

The Influence of Magnesium Hydroxide Morphology on the Mechanical and Visco-elastic Properties of Flexible Thermoplastic Polyolefin

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ABSTRACT

This study deals with the mechanical and visco-elastic behaviour of Flexible thermoplastic polyolefin (FTO) with different amount of halogen-free flame retardants.

In this work, polypropylene and propylene-based elastomer were compounded with two types of magnesium hydroxide (MDH) at different loading. The crystalline structure of the MDH was characterized by X-ray diffraction. Scanning electron microscopy was used to determine particle size of MDH used in the polymer composite and phase morphology. Mechanical properties as tensile yield stress and flexural modulus of polymer composites were measured. The influence of particle size, concentration and morphology of filler MDH on the visco-elastic behaviour of the prepared composites were studied.

INTRODUCTION

Flexible thermoplastic polyolefin mixture is of a polypropylene (PP) or a polyethylene (PE) with an elastomer, such as, ethylene-propylene rubber (EPR), ethylene-propylene-diene rubber (EPDM). [1–3] While the polypropylene provides tensile strength and increased heat resistance, the elastomer provides flexibility, extensibility and good self-hot tack. Since it is well known that FTO are a highly combustible materials, it is usually highly desirable to improve its flame retardancy and reduce the emissions of smoke and poisonous gases.[4,5] To achieve the required flame retardant grade of low smoke and non-toxic

character, metal hydroxides, e.g. MDH, could be added (generally in high filling amount, up to 60% mass fraction). However, high filler loading leads always without exception to a deterioration of the mechanical and visco-elastic performances in the composites. [6–8]

The main goal of the work reported in this paper was to characterise mechanical properties of pressed flexible thermoplastic polyolefin sheets filled with different amount of magnesium hydroxide (FTO/MDH). Beside this, the visco-elastic behaviour of prepared composite systems was evaluated with respect to particle sizes, concentrations and morphologies of utilised fillers.

EXPERIMENTAL

Material

Propylene-based elastomer (PBE) Versify 3401 (Dow Chemical Company, Germany) with density of 0.87 g/cm^3 and melt flow index of 8.0 g/10 min (measured at $230 \text{ }^\circ\text{C}$ under 2.16 kg) and polypropylene random copolymer TOTAL PPR 6298 (Total Petrochemicals & Refining S.A./N.V., Belgium) with density of 0.902 g/cm^3 and melt flow index of 9.0 g/10 min (measured at $230 \text{ }^\circ\text{C}$) in various blends were mixed with two types of magnesium hydroxide $\text{Mg}(\text{OH})_2$ used as halogen free flame retardant additives. Magnesium hydroxide of purity higher than 98% and specific surface area (BET) $6\text{-}10 \text{ m}^2/\text{g}$ marked further in the text as MDH_A (Duslo a.s., Slovakia) was utilized without surface treatment, while the second one with

maximum purity of 95% marked as MDH_B (Europiren B.V., The Netherlands) contained 1.5 wt.% of stearic acid as a surface treatment.

Compounding and specimen preparation

Pellets of the PP and PBE and MDH powder fillers (dried before processing) were compounded by the help of twin screw extruder (Labtech Engineering company, Thailand) with modular co-rotating screws of 26 mm in diameter and length of 48D. Temperature profile of compounder was set from 165 °C (the first heating zone) to 220 °C (the die) and used operation speed of screws was 330 rpm. The polymeric melt strings leaving the die were cooled down in water bath tempered to 15°C, dried with airflow and cut into the pellets. In this way, were prepared various FTO/MDH blends, detailed composition is defined in the Table 1, for comparison mechanical and visco-elastic properties. After compounding process, the samples were produced by the hot press (Fontijne LabEcon 300, Netherlands); this involved preheating of the blends in the mold at 210°C for 2 minutes, followed by compression for 3 minutes and subsequent cooling at temperature of 25°C both under pressure of 200 kPa. In this way were prepared sheets of the thickness 1 and 4 mm.

Table 1. Composition of samples

Code of sample	Unit	PBE	PP	MDH A or B	Ratio PP/PBE
FTO-1	% w/w	0.75	0.25	0	0.33
FTO-2	% w/w	0.70	0.30	0	0.43
FTO-3	% w/w	0.55	0.45	0	0.82
FTO/MDH_15	% w/w	0.65	0.20	0.15	0.31
FTO/MDH_35	% w/w	0.45	0.20	0.35	0.44
FTO/MDH_55	% w/w	0.25	0.20	0.55	0.82

