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Marcos Batistella, Belkacem Otazaghine, Rodolphe Sonnier, Carlos Petter, José-Marie Lopez-Cuesta.  
Fire retardancy of polypropylene/kaolinite composites. *Polymer Degradation and Stability*, 2016, 129,  
pp.260-267. 10.1016/j.polymdegradstab.2016.05.003 . hal-02906432

**HAL Id: hal-02906432**

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Submitted on 26 May 2021

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# Fire retardancy of polypropylene/kaolinite composites

Marcos Batistella <sup>a, c, \*</sup>, Belkacem Otazaghine <sup>b</sup>, Rodolphe Sonnier <sup>b</sup>, Carlos Petter <sup>c</sup>, Jose-Marie Lopez-Cuesta <sup>b</sup>

<sup>a</sup> Federal University of Santa Catarina, R. Eng. Agrônomo Andrei Cristian Ferreira, s/n – Trindade, Florianópolis, SC, CEP 88040-900, Brazil

<sup>b</sup> Ecole des Mines d'Alès, Centre des Matériaux (C2MA) – Pôle Matériaux Polymères Avancés, 6 Avenue de Clavières, 30319, Alès Cedex, France

<sup>c</sup> Federal University of Rio Grande do Sul, Av. Bento Gonçalves, 9500, Porto Alegre, CEP 91501-970, Brazil

## A B S T R A C T

In this study the influence of surface modification of kaolinite with trisilanolisooctyl Polyhedral Oligo-SilSesquioxane (POSS) in polypropylene composites was evaluated in terms of thermal stability and fire retardancy and compared with talc. Thermogravimetric analysis showed that incorporating 30 wt% of kaolinite enhanced the thermal stability by ca. 20 °C compared to neat polymer. Cone calorimeter results demonstrated that kaolinite can greatly reduce the pHRR but not unmodified kaolinite. Rheological measurements showed that surface treatment of kaolinite leads to a decrease in viscosity, which could enhance processability. Finally, a correlation between viscosity and pHRR was found and the fire behavior of PP containing modified kaolinite could be explained.

## Keywords:

Kaolinite

Talc

POSS

PP

Flame retardancy

## 1. Introduction

Kaolinite is a 1:1 aluminosilicate composed of two layers of an alumina like tetrahedral sheet and a silica like octahedral sheet with the formula:  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ . Kaolinite has many industrial applications because of its special characteristics: chemically inert in a wide pH range, great covering power [1] when used as a pigment or as a surface coating for painting applications, low thermal conductivity and a lower cost compared to some current mineral fillers used in polymers. Main uses of kaolinite are in paper and ceramic industries and few studies concern its use in polymers [2–7]. Recently, we [7] studied the fire retardancy of an ultrafine kaolinite in EVA composites and compared this kaolinite with aluminum trihydroxide (ATH). Results showed that EVA filled with kaolinite exhibited better performances in terms of pHRR compared to EVA/ATH composites.

Polypropylene (PP) is commonly used due to its attractive versatility in terms of properties and processability. Nevertheless, poor flame retardancy is the main drawback of PP. To reduce its flammability, several kinds of flame retardant additives such as

halogenated compounds, metal hydroxides, intumescent systems [8,9], and mineral fillers have been used [10–14]. Among these flame retardants, the use of hydrated mineral fillers presents some drawbacks because satisfactory flame retardant properties are only achieved at high loading levels (up to more than 60% wt) leading to adverse impact on processability and mechanical properties. Beyond ATH and MDH (magnesium dihydroxide), other additives have been studied in the literature [9,14–19]. Fina et al. [9] reported the use of methyl-, vinyl- and phenyl polysilsesquioxanes as flame retardants for PP. They showed a decrease in the peak of heat release rate (pHRR) with relatively low concentration (10–20 wt%) of the POSS compounds. Duquesne et al. [12] studied the influence of talc on intumescent PP formulations and showed that composites containing talc were more thermally stable compared to neat polymer. Montezin et al. [19] reported the use of talc and halogenated flame retardants in a PP/PE blend. They showed that the partial replacement of the halogenated flame retardant by talc leads to the same behavior in flame retardancy, reaching V-0 in UL94 test, compared to halogenated alone.

It should be noted that homogeneous dispersion of fillers in polymer matrix and good interfacial adhesion are crucial for the performances of composites. To achieve this goal, several approaches have been considered such as the chemical functionalization of fillers or the use of compatibilizers. In particular, some studies have already reported the modification of layered silicates

\* Corresponding author. Federal University of Santa Catarina, R. Eng. Agrônomo Andrei Cristian Ferreira, s/n – Trindade, Florianópolis, SC, CEP 88040-900, Brazil.  
E-mail address: [marcos.batistella@posgrad.ufsc.br](mailto:marcos.batistella@posgrad.ufsc.br) (M. Batistella).

by POSS compounds in order to improve the properties of composites. Zhao et al. [20] showed that montmorillonite (MMT) modified with aminopropylisooctyl POSS improved the mechanical behavior of polyamide 12 (PA12). Yei et al. [21] also studied the influence of a surface treated MMT with the same POSS on the thermal behavior of polystyrene (PS). The authors showed an increase in onset temperature under nitrogen with functionalized MMT compared to pure polymer or composites filled with untreated MMT.

In the present study, surface modification of kaolinite with trisilanolisooctyl POSS was evaluated in terms of fire reaction of PP composites. Kaolinite performance was also compared to talc in PP. Finally, rheological measurements were carried out to assess the relation between viscosity and flame retardancy of composites.

## 2. Materials and methods

### 2.1. Materials

Trisilanolisooctyl POSS was used as purchased from Hybrid Plastics (Fig. 1). PP was a homopolymer supplied by Sabic (SABIC® PP 505P, MFR 2.0 g/10 min at 230 °C/2.16 kg).

Two ultrafine layered silicates with close particle size and morphology were used in this study: kaolinite (Kaol) kindly supplied by Vale (Ipixuna-Brazil) and talc (TA) kindly supplied by Imerys (Luznac-France). Commercial designation and characteristics of both fillers are shown in Table 1. Specific surface area was determined by B.E.T. (Brunauer–Emmett–Teller (B.E.T) method, using N<sub>2</sub> as adsorbed gas at 77 K on a Beckman Coulter SA3100 instrument and average particle size (d<sub>50</sub>) by laser particle-size analysis (Coulter LS230).

