]

and polyolefin copolymers [12], too. However, the grafting of polyethylene wax (PEW) was not reported.

Aliphatic waxes can be produced with mild, thermal cracking of plastic wastes (polyethylene, polypropylene). Lots of researches suggest that the best utilisation way of the cracking products is the energetic application, so the aim of these investigations is to achieve the biggest yield of liquid product (light oils). However the yield of C30+ hydrocarbons can be considerable at mild reaction parameters [13-14]. The utilisation of this heavier fraction is less described in the literature (e.g. incineration).

An alternative way for utilisation of residue obtained from waste plastic cracking is blending into bitumen. It is well known that polymers have been used as bitumen modifiers to increase mechanical properties [15-17]. There are lots of studies about bitumen modification with various polymers. Elastomers, plastomers and moreover waste plastics and rubbers were used in these experiments. Grain rubber obtained from waste tyre has become one of the most important bitumen modifiers nowadays. However the inhomogeneity of rubber-bitumen composites is a considerable problem during the utilisation [18]. The precipitation of rubber from bitumen can affect the product quality, to avoid precipitation stirred storage tanks were used. An other solution of this problem that functionalised polyolefin wax by maleic-anhydride is added into rubber-bitumen composite. Therethrough the modified PEW works in the rubber-bitumen composites as dispersant additives.

The aim of this paper was to synthesize such modified polyethylene wax which can be used in rubber-bitumen

composites as dispersant additives. Raw material of the synthesis was C30+ hydrocarbon fraction obtained from thermal cracking of polyethylene waste. A further aim of this study was to analyse the grafted products and to evaluate the dispersant effect of the additives in rubber-bitumen composites.

## Experimental

### Materials

Polyethylene wax was produced by thermal cracking of polyethylene waste derived from package industry. The thermal cracking carried out in a horizontal tube reactor system at 530 °C reaction temperature. The produced PEW was analysed and following results were given: I/Br number 45.9 g I/ 100 g PEW; olefin content 42.8%; Mw 990 g/mol. The used reagents for the grafting reaction are monomers (maleic-anhydride (MA), n-decene, styrene), initiator (di-tertiary-butyl-peroxide (DTBP)) and solvent (xylene). Main properties of these materials are shown in *Table 1*. The synthesized additives were evaluated in rubber bitumen composite. The composites were prepared by mixing of grain rubber with two types of bitumen in appropriate amount. *Table 2* shows the properties of these bitumens, while the grain rubber has the following properties: grain size <2 mm; moisture 0.5 w/w%; free from metal contamination and it was grained by water jet system.

*Table 1:* Properties of the used materials

Properties	MA	n-decene	styrene	DTBP
$d_4^{20}$ g/cm <sup>3</sup>	–	0.745	0.909	0.796
Refraction index	–	1.4230	1.5463	1.3891
Molecular weight, g/mol	98.0	140.0	104.1	146.2
Boiling point, °C	200	170	145	–

*Table 2:* Properties of the used bitumens

Bitumen	B160/200	B50/70
Softening point, °C	40	48
Penetration, 0.1 mm	190	51
Fraass breaking-point, °C	-15	-12
Dynamic viscosity 135°C, mPas	194	495
Dynamic viscosity 180°C, mPas	41	90

### Synthesis

A commercial solution grafting process was used to graft MA onto PEW. The reaction recipe was typically as follows: In a sealed vessel 420 g PEW was dissolved in xylene at 140 °C under stirring. After complete dissolution of PEW MA and DTBP were added and moreover in some cases styrene and n-decene were added as co-monomers. The xylene was removed from the grafted PEW by vacuum distillation. The product

was washed with boiling acetone and dried in vacuum at 80 °C for 12 h.

Three types of dispersant additives (modified polyethylene wax) were synthesized with this reaction recipe. In one case only MA was grafted onto the wax PEW/MA/DTBP (PE/1). In other cases besides of MA n-decene or styrene was used to increase the graft degree of MA on PEW. These co-monomers were added PEW/MA/DTBP/n-decene (PE/2) or PEW/MA/DTBP/styrene (PE/3).

The effect of dispersant additives was evaluated in rubber bitumen composites. These composites were prepared with a so called multistage method. This method means that the chemical dispersion of rubber and other additives in bitumen is followed by a mechanical shearing. In all cases the samples contained 15 w/w% grain rubber and the preparation parameters were fixed. Six different composition were produced: a commercial rubber-bitumen without any additives (RB), a composite with a reference additives (RB+R), three composite with the synthesized additives (RB+PE/1, RB+PE/2, RB+PE/3) and the non modified PEW was investigated in rubber-bitumen (RB+PEW). The reference additive was a styrene-butadiene-styrene copolymer, which was tested in a previous work [19].