CHARACTERISATION

Structural characterisation of filler

The crystalline structure and purity of the magnesium hydroxide obtained was characterized by X-ray diffraction (XRD), on a Rigaku Miniflex 600 X-ray diffractometer (Rigaku Europe SE, Germany) operated at 40 kV and 15 mA. Nickel-filtered Co Kα1 radiation (λ = 1.7889 Å) was applied over a 5° to 90° angular region, with the step size and rate set to 0.02° and 10°/min., respectively. The crystallite size (d_{diffr}) of the samples was estimated using the Scherrer equation:

$$d_{diffr} = \frac{0.9\lambda}{\beta \cos\theta} \cdot 100 \quad (1)$$

This involved gauging the line-broadening (β, full width at half-maximum, corrected by the response of the instrument) of the main peak intensity for magnesium hydroxide (001), where λ is the wavelength for Co Kα1 radiation and 2θ is the Bragg angle. Phase composition was evaluated via Rigaku Miniflex 600 software, utilizing the normalized RIR method. The RIR is the ratio between the integrated intensities of the peak of interest and that of a known standard.

The micrographs of the flame retarders were taken on scanning electron microscopes Nova NanoSEM 650 (FEI, Czech Republic). Foregoing coating of examined samples comprising a thin layer of gold/palladium had been applied by a SC 7640 sputter coater (Quorum Technologies, UK).

Mechanical properties of composition

Tensile and three point flexural tests were carried out on a Testometric universal-testing machine M 350-5CT (Testometric Co. Ltd., England), equipped with a load cell of 300 kN. The tensile properties of the polymer composites testing specimens were investigated using a crosshead speed of 50 mm/min and the length of the gauge

equalled 50 mm. The dumb-bell-shaped specimens (Type 2, specified according to the standard ISO 527) of the thickness 1 mm were cut out from prepared sheets by the means of a punching press. In total, six specimens of each material were tested. Five individual samples of dimensions 80 mm x 10 mm x 4 mm (according to the standard ISO 178), for all the compositions, were milled out from the 4 mm pressed sheets using CNC milling machine Charly4U (Mecanumeric Co., Italy) in order to define the flexural strength and modulus. A span of 64 mm was applied, pertaining to a span to depth ratio of 16:1. The samples were positioned in the middle of the supports, and the device was operated at a speed of 2.0 mm/min under ambient temperature conditions.

Visco-elastic behaviour

Visco-elastic measurements of prepared polymer blend FTO and FTO/MDH were performed using a rotational rheometer MCR 502 (Anton Paar, Austria) with a plate-plate geometry in oscillatory mode at 210 °C. Firstly, amplitude sweep measurements were performed in order to define linear visco-elastic region (LVE). Subsequently, the frequency sweep measurements were carried out in frequency range 0.1–100 Hz using strain values of 0.1%.

RESULTS AND DISCUSSION

XRD of filler powders

Powder XRD pattern of the used fillers is shown in Figure 1. All diffraction peaks for filler MDH_A are characteristic for the hexagonal $\text{Mg}(\text{OH})_2$ Brucite structure and they are in a good agreement with the International Center for Diffraction Data database ICDD entry 01-071-5972 (see Fig. 1a). On the other hand, XRD data of the powder MDH_B (presented in Fig. 1b) shows the presence of other substances, where the XRD pattern corresponds to

residues of kaolinite, calcium carbonate, magnesium carbonate and calcium magnesium carbonate. The probable reason why MDH_B contains other substances is the way of preparation of the powder. While the MDH_A was most likely prepared from magnesium silicate ore via MgCl_2 and MgO by Aman process [7], the MDH_B could be mechanically milled from MgCl_2 brine and lime or dolomite lime. The diffraction lines from (001), and (100) planes in $\text{Mg}(\text{OH})_2$ that can be found in the diffractograms at 2θ angle 21.86° and 38.49° were used for diffracting area size d_{diff} estimation via the well-known Scherrer's method. The estimated crystallite sizes are about 45 nm for MDH_A and 62 nm for MDH_B.

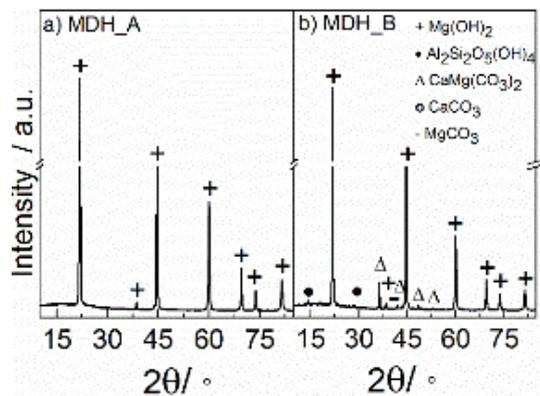


Figure 1 XRD pattern of the samples a) MDH_A, b) MDH_B

SEM of fillers and polymer composites

In the Figure 2 SEM images comparing shape and size of MDH microparticles, dispersion and distribution of MDHs and PP in FTO blends are presented. Figure 2a demonstrates regular hexagonal shape of MDH_A and narrow particle size distributions having the diameter of microparticles up to 5 μm and thickness in hundreds of nanometers. On the other hand, sample MDH_B (Figure 2b) has irregular shape of microparticles having larger particle size distribution compare to MDH_A. Obviously many of MDH_B powder microparticles are bigger than 10 μm .