### 2.2. Surface modification of kaolinite

Surface treatment of kaolinite particles was carried out in ethanol/water mixture (96/4). 10 g of kaolinite, 0.3 g of trisilanolisooctyl POSS and 90 mL of an ethanol/water solution were introduced in a 250 ml flask fitted with a condenser. The mixture was then stirred and heated at solvent reflux for 4 h. The mixture was then centrifuged to remove the liquid phase and washed three times with ethanol. The POSS modified kaolinite was dried at 50 °C for 12 h. Surface treated kaolinite is referred as Kaol-POSS.

### 2.3. Preparation of PP composites

Compositions were extruded using a Clextral BC21 twin-screw extruder (CLEXTRAL SAS & AFREM, Firminy, France). The rotation speed was kept at 150 rpm, temperature ranged between 160 and 200 °C and polymer output was 4.5 kg/h. Square sheets specimens were prepared with dimensions of 100 × 100 × 4 mm<sup>3</sup> by injection molding using a 50 ton Krauss-Maffei equipment (Munich, Germany) and temperature range from 180 to 200 °C. The formulations

are showed in Table 2.

### 2.4. Characterization

Thermogravimetric analyses (TGA) were carried out on 10 ± 2 mg samples at 10 °C/min from 20 to 800 °C under nitrogen flow using a Perkin-Elmer Pyris-1 TGA. A Scanning Transmission Electron Microscopy (FEI Quanta 200 SEM) was used to study the morphology of the samples. All images were obtained under high vacuum at a voltage of 12.5 kV. The cone calorimeter experiments were carried out using a Fire Testing Technology apparatus with an irradiance of 50 kW/m<sup>2</sup> according to ISO 5660 standard. For each composite three samples were tested and mean values were reported. Viscosity measurements were carried out in dynamic mode at 200 °C using 0.5% strain and a frequency ranging from 10<sup>-1</sup> to 10<sup>2</sup> s<sup>-1</sup> (ARES, Rheometric Scientific) using parallel plates geometry. Shear storage modulus (G') and damping factor (tan δ) were evaluated.

## 3. Results and discussion

### 3.1. Surface modification of kaolinite

The effect of surface treatment was evaluated by FTIR analysis and showed in Fig. 2. Kristo et al. [22] have reported that kaolinite has five infrared active modes in the 3800–3400 cm<sup>-1</sup> region, centered at 3693 (ν<sub>1</sub>), 3681 (ν<sub>4</sub>), 3667 (ν<sub>2</sub>), 3651 (ν<sub>3</sub>), ascribed to the “outer hydroxyls” and 3619 (ν<sub>5</sub>) cm<sup>-1</sup> (“inner hydroxyl groups”). It should be noted that active mode at 3681 cm<sup>-1</sup> is only observed using Raman spectroscopy. The kaolinite used in the present work displays bands at 3692, 3665, 3650, and 3617 cm<sup>-1</sup>, in agreement with the literature. The Kaol-POSS sample shows a band centered at 2900 cm<sup>-1</sup> characteristic of C–H bonds and indicates that the POSS was successfully grafted on the kaolinite surface (Fig. 2).

Thermal stability of POSS, Kaol and Kaol/POSS observed by TGA are shown in Fig. 3. The first stage of mass loss observed for the POSS (at approximately 140 °C) may be related to the degradation of silanol groups, while the second mass loss which starts at about 320 °C occurs due to the degradation of isooctyl branches and Si–O cage [23]. Kaol shows a single degradation steep in mass loss between 400 and 550 °C corresponding to the release of structural water (about 14%). Kaol-POSS shows a decrease in the thermal stability in comparison to Kaol. The mass loss starts at about 320 °C which corresponds to the degradation of the Si–O cage from the grafted POSS. The mass loss for Kaol-POSS is about 16.7%, corresponding to a grafting rate of about 5% wt., considering the mass loss of POSS and kaolinite.

### 3.2. Thermal stability of PP composites

TGA measurements are shown in Fig. 4 and complete results in Table 3. Thermal degradation of PP under nitrogen was well studied and consists in a single mass loss step which starts at about 310 °C [24–27]. PP thermally degrades to volatile products through a radical chain process originated by carbon-carbon bond scission. The addition of Kaol or Kaol-POSS leads to a significant improvement of the thermal stability of PP composites: the initial pure PP decomposition temperature corresponding to a mass loss of 2% wt. is about 347 °C whereas this temperature is shifted to 389 °C for PP filled with talc (PP/TA), 400 °C for PP/Kaol and 400–420 °C for PP/Kaol-POSS as a function of filler loading.

As reported in Table 3 the peak of mass loss rate is 438 °C for pure PP. This temperature is shifted to about 460 °C for all PP/Kaol composites (10, 20 and 30 wt%). For PP/Kaol-POSS an increase was

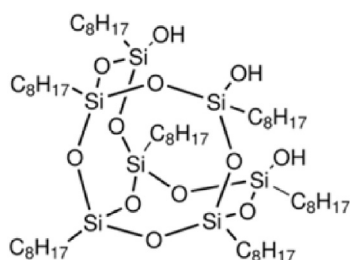


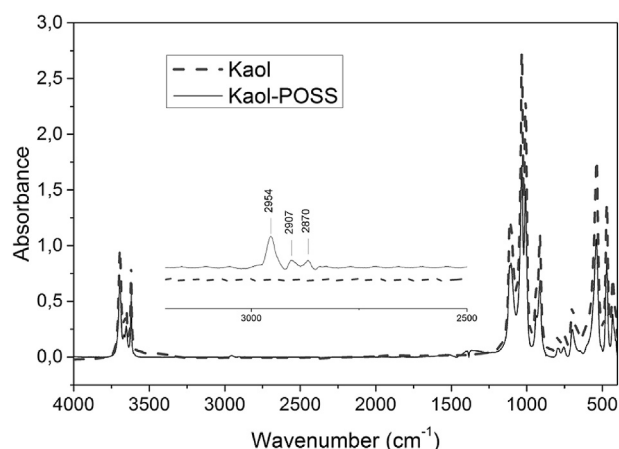
Fig. 1. Trisilanolisooctyl POSS structure.