### Analysis procedures

The molecular structure of the additives were determined by a Fourier Transform-Infrared (FTIR) technique with a TENSOR 27 type spectrometer (resolution: 4 cm<sup>-1</sup>, illumination: SiC Globar light, monochromator: KBr prism, detector: RT-DLaTGS type detector) in the 4000–400 cm<sup>-1</sup> wave number range. Opus5.5 software was used for the spectrometer control and the data processing.

Utilization properties of the prepared rubber-bitumen composites were tested by the following examinations: penetration (ASTM D 597), softening point (ASTM D 3695), elastic recovery (ASTM D 6084-04), Brookfield viscosity at 180°C (ASTM D 4402), storage stability (EN 13399).

## Results and discussion

### Infrared spectroscopy

The FTIR spectra of the pure PEW and the modified polyethylene waxes are shown in *Fig. 1*. Peaks in 3000–2800 cm<sup>-1</sup> wave number range are typical of the bond vibrations of saturated hydrocarbons. Moreover other typical groups of paraffin infrared bands can be seen in *Fig. 1*.

The wax obtained from the thermal cracking of polyethylene consisted paraffinic and olefinic hydrocarbons, these olefinic molecules were mostly  $\alpha$ -olefins. The  $\alpha$ -olefins molecules are more reactive than the other olefins or paraffin hydrocarbons, therefore

these molecules are advantageous in the MA grafting. The C–H deformation bond vibrations at region 1000–850  $\text{cm}^{-1}$  are typical of unsaturated hydrocarbons (Fig. 1). The band pair of vinyl group ( $\text{RHC}=\text{CH}_2$ ) appeared at 990 and 910  $\text{cm}^{-1}$  wavenumber, where the later band has double intensity. In case of vinylidene group ( $\text{R}_1\text{HC}=\text{CHR}_2$ ) two bands could be seen at 980 and 960  $\text{cm}^{-1}$ .

The comparison of the infrared spectrums of synthesized additives and the raw material showed significant differences. These differences confirm the reaction of PEW and MA, because new adsorption bands at 1795–1775  $\text{cm}^{-1}$  and at 1870–1850  $\text{cm}^{-1}$  can be assigned to grafted anhydride, which are due to symmetric ( $\nu_s\text{C}=\text{O}$ ) (strong) and asymmetric ( $\nu_{as}\text{C}=\text{O}$ ) (weak) stretching vibration of five members cyclic anhydrides [12], respectively. Appearing of peaks between 1140 and 1000  $\text{cm}^{-1}$  are the consequences of anhydride  $\nu_{as}\text{C}-\text{O}-\text{C}$  vibrations, moreover other typical anhydride bands can be seen at range 1300–1180  $\text{cm}^{-1}$  and 1050–900  $\text{cm}^{-1}$ . An other evidence shows the successful PEW grafting, because in case of the using

styrene co-monomer vibration bands can be observed, at 780–690  $\text{cm}^{-1}$  which are typical of aromatic hydrocarbons.

Fig. 2 shows the enlarged infrared spectrum of product and PEW at 1600–1900  $\text{cm}^{-1}$  wave number range. In the spectrum of additives at 1870–1850  $\text{cm}^{-1}$  and 1795–1775  $\text{cm}^{-1}$  the grafted MA content can be observed on the PEW. Intensity of both peaks show that the grafting rate increased with the using of co-monomers. In case of pour MA grafting the grafting rate was the lowest and styrene makes the largest improvement in the grafting ration. In the literature it was presented that the co-monomer enhanced the MA grafting on to polymers [10]. The maximum intensity at 1775  $\text{cm}^{-1}$  indicates that the MA attached to the styrene monomers to form short oligomers and after that this oligomers grafted onto the PEW. Li et al. [10] reported that the FTIR spectrum has maximum intensity at 1770  $\text{cm}^{-1}$  than single MA grafting occurred, in case of the maximum intensity at 1790  $\text{cm}^{-1}$  the polymeric MA grafting was the main reaction. In our FTIR spectra the maximum intensity of vibration bands appeared between 1790 and 1770  $\text{cm}^{-1}$  wave number.

