# Influence of various fire retardants on rheological behavior of polypropylene

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ABSTRACT

This contribution deals with effect of particle fire retardant fillers on the rheological properties of polypropylene. The prepared composites exhibit higher viscosity and storage modulus values, when compared to original neat polypropylene. Magnesium hydroxides plate-like particles contribute to an increase in rheological parameters more significantly than irregular particles of intumescent fire retardant system. A dependence of imaginary part of complex viscosity over its real part have been further plotted in order to investigate homogenity of the samples.

## INTRODUCTION

Particle filler is commonly used in plastics to enhance their applicability or due to economic reasons. One important property of plastics that has to be commonly provided by addition of some external filler is a flammability resistance. Conventional plastics, such as polyethylene or polypropylene (PP), have no intrinsic ability to supress their burning after their exposure to a fire and, thus, in order to fulfil demands for their utilization in many applications it is necessary to use fire retardants. Nowadays, there are efforts to use halogen-free fire retardants. Mainly nanofillers[1-3], and even aluminium hydroxide ($Al(OH)_3$; AH) or magnesium hydroxide ($Mg(OH)_2$; MH)[4] are often used as efficient fire retardants in polyolefins, however, good distribution of used nanofiller within the polyolefinic matrix is very challenging. Moreover, in the case of hydroxides another complications are arisen because for achievement of sufficient reduction in flammability, high loadings of particles have to be used. This affects mechanical performance together with rheological properties and processing abilities of the systems. Therefore, recently, there are efforts to find a synergistic effect between various types of fire retardants[5-7] in order to find novel effective systems with lower loadings of the fillers in the matrix. Another approach is a use of intumescent flame retardant (IFR) systems, which has gotten broad attention in last years. These systems are very efficient and need only loading up to 35 wt% (normally the loading is 20-25 wt%) to fulfil the most challenging limits. A combination of IFR systems with another fire retardants further enhance the resistance of fire, enables lower loading particles and, consequently, can provide economic benefits[8-10]. Chiu et al.[11] has confirmed the possibility to combine IFR systems together with MHs to obtain a composite with superior flammability resistance. The similar results were found by Qin et al., who combined an IFR system with nano-AH particles[12]. Unlikely solid particles such us AHs, MHs, nanofillers, *etc*., it has been reported that IFR systems can cause a reduction in storage modulus, $G'$, of PP due to plasticizing phenomenon and an increase in total free volume[13] or increase the

viscosity of the system only very slightly at high loadings (>25 wt%)[14].

Since, there is a lack of papers combining the IFR systems with MH or AH, and the information about rheology of such composites could not be found, the main goal of this study was to evaluate a possibility to use together IFR systems with MHs as an effective fire retardant system regarding the rheological properties of the composites.

## EXPERIMENTAL SECTION

### Materials

A commercial IFR system based on the ammonium phosphate and MH were used as supplied. As a PP matrix PP Hostalen H1022 was used.

### Composite preparation

The matrix was mixed together with filler using an internal mixer (Plastograph; Brabender W50 EHT PL, Germany) at 50 rpm at 200 °C for 4 min. Subsequently, the mixture was removed and put into the mixer for another 3 min.

The homogenized mixtures were moulded at 200 °C to create plates of a thickness ~1.6 mm that were further used for an investigation of rheological properties. The composition of prepared mixtures is defined in Table 1.

Table 1. The compositions of prepared PP mixtures with fire retardants (in wt%).

| Mixture | PP (wt%) | IFR (wt%) | MH (wt%) |
|---|---|---|---|
| **PP-0-0** | 100 | 0 | 0 |
| **PP-15-30** | 55 | 15 | 30 |
| **PP-10-45** | 45 | 10 | 45 |
| **PP-15-45** | 40 | 15 | 45 |
| **PP-20-45** | 35 | 20 | 45 |
| **PP-25-45** | 30 | 25 | 45 |
| **PP-15-60** | 25 | 15 | 60 |

### Characterization techniques

Scanning electron microscopy (SEM; VEGA II LMU, Tescan, Czech Republic) was used to observe morphology and size of the used fillers. Rheological measurements in oscillatory mode were performed using a rotational rheometer (MCR 502 Anton Paar, Austria) at 200 °C with a plate-plate geometry of a diameter 25 mm. Firstly, linear viscoelastic region was determined in order to define the strain value in elastic region that was further used (0.03 %) for the dynamic frequency sweep measurements in angular frequency, $\omega$, region 0.1 – 100 rad $s^{-1}$.