**Table 1**  
Characteristics of fillers.

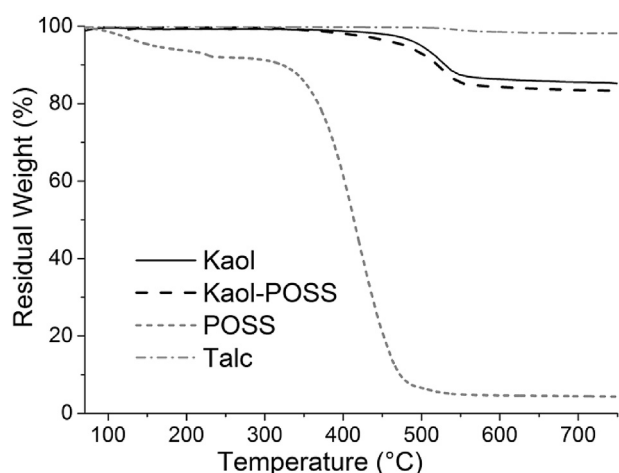
	Commercial designation	Median diameter ( $\mu\text{m}$ )	Specific surface area ( $\text{m}^2/\text{g}$ )
Kaolinite	Paralux	0.9	12
Talc	Jetfine 0.7C	0.7	19

**Table 2**  
Formulations used in this study (wt%).

	Kaolinite	Talc	Kaol/POSS
PP 505P	—	—	—
PP/Kaol-10	10	—	—
PP/Kaol-20	20	—	—
PP/Kaol-30	30	—	—
PP/Kaol-POSS-10	—	—	10
PP/Kaol-POSS-20	—	—	20
PP/Kaol-POSS-30	—	—	30
PP/TA-10	—	10	—
PP/TA-20	—	20	—
PP/TA-30	—	30	—

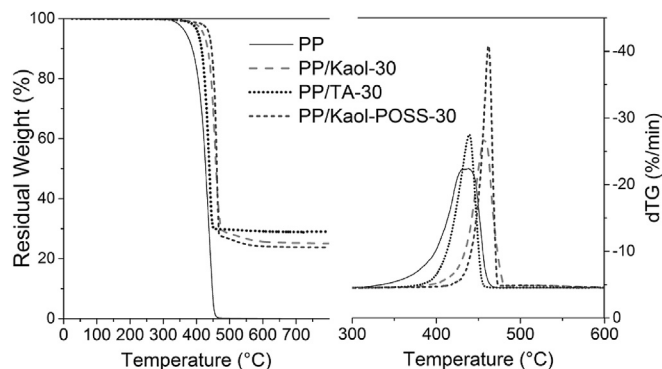


**Fig. 2.** FTIR of Kaol and Kaol-POSS samples.



**Fig. 3.** TGA of Kaol, Kaol-POSS and POSS samples under  $\text{N}_2$  at  $10^\circ\text{C}/\text{min}$ .

found as a function of filler loading: from 448 to 461  $^\circ\text{C}$ . Interestingly, a decrease was observed for PP/TA composite as a function of filler loading: from 453 to 438  $^\circ\text{C}$ . The increase of degradation temperature has been already observed in the literature and some



**Fig. 4.** Representative curves of TGA results of PP/composites filled at 30 wt% under  $\text{N}_2$  at  $10^\circ\text{C}/\text{min}$ .

studies explain that some fillers could act as volatile decomposition products shields [27,30]. Moreover it should be noted that PP decomposes completely at about 460  $^\circ\text{C}$ . The amount of composite residues is about 26 wt% for PP/Kaol-30, 24 wt% for PP/Kaol-POSS-30 and 28 wt% for PP/TA-30 which corresponds closely to fillers content and seems to indicate that no char was formed. It should be noted that thermal degradation of talc is well studied in the literature and consists of a single mass loss between 600 and 1000  $^\circ\text{C}$  corresponding to the dehydroxylation, with a mass loss of about 5% [28–30].

### 3.3. Cone calorimeter tests

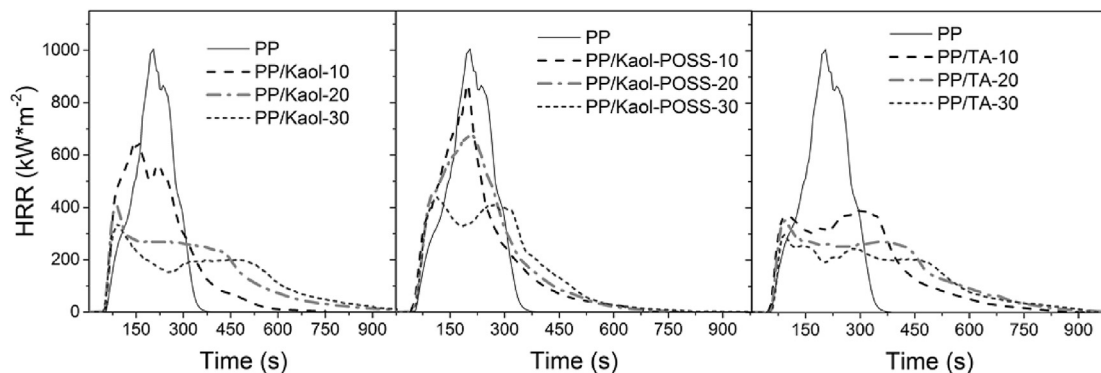
HRR plots of PP, PP/TA, PP/Kaol and PP/Kaol-POSS composites are shown in Fig. 5 and complete results in Table 4. The behavior of PP is typical of a non-charring polymer with a high pHRR (c.a. 1000  $\text{kW}/\text{m}^2$ ) without formation of residue. The incorporation of kaolinite or talc showed a reduction in pHRR even for 10 wt% loading. At higher filler content, both fillers (kaolinite and talc) showed approximately the same pHRR reduction (c.a. 70–80%) with a longer time burning. The incorporation of Kaol-POSS leads to poor performances. These results are not in agreement with the thermal stability observed by TGA. Indeed, PP filled with Kaol-POSS showed the best thermal stability improvement in comparison to PP, while talc does not change the temperature of the peak of mass loss rate. It means that the fire performance in cone calorimeter test is due to other phenomena as discussed in the following. It should be noted that TGA measurements were conducted in nitrogen whereas cone calorimeter tests were carried out in air. However, it is considered that the pyrolysis in cone calorimeter is anaerobic after ignition because oxygen is consumed in the flame.

From Table 4, time to ignition obtained for PP/Kaol, PP/Kaol-POSS and PP/TA are slightly different from the value of pure PP: Kaol and Kaol-POSS tends to decrease the TTI while talc tends to increase its value. It should be noted that TTI depends on many parameters [31–33], but the identification of these parameters is not the aim of this study.