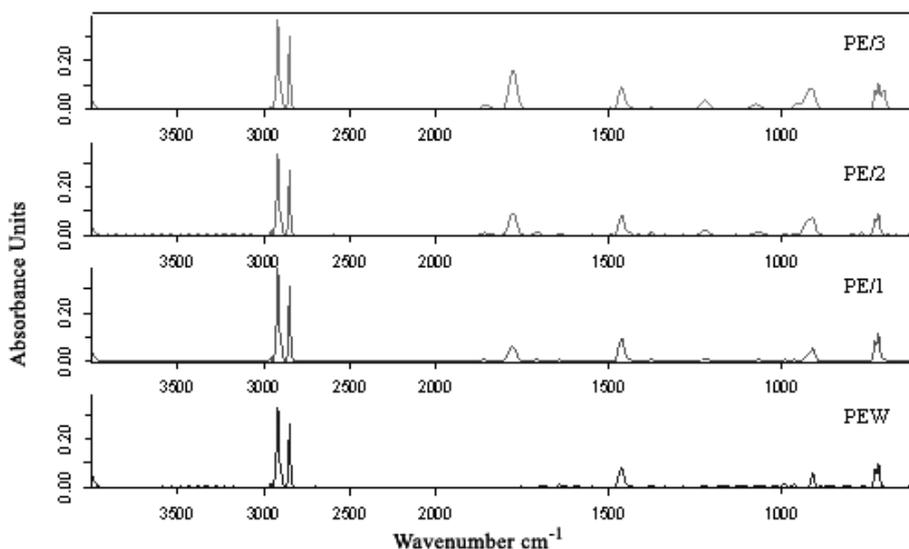


Figure 1: FTIR spectra of PEW and the grafted PEW

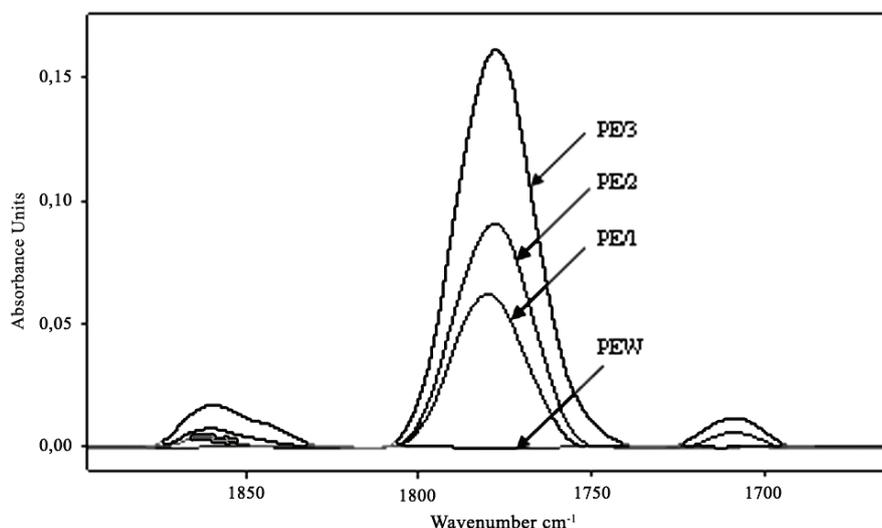


Figure 2: FTIR spectra of additives at region 1900–1650  $\text{cm}^{-1}$

*Analysis of rubber bitumen composites*

*Softening point*

Fig. 3 shows the softening point data of the rubber bitumen samples. In all cases the dispersant additives decreased the softening point of the composites, although this effect was not significant. The softener effect of the PEW and the additives can be advantageous property, because adding small amount from them can modify the rubber bitumen composition.

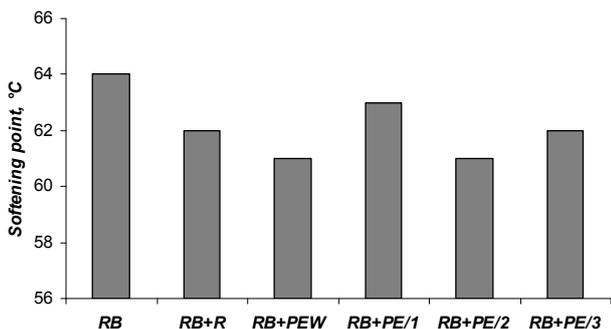


Figure 3: Softening points of rubber bitumen composites

*Penetration*

It can be seen in Fig. 4 that the additives and the PEW increased the penetration of the rubber bitumen samples. The properties of rubber bitumen can be modified with the synthesized additives. Usually the penetration data are in connection with the softening point, but in this case the additives did not affect significantly the softening point of the rubber bitumen composites, however the penetration was increased with the modification.

