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### Effect of Ultrafine Full-Vulcanized Powdered Rubber on the Properties of the Intumescent Fire Retardant Polypropylene

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# Effect of Ultrafine Full-Vulcanized Powdered Rubber on the Properties of the Intumescent Fire Retardant Polypropylene

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*Ultrafine full-vulcanized powdered rubber (UFPR) was added into intumescent fire retardant polypropylene (IFR-PP) composites, and fire retardance, morphology, and properties of the composite were analyzed. Ammonium polyphosphate and pentaerythritol were used as the intumescent fire retardants (IFR). The mechanical properties (elongation at break increased from 70% to 110%) and the melt flowability of IFR-PP improved by adding a small quantity of UFPR (less than 0.5 phr) but decreased when the UFPR was more than 0.5 phr. At the same time, the fire retardance, as measured by the limiting oxygen index and the UL94 vertical test rating, and other mechanical properties decreased appreciably with adding UFPR. The reasons were analyzed by using SEM micrographs, and a model was proposed to explain the reasons.*

**Keywords** elongation at break, intumescent fire retardant, mechanical properties, melt flowability, polypropylene, ultrafine full-vulcanized powdered rubber

## Introduction

In recent years, polypropylene (PP) has been widely used in cars, architectural materials, electronic cases, and other applications because of its low cost, low density, fine mechanical properties, easy processing, etc. But the limiting oxygen index (LOI) of pure PP is only 17.4; it is a flammable material. Halogen based fire retardant PP has been used in the past, but researchers have found that the halogen is a noxious material; generally, they evolve halogen acids and metal halides on burning, and increase the formation of toxic gases and corrosive smoke.<sup>[1]</sup> Therefore, halogen-free fire retardants are becoming more and more important for PP.

Metallic hydroxide fire retardants and intumescent fire retardants (IFR) are widely used in polymers as halogen-free fire retardants, nowadays. IFR has been used in PP matrix as a conventional halogen-free fire retardant. It contains three active ingredients: an acid source as a catalyst, a carbonization compound, and a blowing agent. Usually, ammonium polyphosphate (APP) has been used as acid source and blowing agent and pentaerythritol (PER) as the carbonization compound.<sup>[2]</sup> On the one hand, selecting an appropriate ratio of

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APP and PER and adding the mixture into polypropylene can effectively improve the fire retardance of compound. But on the other hand, IFR decreases the mechanical properties and flowability of PP matrix.

PER is an important carbonization compound due to its high hydroxy content. Moreover, using Polyamide 6 (PA6) to replace PER as a carbonization agent in association with APP was shown to be successful in the PP system.<sup>[3]</sup> To become a carbonization agent in an intumescent fire retardant, a compound must have high hydroxyl and carbon content, such as PER or other carbonizer, and carbonifying catalytic activity, such as PA6, forming a swollen multicellular char layer to prevent expansion of fire and heat when the resin burns. Actually, some rubbers play the same role as PA6 in terms of carbon content and fire retardant synergist because of their benzene ring structure,<sup>[4]</sup> the latter exists in some self-extinguishing resins such as polyphenylene oxide<sup>[5]</sup> and poly(sulfonyldiphenylene phenylphosphonate),<sup>[6]</sup> and increases their fire retardancy. Therefore, it was hoped that styrene-butadiene rubber (SBR) would have a synergistic effect with IFR and improve fire retardancy of the composite. However, ordinary rubber is not fit for processing with PP, such as by extrusion and injection molding, because of its high degree of vulcanization.

In this paper, a new form of SBR was used in the form of ultrafine full-vulcanized powdered rubber (UFPR) produced by a special method.<sup>[7]</sup> It has previously been reported to have been used in polyvinyl chloride,<sup>[8,9]</sup> polystyrene,<sup>[10]</sup> PA6,<sup>[11]</sup> and other polymer matrices<sup>[12,13]</sup> to increase the toughness and other mechanical properties. In addition, Gui<sup>[14]</sup> found that UFPR had a synergistic effect on fire retardancy with magnesium hydroxide in EVA. However, there has been no report about the fire retardancy and mechanical properties of PP/UFPR/IFR composites.

The synergistic effects of UFPR on the fire retardance, mechanical properties, and melt flowability in PP/IFR composites are described in this paper. Various amounts of UFPR were added to the composites and the fire retardancy, thermogravimetric analysis, mechanical properties, melt flowabilities, and morphologies of the composites were observed.