At the end of combustion, there is no residue for PP (Table 4). PP/Kaol, PP/Kaol-POSS and PP/TA showed a different behavior: for PP/Kaol and PP/TA composites a swelled residue was observed

**Table 3**TGA results of PP composites under N<sub>2</sub> at 10 °C/min.

	Onset temperature (°C)	Peak temperature (°C)	Residue at 800 °C (%)
PP 505P	347	438	—
PP/Kaol-10	396	458	8.4
PP/Kaol-20	400	462	16.7
PP/Kaol-30	400	456	26
PP/Kaol-POSS-10	405	448	7.8
PP/Kaol-POSS-20	410	455	15.2
PP/Kaol-POSS-30	420	461	23.7
PP/TA-10	380	453	9.4
PP/TA-20	389	445	18.8
PP/TA-30	390	438	27.8

**Fig. 5.** HRR plots of different PP composites at 50 kW/m<sup>2</sup>.**Table 4**

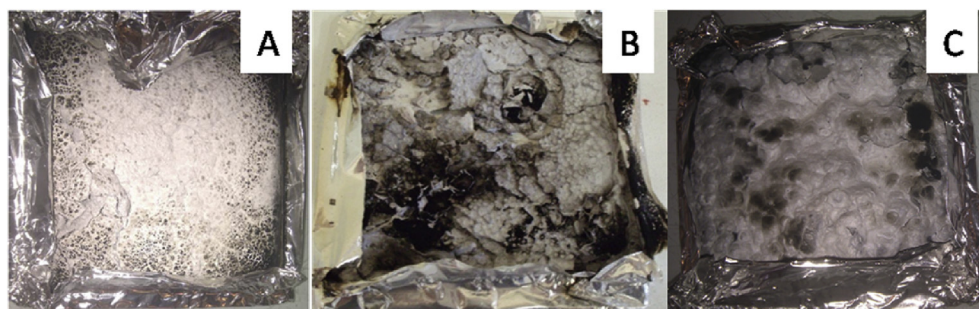
Cone calorimeter results for PP/Kaolinite and PP/Kaol-POSS composites.

	PHRR (kW/m <sup>2</sup> )	TTI (s)	THR (MJ/m <sup>2</sup> )	EHC (kJ/g)	Experimental mass residue (%)	Theoretical mass residue <sup>a</sup> (%)
PP 505P	1000 ± 98	44 ± 3	145	37	0	0
PP/Kaol-10	634 ± 28	35 ± 3	144	36	9.8	8.6
PP/Kaol-20	396 ± 20	38 ± 2	136	36	20.9	17.2
PP/Kaol-30	348 ± 22	41 ± 2	126	35	29.4	25
PP/Kaol-POSS-10	850 ± 32	35 ± 1	140	34	7	8
PP/Kaol-POSS-20	650 ± 28	38 ± 2	141	34	15.8	16
PP/Kaol-POSS-30	430 ± 22	50 ± 5	137	36	23	24
PP/TA-10	377 ± 28	49 ± 4	128	35	19	9.6
PP/TA-20	341 ± 20	56 ± 3	118	34	28	19.6
PP/TA-30	295 ± 12	50 ± 3	112	33	39	28.6

<sup>a</sup> Theoretical mass calculated as the sum of the mass losses from the filler and the neat polymer in TGA.

whereas for treated kaolinite a fine gray residue was observed (Fig. 6). Also, it is interesting to note that for samples filled with untreated kaolinite and talc, mass at the end of the test is higher than expected (considering complete degradation of polymer and

water mass loss from kaolinite). As in TGA no char was observed, an explanation is that both untreated kaolinite and talc particles could form a protective surface layer that insulates the polymer and prevents its complete degradation with better results for talc. This

**Fig. 6.** Cone calorimeter residues for PP/Kaol-30 (A), PP/Kaol-POSS-30 (B) and PP/TA-30 (C) composites.



also explains the decrease in THR for PP/Kaol and PP/TA.

The Effective Heat of Combustion (EHC) is an important parameter to understand how the flame retardant acts. Small changes were observed for different composites as a function of filler type: a small decrease was observed for Kaol or Kaol-POSS composites compared to neat PP. Addition of talc particles leads to an increasing reduction of EHC as function of loading. This decrease could be attributed to a physical effect of filler protecting the underlying polymer, i.e. a part of the polymer is not fully degraded and then the EHC is not necessarily equal to the EHC of pure PP.

TGA measurements of different sections of cone calorimeter residues from PP/TA and PP/kaol were performed. Fig. 7 shows the result of TGA at the center and at the edge of the cone calorimeter residue. For both fillers, no mass loss due to the presence of an organic part was observed for the sample extracted from the center of the residue. For the samples from the edge of the residues, significant differences were found: a mass loss of 6% wt. and 70% wt. were observed for PP/Kaol-30 and PP/TA-30 respectively. This result supports the hypothesis that the residue at the end of cone calorimeter tests is in fact undegraded polymer and filler forming a surface protective barrier.

During burning, the efficiently flame retarded composites must exhibit a residue that covers the entire sample surface without any openings. No vigorous bubbling must occur to allow the formation of a barrier layer and to avoid a fast transport of degradation products from the pyrolysis front to the gas phase. This effect was observed for PP/Kaol and PP/TA composites. On the contrary, the use of surface treated kaolinite leads to the formation of many cracks during the composites burning. Moreover, contrary to the PP/Kaol samples, the final residue was only due to the mineral filler and no swelling was observed. Then, the PP filled with modified kaolinite shows a decrease in fire performance compared to PP/Kaol composites.