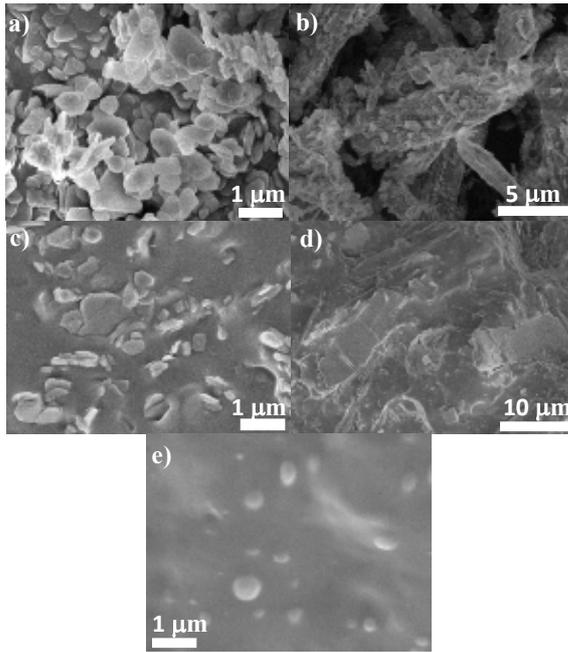


Figure 2 a) MDH_A, b) MDH_B, c) FTO/MDH_A_55, d) FTO/MDH_B_55, e) FTO_3

A good wettability and particles distribution of MDHs in the polymer at a 55 wt.% loading could be judged in Figure 2c and 2d. Evidently, it is clear that the compounding process did not changed the morphology of the fillers. Finally, phase morphology of PP-PBE in FTO is shown in Figure 2e. Spherical particles of PBE having globular shape with diameter about 1 μm or smaller.

Mechanical properties of polymer composites

Flexural tests of samples were performed according to the ISO 178 standard at a speed 2 mm/min. Trend of flexural modulus of FTO and FTO/MDH with changed ratio of PP/PBE and MDH is displayed in Figure 3a. It could be seen that flexural modulus grows with increasing ratio PP/PBE as well as with level of MDH. The significant impact on flexural modulus of polymer blends has obviously high concentration of used MDH, namely MDH_A has higher stiffening effect on polymer matrix. Flexural modulus of

particulate polymer composites depends on the interfacial adhesion between the polymer and filler and the deformability of the polymer matrix under an external force. It means there exists stronger interfacial bonding between the MDH_A particles and FTO matrix relating to smaller particle size.

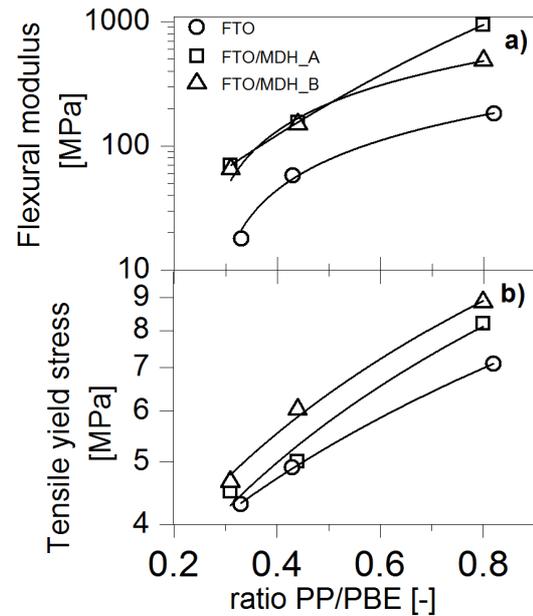


Figure 3 Flexural modulus and tensile yield stress of the samples

Figure 3b exhibit tensile yield stress of samples FTO and FTO/MDH. The tensile yield stress is important properties of material, since it gives information on the maximum allowable load without considerable plastic deformation. The tensile yield stress is increased with increases ratio PP/PBE and MDH. Contrary to modulus values, the tensile yield stress is only insignificantly changed with increased loading level. Definitely higher effect on tensile stress has increasing amount of PP used in FTO.