## RESULTS AND DISCUSSIONS

The used IFR system consists of particles of irregular oval-like shape with its longer axis of a size 10 μm (Fig. 1a). On the other

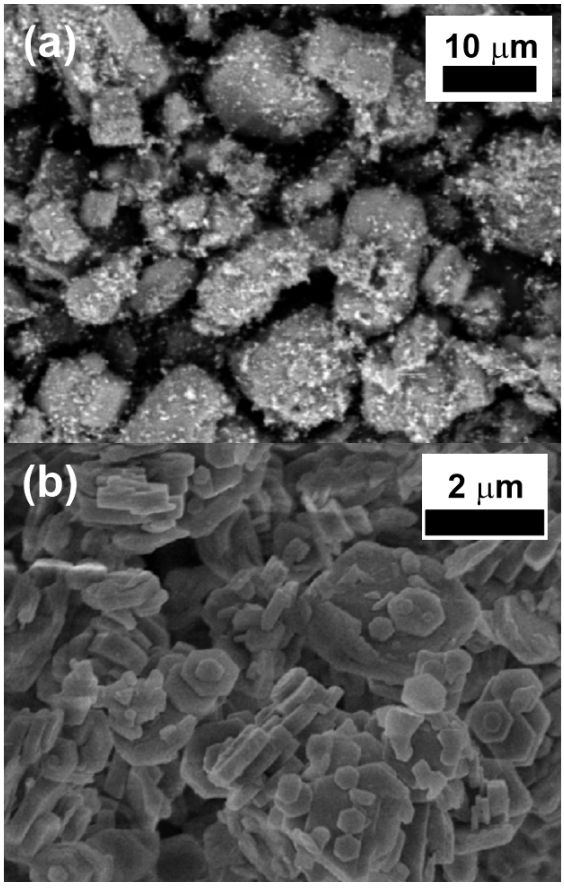


Figure 1. SEM images of used fire retardants: (a) the IFR system; (b) MH.

side, the used MH particles possess hexagonal plate-like morphology with high polydispersity and size up to and size up to 2 μm (Fig. 1b).

Influence of particle fillers on the rheological properties of prepared samples can be seen in Fig. 2 and Fig. 3. The particles of MH with plate-like morphology cause a significant increase in both $G'$ and complex viscosity, $\eta^*$, when compared to IFR systems. It is well-known that systems consisting of rod-like or plate-like particles generally exhibit higher drag in a dynamic regime at small strains due to higher energy needed for the orientation of the particles in velocity gradient direction[15], which can well explain the abrupt increase in $G'$ and $\eta^*$ of the sample PP-15-60. This increase can be further attributed to the higher interface forces between polymer matrix and the filler due to smaller size of the MH particles. At higher $\omega$ the rheological parameters of prepared composites are closer to the values of pure PP, which can be attributed to the movement of polymer chains, which was probably not so considerably affected by the particles[13], or to shear-thinning behaviour of plate-like filler

In Fig. 4 a dependence of imaginary part, $\eta''$, on the real part of the complex viscosity, $\eta'$, can be found. This dependence is often used to express miscibility and homogeneity of polymer composites or blends[16]. In the case of the good homogeneity of the sample, this "Cole-Cole" dependence should creates smooth the semi-circular shape. The dependences for PP-0-0 and PP-15-30 show smooth curves, unfortunately, the semi-circular shape is only slightly outlined.