#### 3.4. Viscosity vs. fire behavior

In the literature the filler surface treatment was shown to have different effects in composites: it improves dispersion and could act as a lubricant between filler and matrix. If the coupling agent improves dispersion, an expected result in cone calorimeter is the formation of a more effective layer which insulates the underlying material and protects it against heat. However, this lubricant effect may lead to an undesirable effect: the formation of the protective layer could be decreased due to the improved wetting of the filler

by the polymer. It should be mentioned that surface treatment has an influence in viscosity of the composites and viscosity could influence fire behavior in cone calorimeter [7,34,35]. Kashiwagi et al. [34] studied the influence of viscosity in PMMA and PS nanocomposites and showed a decrease in pHRR with an increase in storage modulus ( $G'$ ). In the previous work [7], the effect of various fillers on viscosity and fire behavior (pHRR) on EVA was studied. It showed that an increase in  $G'$  could lead to a decrease in pHRR due to limited transfer rate of combustible products to gas phase. Courtat et al. [35] studied the effect of surface treatment of silica nanoparticles in PP composites and showed that unmodified filler led to a better fire performance in terms of pHRR. The authors attributed this result to the rheological behavior: a higher storage modulus ( $G'$ ) leads to a greater decrease of pHRR. To understand the relation between surface modification of kaolinite, viscosity and fire behavior, rheological measurements were conducted using the procedure yet described in the literature [7,34,35].

Fig. 8 compares the storage modulus ( $G'$ ) and damping factor ( $\tan \delta$ ) of pure polypropylene, PP/Kaol, PP/Kaol-POSS and PP/TA composites at 30 wt% of fillers. The incorporation of unmodified kaolinite and talc dramatically changes the linear viscoelastic response to shear deformation with an increase in the storage modulus at lower frequencies. Storage modulus of PP/Kaol-POSS has not changed in comparison with pure polymer. Generally, it is suggested in the literature that the modification of the particles surface increases the viscosity and modulus values if chemical

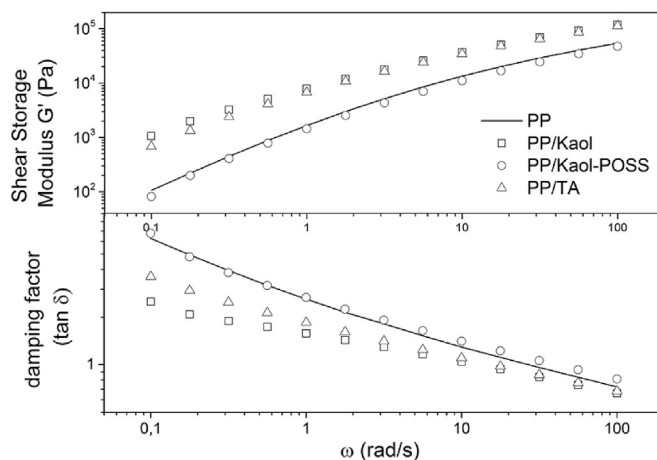


Fig. 8. Rheological behavior of PP composites for 30 wt% of mineral fillers.

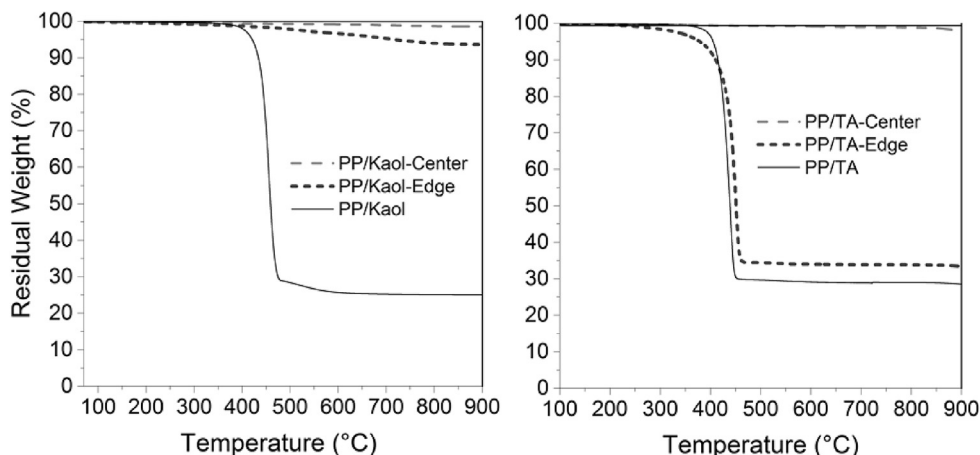


Fig. 7. TGA results of cone calorimeter residues of PP/Kaol and PP/TA composites at 30 wt%.

bonding or entanglement occurs between coupling agent and matrix [36–38]. In other cases, some coupling agents could also act as wetting or dispersant agents. In PP/Kaol-POSS composites, the reduction in viscosity and modulus may be due to a lubricating effect at the particle-polymer interface [36] and because carbon short-chains of POSS are not long enough to entangle with PP matrix. Moreover, it seems that wetting of the filler by PP is decreased leading to an improvement of filler dispersion in the polymer matrix (Fig. 9). The combination of these factors (improved dispersion and lubricating effect) may explain the observed decrease in storage modulus.

As already mentioned, Kashiwagi et al. [34] showed that an increase in viscosity favors the formation of a protective surface layer that insulates the polymer and reduces the mass transfer of volatile gases leading to a decrease in pHRR. In the above mentioned work [7] it was reported that an increase in melt viscosity by the addition of fillers with different surface area or aspect ratio leads to a decrease in pHRR in EVA composites. This work reported two distinct tendencies: in a first regime, normalized pHRR decreases quickly when normalized elastic modulus increases. From a threshold value (5 for normalized  $G'$ ) a second regime was observed: normalized pHRR remained almost constant, whatever a further increase of normalized elastic modulus.

These results suggest that the higher the elastic modulus is, the better the fire behavior is (at least up to a threshold value). As reported in the literature [7,34,35] such an improvement of fire behavior can be assigned to an easier accumulation of the inert additives near the surface then limiting the heat transfer between the flame and the condensed phase. Thus, this accumulation can act as a protective layer. Moreover, an increase of viscosity can slow down the gases transfer between the composite and the flame.

In order to understand the difference of burning behavior between composites containing talc, kaolinite and grafted kaolinite, rheological properties were compared with cone calorimeter results according to the method already reported [7,34,35]. The differences in terms of pHRR for surface modified kaolinite as compared to untreated kaolinite at different mass concentrations can be seen by comparing the relationship between the normalized storage modulus measured at a low frequency (0.1 rad/s) and the normalized pHRR of the different composites, as shown in Fig. 10. It should be noticed that rheological analyses were performed at 200 °C, while the temperature of the condensed phase during the cone calorimeter tests were increased from ambient to polymer pyrolysis temperature (i.e. approximately 450–500 °C for PP). Nevertheless we assume that the differences in viscous behavior between composites are qualitatively similar at processing temperature (200 °C) and during cone calorimeter test.