## Experimental

### Materials

PP (T30S) with a melt flow rate (MFR) of 2.5 g/10 min (230°C/2.16 kg) and 1.9 g/10 min (190°C/2.16 kg) was supplied as powder by Phoenix Petrochemical Company, Wuhan, China. Ammonium polyphosphate (APP),  $(\text{NH}_4\text{PO}_3)_n$ ,  $n \geq 1000$ , average particle size less than 10  $\mu\text{m}$ ) with a density of 1.9 g/cm<sup>3</sup> and bulk density of 4.1 g/L was supplied by Yaxin Chemical Material Company Ltd., Guangzhou, China. Pentaerythritol with the density of 1.9 g/cm<sup>3</sup> and bulk density of 7.7 g/L was supplied by Perstorp Specialty Chemicals AB, Sweden. Ultrafine full-vulcanized powdered rubber (UFPR, SBR, with the density of 1.3 g/cm<sup>3</sup>, bulk density of 1.5 g/L and average particle size less than 0.2  $\mu\text{m}$ ) was supplied by SINOPEC Beijing Research Institute of Chemical Industry.

### Processing and Formulations

The formulations of the composites are listed in Table 1, in which the weight ratio of APP/PER was 4 and the total of IFR was 30 wt% in the composite. First, the UFPR was dried for 4 hr at 50°C in a vacuum oven, and then the PP, IFR, and UFPR were mixed by using a high-speed mixing agitator for 5 min. The compounds were extruded together in a

**Table 1**  
Formulation of PP/IFR/UFPR composites

Sample	PP (phr)	IFR		
		APP (phr)	PER (phr)	UFPR (phr)
IPR-PP	70	24	6	0
UFPR-1	70	24	6	0.1
UFPR-2	70	24	6	0.2
UFPR-3	70	24	6	0.5
UFPR-4	70	24	6	1
UFPR-5	70	24	6	2

twin-screw extruder (diameter = 20 mm, length-to-diameter ( $L/D$ ) = 35) and pelleted. The pellets were dried for 2 hr at 80°C and injection molded to form specimens with suitable size and thickness.

### *Fire Testing*

The limiting oxygen index was measured using a HC-2 type instrument (Jiangning Country Analyze Instrument Factory, Jiangsu, China). The dimensions of the specimens were 150 mm × 6 mm × 3 mm, according to ASTM D2863.

The UL94 vertical test was performed using a CZF-3 type instrument (Jiangning Country Analyze Instrument Factory, Jiangsu, China). The dimensions of the specimens were 127 mm × 12.7 mm × 3.2 mm and 127 mm × 12.7 mm × 1.6 mm, according to the UL94 test and ASTM D635, respectively.

### *Thermogravimetric Analysis*

Thermogravimetric analysis was carried out using a SDT/Q600 thermogravimetric analyzer (TA Instruments Inc., USA) at a linear heating rate of 10°C/min under a nitrogen atmosphere (100 mL/min) at temperatures ranging from room temperature to 850°C. The weight of all samples was kept within 7–10 mg.

### *Tensile Testing*

Tensile testing of the specimens was performed on an AGS-J universal testing machine (Shimadzu Co. Ltd., Japan); the crosshead speed was 50 mm/min. The tensile measurements were performed at 23°C, and geometry of the specimens, number of the specimens, the test conditions, the procedure, and calculations were according to ASTM D-638.

### *Melt Flowability Testing*

The melt flowability of the PP/IFR composite was examined on a XNR-400 MFR testing instrument (Chengde Instruments Inc., China) at 190°C with a load of 2.16 kg, according to ASTM D-1238.

**Table 2**  
Fire testing of PP/IFR/UFPR composites

Sample	Flammability test		
	LOI (vol%)	UL94 rating (3.2 mm)	UL94 rating (1.6 mm)
IPR-PP	32	V-0	V-1
UFPR-1	32	V-0	V-1
UFPR-2	32	V-0	V-1
UFPR-3	32	V-0	V-1
UFPR-4	31	V-0	V-1
UFPR-5	29	V-0	V-1

The capillary rheological property was evaluated by a capillary rheometer (RHEOGRAPH 2002, GÖTTFEAT) at 190°C. The length-to-diameter of the capillary was 30/1.

### Scanning Electron Microscopy

Scanning electron microscopy (SEM) micrographs were obtained by using a JSM-5900LV scanning electron microscope (JEOL Co. Ltd., Japan). The samples were frozen in liquid nitrogen and then fractured for the morphology observation. The acceleration voltage was 20 kV, and the specimens were previously coated with a conductive gold layer.