Visco-elastic flow properties

Figure 4 and 5 shows the variation of the storage modulus, loss modulus and complex

viscosity values of the three evaluated FTO blends (PP/PBE ratio of 0.33, 0.43, and 0.82) and their composites with three different filler concentration (15, 35 and 55 wt.%) of two MDH types (MDH_A, MDH_B) defined in angular frequency range from 0.01 to 100 Hz at 210°C.

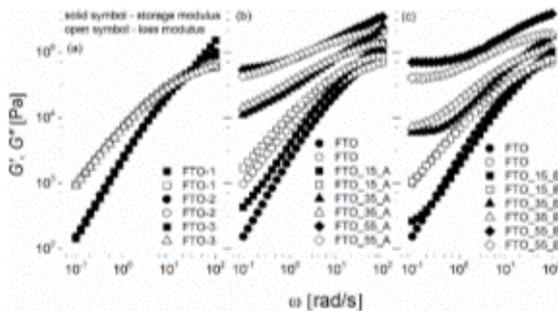


Figure 4 The log-log dependence of the G' and G'' on the frequency at 210°C for samples with various PP/PBE ratio (a) and various concentration of MDH (b), and (c)

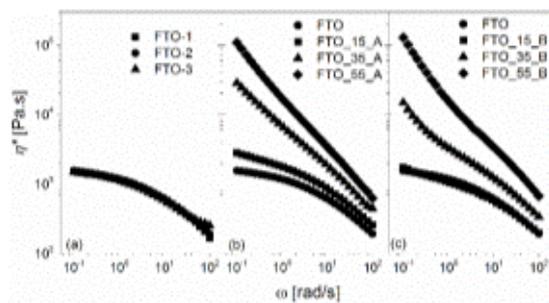


Figure 5 The log-log dependence of the η^* on the frequency at 210°C for samples with various PP/PBE ratio (a) and various concentration of MDH (b), and (c)

In general, it could be seen that the values of dynamic moduli G' and G'' , as well as complex viscosity η^* , as a function of frequency are almost unchanged with the variation of PP/PBE ratio. On the other hand, increasing amount of the filler concentration significantly increase both the modulus and viscosity level.

Comparing influence of filler MDH_A and MDH_B, it is obvious that several differences could be defined. While the loss

and storage moduli do not change significantly for low concentration of MDH_B (15 wt.%), there is visible increase of G' and η for the same amount of MDH_A having smaller filler size (higher surface area). In addition, more meaningful increase of the visco-elastic properties are determined for all other concentration of MDH_A. (compare Figure 4b and 4c, and 5b and 5c). Further, it could be seen that G' and G'' for higher concentration (35 and 55 wt.%) of MDH_A is almost equivalent for whole frequency range, while higher level of G' was determined for MDH_B concentration of 35 wt.% contrary to higher level of G'' for concentration of 55 wt.%.

Obviously, it could be highlighted that the increasing amount of filler concentration in tested composite decrease the change in dynamic moduli contrary to increase change of complex viscosity. Moreover, while linear change of moduli is found for MDH_A, there is S-shape curving of moduli dependencies for MDH_B. The appearance of nonterminal region for storage modulus in low frequency could be explain as an indication of three-dimensional filler network formation in composites caused by filler-filler and polymer-filler interactions.

Regarding complex viscosity values, it could be stated that all tested composites behaves pseudoplastically. At lower frequencies, the complex viscosity is significantly increased by filler loading while at higher frequencies a different behaviour is observed. The behaviour of polymer melt is insignificantly influence by increasing ratio of PP/PBE. The complex viscosity of unfilled FTO melts, as well as the 15 wt.% MDH filled polymer systems, shows a Newtonian plateau in the low frequency region. On the other hand, no Newtonian flow region is found at low

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frequencies for the system containing 35 wt.% or 55 wt.% of MDH. For these highly filled FTO have MDH_A higher complex viscosity than systems filled MDH_B. The very high viscosity of FTO/MDH_A_55 as well as FTO/MDH_A_35 is connected with increased particle interaction and higher particle surface area due to the relatively small particle size (as seen in Figure 2).

CONCLUSION

In this study, effects of variations in ratio of PP/PBE in flexible thermoplastic polyolefin blends are compared together with different filling of composite prepared using twins screw extruder from FTO and two types of magnesium hydroxide filler via evaluation of the mechanical and visco-elastic properties. While the change in PP/PBE ratio insignificantly influence both mechanical and visco-elastic properties, they are significant influenced by the level of MDH filling. Namely, the highest effect on flexural modulus, storage and loss moduli and complex viscosity was determined for the highest filler loading (55 wt.%) of MDH_A, which could be explained as a reason of the biggest specific surface area of relatively small particles of MDH_A as was proved by SEM and XRD.

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