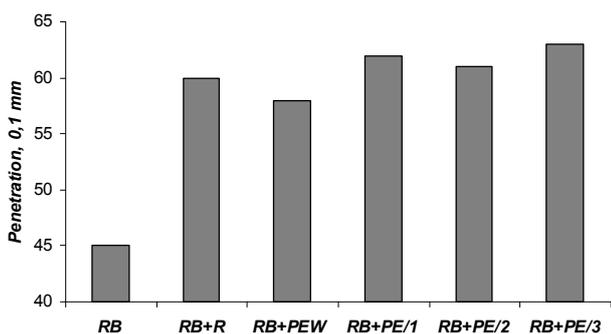


Figure 4: Penetration data of rubber bitumen composites

*Storage stability*

The best way to evaluate the efficiency of the dispersant additives is the studding of the storage stability properties of the samples. In all cases the additives improved the storage stability. Quality requirements of the rubber bitumens consist the storage stability and the maximum limit is 5 °C differences between upper and lower layer

softening point. In case of PEW the precipitation of rubber from the bitumen was occurred, that can be seen in Fig. 5. However it is considerable that the storage stability of PEW modified rubber bitumen was the same as the original rubber bitumen, so the PEW did not decreased this property. All of the additives had similar increasing affect as the reference additive, therefore the 5 °C limit could be maintained.

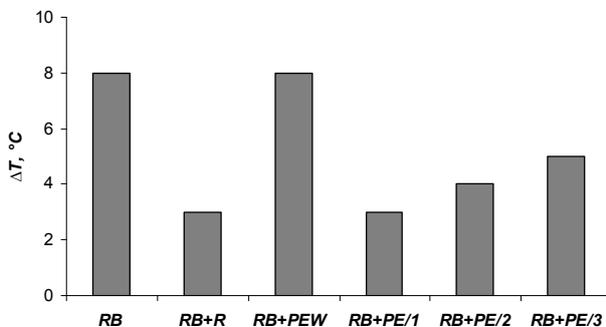


Figure 5: Storage stability of rubber bitumen composites

*Temperature dependence of viscosity*

It is beneficial to determine the temperature dependence of viscosity of rubber bitumens, because it is important for the further utilisation of the products. Fig. 6 shows the temperature-viscosity characteristics of the rubber bitumen samples. According to practical experiences 500 mPas viscosity is suitable for the bitumen mixing in the industry at 180 °C. The softening affect of PEW and the additives appeared at this property too, because the original rubber bitumen sample has 1020 mPas viscosity than after modification this decreased to 520–610 mPas.

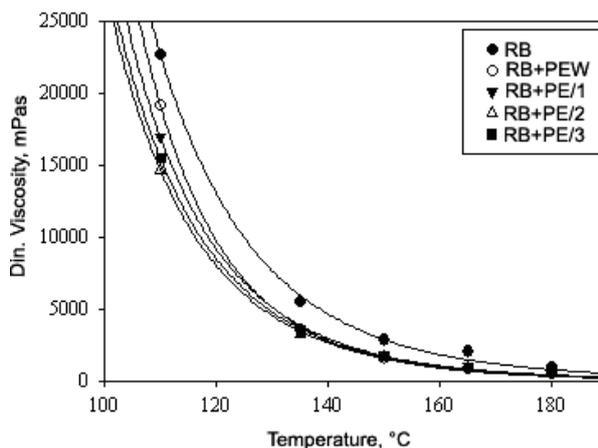


Figure 6: Temperature-viscosity characteristic of rubber bitumen samples

*Elastic recovery*

Elastic recovery shows the flexibility properties of rubber bitumens, the most flexible composite has the biggest relaxation time. Fig. 7 shows the elastic recovery results of the samples. According to Fig. 7 it can be established

that the rubber gives the flexibility of the composite, because the behaviour of the curves are similar.