To obtain full semi-circulars experiments at broader frequency range or at higher temperatures to provide higher mobility of chains should be performed. The sample PP-10-45 and PP-15-45 also shows regular curve predicting good homogeneity.

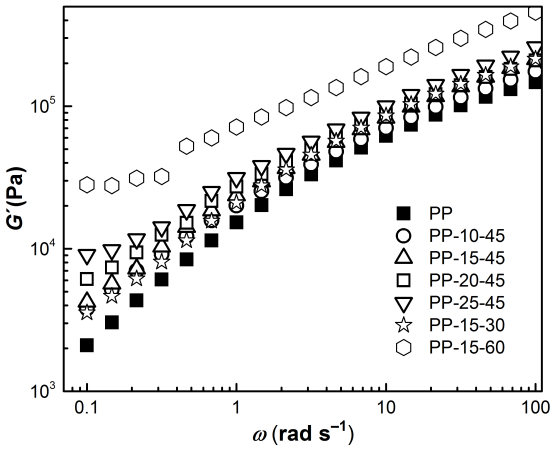


Figure 2. Dependence of storage modulus, $G'$, on angular frequency, $\omega$, for the prepared composite systems at 200 °C.

However, the rest of the samples (PP-20-45, PP- 25-45, PP-15-60) exhibit high distortion indicating lower homogeneity of the samples. In these higher loaded samples the particles can easily create agglomerates leading to spaces of inhomogeneity.

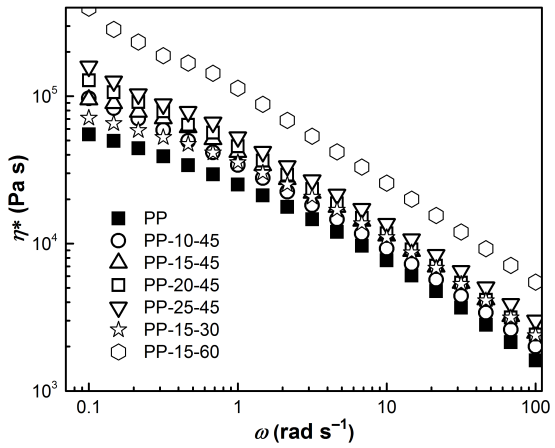


Figure 3. Dependence of complex viscosity, $\eta^*$, on angular frequency, $\omega$, for the prepared composite systems at 200 °C.

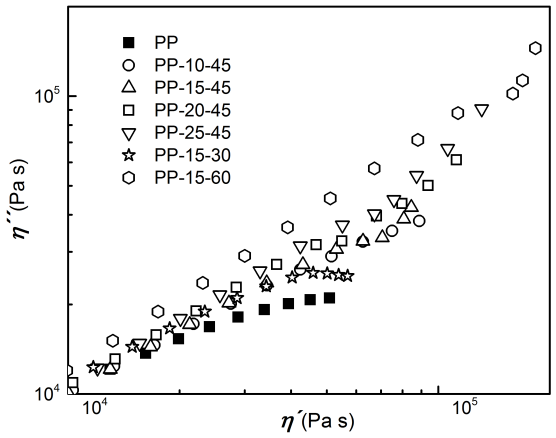


Figure 4. Cole-Cole plot of imaginary part, $\eta''$, of complex viscosity on its real part, $\eta'$, for the prepared composite systems at 200 °C.

## CONCLUSIONS

Rheological properties of prepared polymer composites based on polypropylene filled with magnesium hydroxide and intumescent flame retardant system have been investigated. The small plate-like shaped particles of magnesium hydroxide contributes to increase in complex viscosity and storage modulus of prepared composites more significantly than bigger irregularly shaped particles of intumescent fire retardant system. It was further shown that at lower loadings composites with good homogeneity can be obtain by plotting the dependence of imaginary part of complex viscosity over the real part. At higher loading of the particles, however, some distortion from semi-circular dependences have been observed probably due to a possible creation of agglomerates.

## ACKNOWLEDGMENTS

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