As in our previous study, two distinct tendencies could be observed as a function of filler type and surface treatment. When normalized  $G'$  is higher than 2, normalized pHRR is stable around

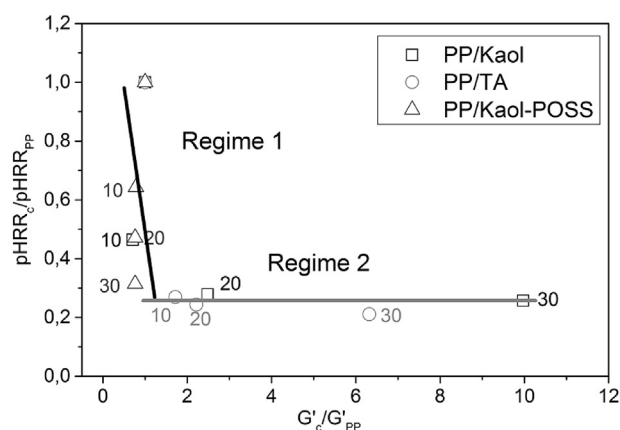


Fig. 10. Comparison of normalized  $G'$  vs. normalized PHRR.

0.25, regardless the filler rate. This tendency at high  $G'$  was called Regime 2. For example, 20 or 30 wt% of kaolinite leads to similar pHRR even if normalized  $G'$  is very different: 2.2 and 10 respectively. PP composites filled with at least 20 wt% kaolinite or talc are all in the Regime 2.

On the contrary, when normalized  $G'$  is low, pHRR is relatively high. This is the case for all PP composites filled with modified kaolinite for all loadings. This tendency at low  $G'$  value was called Regime 1 as in our previous work [7]. In this study, a more precise tendency was found: normalized pHRR decreases when normalized  $G'$  increases. It seems that surface treatment has a negative impact on fire performance of composites allowing bubbling and mass transfer of combustible gases to the flame. This behavior was also observed in recent studies in PS and PMMA nanocomposites [34] and in PP/silica composites [35]. Kashiwagi et al. [34] proposed that there exists a threshold viscosity which permits the formation of the protective surface barrier to limit bubbling and mass transfer. Results found in this study supports that hypothesis, i.e. a more rigid composite (i.e. a higher  $G'$ ) could lead to an improved fire behavior by limiting the bubbling, convection into the condensed phase and pyrolysis gases transfer to the flame. When these phenomena are limited enough (i.e. when elastic modulus becomes higher than a threshold value) the pHRR is stabilized and does not decrease anymore. Moreover, during cone calorimeter test, an intense bubbling was observed for PP/Kaol-POSS composites whereas no bubbling was observed for PP/Kaol composites. Also, the observation of the residues formed with untreated and surface modified kaolinites (Fig. 6 A and B) shows that the cohesion of the residual structure decreases with the surface treatment. The decrease in viscosity may allow a more intense bubbling leading to a smashing of the protective mineral layer. Then the mass transfer

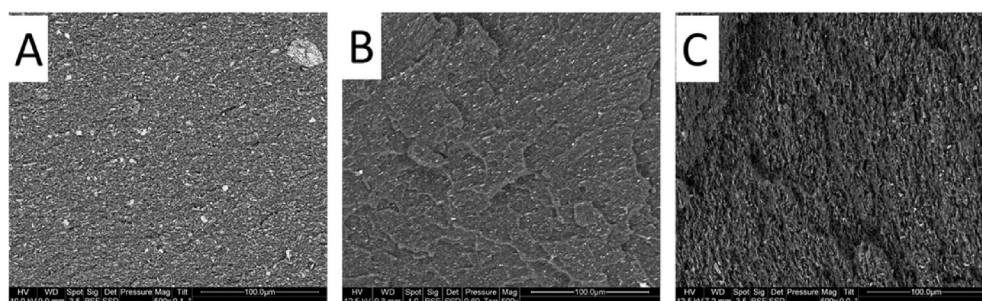


Fig. 9. Representative SEM images of PP/Kaol-30 (A), PP/Kaol-POSS-30 (B) and PP/TA-30 (C) composites.

to gas phase is amplified, with an increase of pHRR compared to untreated kaolinite. Indeed, in order to have a more effective physical effect, the fillers in the PP composites must form a homogeneous and cohesive layer without cracks.

#### 4. Conclusions

Kaolinite was modified with trisilanolisooctyl POSS in order to improve its compatibility with PP. Results showed that the surface treatment of kaolinite leads to a better dispersion of the filler in PP. SEM images showed the presence of agglomerates ranging from a few micrometers to 50–60  $\mu\text{m}$  for untreated kaolinite. Surface treatment leads to agglomerates of only a few micrometers. Furthermore, the surface modification led to a lack of interfacial cohesion between filler and polymer, leading to changes in viscosity of composites. When modified kaolinite was used, similar viscosity as pristine PP was observed which could be attributed to a sliding phenomenon between filler and matrix. Compared to talc, untreated kaolinite leads to the same increase in viscosity.

The addition of kaolinite with or without surface treatment leads to an improvement in thermal stability of PP through an increase of the onset and peak temperatures compared to composites filled with talc or neat PP. For all fillers, cone calorimeter results showed a reduction in pHRR mainly due to the formation of a protective barrier layer that insulates material and protects the non-degraded polymer. Furthermore, differences in bubbling were observed for composites. When unmodified kaolinite and talc were used, no bubbling was observed and a surface protective layer was formed before ignition whereas for composites filled with kaolinite treated with POSS, an intense bubbling was observed. Talc particles form a more efficient surface protective layer that insulates the degrading polymer and protects it against heat. This behavior was confirmed by thermal analysis of different sections of cone calorimeter residues: in the edge of samples, the polymer was protected against heat and in the center no polymer was found after cone calorimeter test.

Finally, a decrease in pHRR was observed with the increase of relative storage modulus up to a threshold value. Rheological measurements showed that the composite viscosity has a major effect in the pHRR reduction, at least up to a certain value of storage modulus. Above this threshold, pHRR decreases quickly when fillers are incorporated into PP because the increase in elasticity limits bubbling and mass transfer from pyrolysis front to the flame. Below this threshold, pHRR remains constant and independent on the further increase in elasticity. These results confirmed previous works which pointed out that a high viscosity could limit the pyrolysis gases transfer to the gas phase.