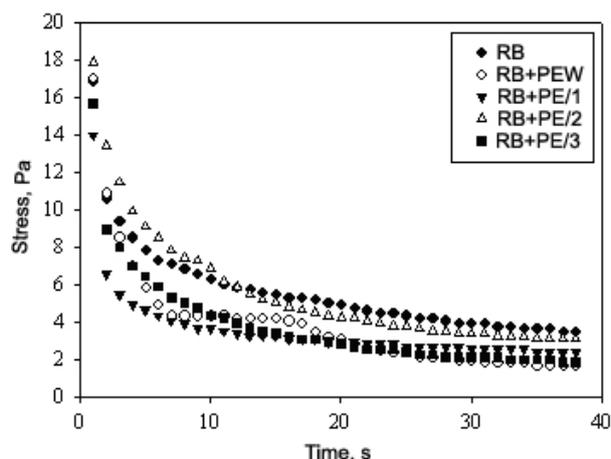


Figure 7: Elastic recovery of the rubber bitumen composites

### Conclusion

In our experimental work additives were synthesised as dispersant for rubber bitumen composites with copolymerisation of olefins and maleic-anhydride. Raw material was polyethylene wax (PEW) obtained from mild thermal cracking of polyethylene waste. The infrared spectrum of PEW and the synthesised additives was determined at 600–4000  $\text{cm}^{-1}$  wavenumber range and it was stated that there were significant differences between the characteristic of polymers, so the grafting of MA onto PEW was successful. The dispersant effect of the additives was studied in rubber-bitumen composites. All additives increased the stability of rubber-bitumen composites and other properties were increased. Advantageous softening points and viscosity data could be achieved with the using of additives. The PEW increased these properties too. From the results of the experiments it was stated that the modified polyethylene wax obtained from polyethylene waste can solve the instability problem of rubber-bitumen composites.

### REFERENCES

- BOUCHER E., FOLKERS J. P., HERVET H., LEGER L., CRETON C.: Effects of the formation of copolymer on the interfacial adhesion between semicrystalline polymers. *Macromolecules* (1996) 29, 774-782.
- KUDVA R. A., KESKKULA H., PAUL D. R.: Morphology and mechanical properties of compatibilized nylon 6/polyethylene blends. *Polymer* (1999) 40, 6003-6021.
- QIU W. L., ZHANG F. R., ENDO T., HIROTSU T.: Preparation and characteristics of composites of high-crystalline cellulose with polypropylene: effects of maleated polypropylene and cellulose content. *J Appl Polym Sci* (2003) 87, 337-345.
- QIU W., ENDO T., HIROTSU T.: A novel technique for preparing of maleic anhydride grafted polyolefins. *J Appl Polym Sci* (2005) 41, 1979-1984.
- RUSSELL K. E.: Free radical graft polymerization and copolymerization at higher temperatures. *Prog Polym Sci* (2002) 27, 1007-1038.
- MACHADO A. V., COVAS J. A., VAN DUIN M.: Effect of polyolefin structure on maleic anhydride grafting. *Polymer* (2001) 42, 3649-3655.
- KELAR K., JURKOWSKI B.: Preparation of functionalised lowdensity polyethylene by reactive extrusion and its blend with polyamide 6. *Polymer* (2000) 41, 1055-1062.
- CARTIER H., HU G. H.: *J Polym Sci, Part A Polym Chem* (1998) 36(7), 1053-1063
- XIE X. M., CHEN N. H., LI S.: *Acta Polym Sin* (1999) 5, 527-530
- YING L, XU-MING X, BAO-HUA G.: Study of styrene-assisted melt free-radical grafting of maleic anhydride onto polypropylene. *Polymer* 42, (2001) 3419-3425
- HUA-MING LI, HONG-BIAO CHEN, ZHI-GANG SHEN, SHANGAN LIN: Preparation and characterization of maleic anhydride-functionalized syndiotactic polystyrene. *Polymer* (2002) 43, 5455-5461
- GRIGORYEVA O. P., KARGER-KOCSIS J.: Melt grafting of maleic anhydride onto an ethylene-propylene-diene terpolymer (EPDM). *Eur. Polymer J.* (2000) 36, 1419-1429
- PREDEL M., KAMINSKY W.: *Polym Degrad Stab* 70 (2000) 373-385
- ANGYAL A., MISKOLCZI N., BARTHA L.: *J. Anal. Appl. Pyrolysis* 79 (2007) 409-414
- BECKER Y., MÉNDEZ M. P., RODRÍGUEZ Y.: Polymer modified asphalt, *Vision tecnologica*, 9, 1, 2001
- XIAOHU LU, ISACSSON U.: Low-temperature properties of styrene]butadiene]styrene polymer modified bitumens. *Construction and Building Materials* 12 (1998) 405-414
- HINISLIOGLU S., AGAR: Use of waste high density polyethylene as E. bitumen modifier in asphalt concrete mix. *Materials Letters* 58 (2004) 267-271
- NAVARRO F. J., PARTAL P., MARTÍNEZ-BOZA F., GALLEGOS C.: Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. *Fuel* 83 (2004) 2041-2049
- BÍRÓ SZ., GEIGER A., BARTHA L., DEÁK GY., MISKOLCZI N.: Crumb rubber as active bitumen modifying agent, *WasteTech-2005 Congress*, 31 May