#### APPENDIX

#### References

- [1] H.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: a general overview, *Appl. Clay Sci.* 17 (5–6) (2000) 207–221.
- [2] D.M. Ansari, G.J. Price, Correlation of mechanical properties of clay filled polyamide mouldings with chromatographically measured surface energies, *Polymer (Guildf)* 45 (11) (2004) 3663–3670, <http://dx.doi.org/10.1016/j.polymer.2004.03.045>.
- [3] A. Astruc, E. Joliff, J.-F. Chailan, E. Aragon, C.O. Petter, C.H. Sampaio, Incorporation of kaolin fillers into an epoxy/polyamidoamine matrix for coatings, *Prog. Org. Coat.* 65 (1) (2009) 158–168, <http://dx.doi.org/10.1016/j.porgcoat.2008.11.003>.
- [4] S.N. Maiti, B.H. Lopez, Tensile properties of polypropylene/kaolin composites, *J. Appl. Polym. Sci.* 44 (2) (1992) 353–360, <http://dx.doi.org/10.1002/app.1992.070440219>.
- [5] L. Domka, A. Malickaa, N. Stachowiak, A. Malicka, N. Stachowiak, The effect of kaolin modification of silane coupling agents on the properties of the polyethylene composites, *Pol. J. Chem. Technol.* 10 (2) (2008) 5–10, <http://dx.doi.org/10.2478/v10026-008-0020-8>.
- [6] H. Vahabi, M.A. Batistella, B. Otazaghine, C. Longuet, L. Ferry, R. Sonnier, J.-M. Lopez-Cuesta, Influence of a treated kaolinite on the thermal degradation and flame retardancy of poly(methyl methacrylate), *Appl. Clay Sci.* 70 (2012) 58–66, <http://dx.doi.org/10.1016/j.clay.2012.09.013>.
- [7] M. Batistella, B. Otazaghine, R. Sonnier, C. Petter, A.-S. Caro-Bretelle, C. Petter, J.-M. Lopez-Cuesta, Fire retardancy of ethylene vinyl acetate/ultrafine kaolinite composites, *Polym. Degrad. Stab.* 100 (2013) 54–62, <http://dx.doi.org/10.1016/j.polydegradstab.2013.12.026>.
- [8] L. Morice, S. Bourbigot, J.M. Leroy, Heat transfer study of polypropylene-based intumescent systems during combustion, *J. Fire Sci.* 15 (5) (1997) 358–374, <http://dx.doi.org/10.1177/073490419701500502>.
- [9] A. Fina, D. Tabuani, G. Camino, Polypropylene-polysilsesquioxane blends, *Eur. Polym. J.* 46 (1) (2010) 14–23, <http://dx.doi.org/10.1016/j.eurpolymj.2009.07.019>.
- [10] H. Md Akil, M.F.A. Rasyid, J. Sharif, Effect of compatibilizer on properties of polypropylene layered silicate nanocomposite, *Proced. Chem.* 4 (2012) 65–72, <http://dx.doi.org/10.1016/j.proche.2012.06.010>.
- [11] A.B. Shehata, M.A. Hassan, N.A. Darwish, Kaolin modified with new resin-iron chelate as flame retardant system for polypropylene, *J. Appl. Polym. Sci.* 92 (5) (2004) 3119–3125, <http://dx.doi.org/10.1002/app.2022>.
- [12] S. Duquesne, F. Samyn, S. Bourbigot, P. Amigouet, F. Jouffret, K. Shen, Influence of talc on the fire retardant properties of highly filled intumescent polypropylene composites, *Polym. Adv. Technol.* 19 (6) (2008) 620–627, <http://dx.doi.org/10.1002/pat.1127>.
- [13] H. Qin, S. Zhang, C. Zhao, M. Feng, M. Yang, Z. Shu, S. Yang, Thermal stability and flammability of polypropylene/montmorillonite composites, *Polym. Degrad. Stab.* 85 (2) (2004) 807–813, <http://dx.doi.org/10.1016/j.polydegradstab.2004.03.014>.
- [14] M. Longerey, J.-M. Lopez-Cuesta, P. Gaudon, A. Crespy, Talcs and brominated trimethylphenyl indane/Sb<sub>2</sub>O<sub>3</sub> blend in a PP/PE copolymer, *Polym. Degrad. Stab.* 64 (1999) 489–496, [http://dx.doi.org/10.1016/S0141-3910\(98\)00147-5](http://dx.doi.org/10.1016/S0141-3910(98)00147-5).
- [15] T.R. Hull, A. Witkowski, L. Hollingsbery, Fire retardant action of mineral fillers, *Polym. Degrad. Stab.* 96 (8) (2011) 1462–1469, <http://dx.doi.org/10.1016/j.polydegradstab.2011.05.006>.
- [16] L. Clerc, L. Ferry, E. Leroy, J.-M. Lopez-Cuesta, Influence of talc physical properties on the fire retarding behavior of (ethylene–vinyl acetate copolymer/magnesium hydroxide/talc) composites, *Polym. Degrad. Stab.* 88 (3) (2005) 504–511, <http://dx.doi.org/10.1016/j.polydegradstab.2004.12.010>.
- [17] A. Durin-France, L. Ferry, J.-M.M. Lopez-Cuesta, A. Crespy, Magnesium hydroxide/zinc borate/talc compositions as flame-retardants in EVA copolymer, *Polym. Int.* 49 (10) (2000) 1101–1105 doi: 10.1002/1097-0126(200010)49:10<1101::AID-PI523>3.0.CO;2-5.
- [18] X. Almeras, M. Le Bras, P. Hornsby, S. Bourbigot, G. Marosi, S. Keszei, F. Poutch, Effect of fillers on the fire retardancy of intumescent polypropylene compounds, *Polym. Degrad. Stab.* 82 (2) (2003) 325–331, [http://dx.doi.org/10.1016/S0141-3910\(03\)00187-3](http://dx.doi.org/10.1016/S0141-3910(03)00187-3).
- [19] F. Montezin, J.-M. Lopez Cuesta, A. Crespy, P. Georlette, Flame retardant and mechanical properties of a copolymer PP/PE containing brominated

	Storage modulus at 0.1 rad/s (Pa)	$\tan \delta$	Normalized storage modulus	Normalized pHRR
PP 505P	106.36	6.27	1	1
PP/Kaol-10	75.55	7.89	0.70	0.46
PP/Kaol-20	263.54	4.66	2.48	0.28
PP/Kaol-30	1057.7	2.50	9.97	0.25
PP/Kaol-POSS-10	83.91	7.23	0.78	0.64
PP/Kaol-POSS-20	9.50	11.94	0.76	0.47
PP/Kaol-POSS-30	81.24	6.75	0.76	0.31
PP/TA-10	182.24	4.40	1.71	0.27
PP/TA-20	235.65	5.71	2.21	0.24
PP/TA-30	678.69	3.60	6.32	0.21



- compounds/antimony trioxide blends and magnesium hydroxide or talc, *Fire Mater.* 21 (1997) 245–252 doi: 10.1002/(SICI)1099-1018(199711/12)21:6<245::AID-FAM616>3.0.CO;2-F.
- [20] F. Zhao, X. Bao, A.R. McLauchlin, J. Gu, C. Wan, B. Kandasubramanian, Effect of POSS on morphology and mechanical properties of polyamide 12/montmorillonite nanocomposites, *Appl. Clay Sci.* 47 (3–4) (2010) 249–256, <http://dx.doi.org/10.1016/j.clay.2009.10.018>.
- [21] D.R. Yei, S.W. Kuo, Y.C. Su, F.C. Chang, Enhanced thermal properties of PS nanocomposites formed from inorganic POSS-treated montmorillonite, *Polymer (Guildf)* 45 (8) (2004) 2633–2640, <http://dx.doi.org/10.1016/j.polymer.2004.02.020>.
- [22] J. Kristó, R.L. Frost, A. Felinger, J. Mink, FTIR spectroscopic study of intercalated kaolinite, *J. Mol. Struct.* 410 (96) (1997) 119–122, [http://dx.doi.org/10.1016/S0022-2860\(96\)09488-4](http://dx.doi.org/10.1016/S0022-2860(96)09488-4).
- [23] R. Florio, V. Pistor, A.J. Zattera, C.L. Petzhold, Polymerization kinetics of polyurethanes containing trisilanolisooctyl polyhedral oligomer-silsesquioxane, *J. Elastomers Plast.* 46 (7) (2014) 594–610.
- [24] M. Zanetti, G. Camino, P. Reichert, R. Mülhaupt, Thermal behavior of poly(propylene) layered silicate nanocomposites, *Macromol. Rapid Commun.* 22 (3) (2001) 176–180 doi: 10.1002/1521-3927(200102)22:3<176::AID-MARC176>3.0.CO;2-C.
- [25] J.D. Peterson, S. Vyazovkin, C.A. Wight, Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and poly(propylene), *Macromol. Chem. Phys.* 202 (6) (2001) 775–784 doi: 10.1002/1521-3935(20010301)202:6<775::AID-MACP775>3.0.CO;2-G.
- [26] J.H. Chan, S.T. Balke, The thermal degradation kinetics of polypropylene: part III. Thermogravimetric analyses, *Polym. Degrad. Stab.* 57 (2) (1997) 135–149, [http://dx.doi.org/10.1016/S0141-3910\(96\)00160-7](http://dx.doi.org/10.1016/S0141-3910(96)00160-7).
- [27] T.E. Davis, R.L. Tobias, E.B. Peterli, Thermal degradation of polypropylene, *J. Polym. Sci.* 56 (164) (1962) 485–499, <http://dx.doi.org/10.1002/pol.1962.1205616420>.
- [28] R. Ward, Kinetics of talc dehydroxylation, *Thermochim. Acta* 13 (1) (1975) 7–14, [http://dx.doi.org/10.1016/0040-6031\(75\)80061-X](http://dx.doi.org/10.1016/0040-6031(75)80061-X).
- [29] M. Wesoloski, Thermal decomposition of talc: a review, *Thermochim. Acta* 78 (3) (1984) 395–421, [http://dx.doi.org/10.1016/0040-6031\(84\)87165-8](http://dx.doi.org/10.1016/0040-6031(84)87165-8).
- [30] X. Liu, X. Liu, Y. Hu, Investigation of the thermal decomposition of talc, *Clays Clay Minerals* 62 (2) (2014) 137–144, <http://dx.doi.org/10.1346/CCMN.2014.0620206>.
- [31] M.A. Delichatsios, J. Zhang, An alternative way for the ignition times for solids with radiation absorption in-depth by simple asymptotic solutions, *Fire Mater.* 36 (1) (Jan. 2012) 41–47.
- [32] A. Fina, J. Feng, F. Cuttica, In-depth radiative heat transmittance through polypropylene/nanoclay composites, *Polym. Degrad. Stab.* 98 (5) (Feb. 2013) 1030–1035.
- [33] T.R. Hull, A.A. Stec, S. Nazare, Fire retardant effects of polymer nanocomposites, *J. Nanosci. Nanotechnol.* 9 (7) (Jul. 2009) 4478–4486.
- [34] T. Kashiwagi, M. Mu, K. Winey, B. Cipriano, S.R. Raghavan, S. Pack, M. Rafailovich, Y. Yang, E. Grulke, J. Shields, R. Harris, J. Douglas, Relation between the viscoelastic and flammability properties of polymer nanocomposites, *Polymer (Guildf)* 49 (20) (2008) 4358–4368, <http://dx.doi.org/10.1016/j.polymer.2008.07.054>.
- [35] J. Courtat, F. Melis, J.-M. Taulemesse, V. Bounor-Legare, R. Sonnier, L. Ferry, P. Cassagnau, Effect of phosphorous-modified silica on the flame retardancy of polypropylene based nanocomposites, *Polym. Degrad. Stab.* 119 (2015) 260–274, <http://dx.doi.org/10.1016/j.polymdegradstab.2015.05.022>.
- [36] D.M. Bigg, Rheological analysis of highly loaded polymeric composites filled with non-agglomerating spherical filler particles, *Polym. Eng. Sci.* 22 (8) (1982) 512–518, <http://dx.doi.org/10.1002/pen.760220810>.
- [37] C.D. Han, T. Van Den Weghe, P. Shete, J.R. Haw, Effects of coupling agents on the rheological properties, processability, and mechanical properties of filled polypropylene, *Polym. Eng. Sci.* 21 (4) (1981) 196–204, <http://dx.doi.org/10.1002/pen.760210404>.
- [38] A.V. Shenoy, *Rheology of Filled Polymer Systems*, Kluwer Academic Publishers, AA Dordrecht, 1999.