## Results and Discussion

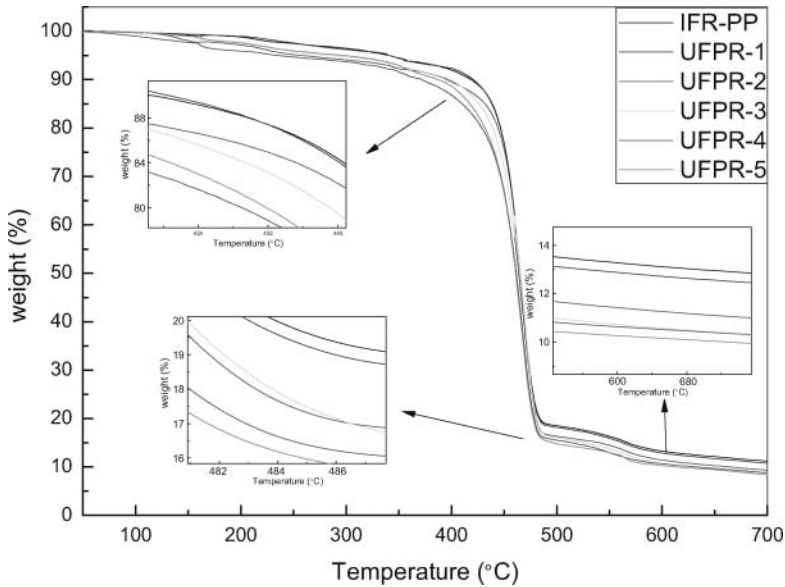
### Fire Testing

The LOI values and UL94 rating data of the various PP/IFR/UFPR composites are given in Table 2. The LOI values of the composites decrease slightly with increasing UFPR content. But there was no difference in the UL94 test for the composites with different UFPR contents and two different thicknesses.

The data suggest that there is no synergistic fire retardance effect between UFPR and IFR in the composites, and the UFPR decreases the fire retardance. But if we treat the UFPR

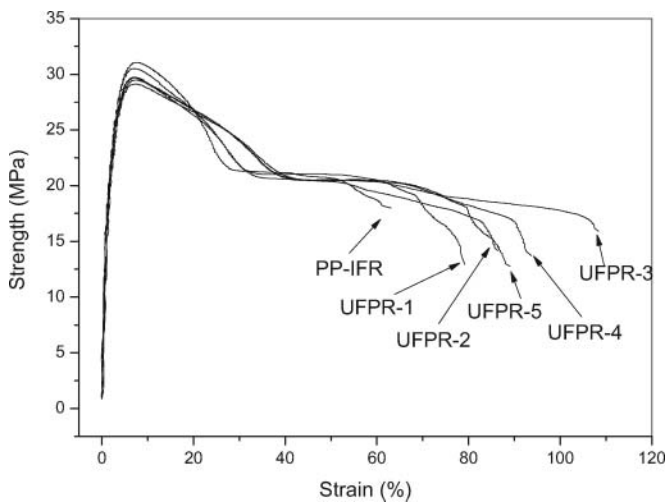
**Table 3**  
TG data of PP/IFR/UFPR composites

Sample	$T_{\text{onset}}$ (°C)	$T_{\text{max}}$ (°C)	Residue (wt%, 400°C)	Residue (wt%, 500°C)	Residue (wt%, 700°C)
IFR-PP	372	467	92.33	18.53	11.14
UFPR-1	370	467	91.91	18.20	10.74
UFPR-2	383	468	89.90	16.42	9.28
UFPR-3	379	467	89.53	16.03	8.75
UFPR-4	366	466	88.49	15.54	8.59
UFPR-5	382	467	86.77	14.75	8.35

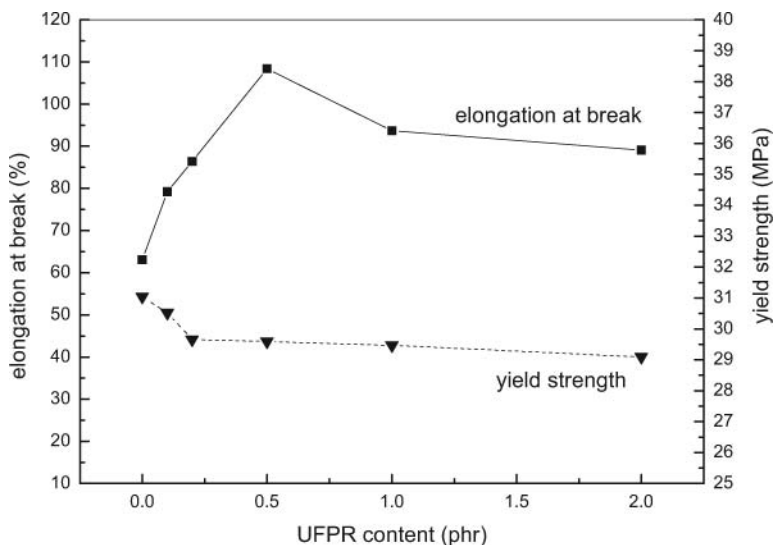


**Figure 1.** TG curves of PP/IFR/UFPR composites with different UFPR contents.

as part of the polymer matrix, as mentioned in the literature above,<sup>[5-12]</sup> the IFR content was reduced by adding UFPR. However, this still leads to decrease in the LOI values. Moreover, the same UL94 rating data for the two thicknesses show that the composites achieved the same fire retardance level by adding less fire retardant. The reason why the fire retardance decreased is the UFPR was added as part of the polymer matrix and the IFR content was decreased. Therefore, the results of fire test imply that the composites keep similar LOI values and UL94 rating with less IFR and no more than 0.5 phr UFPR.



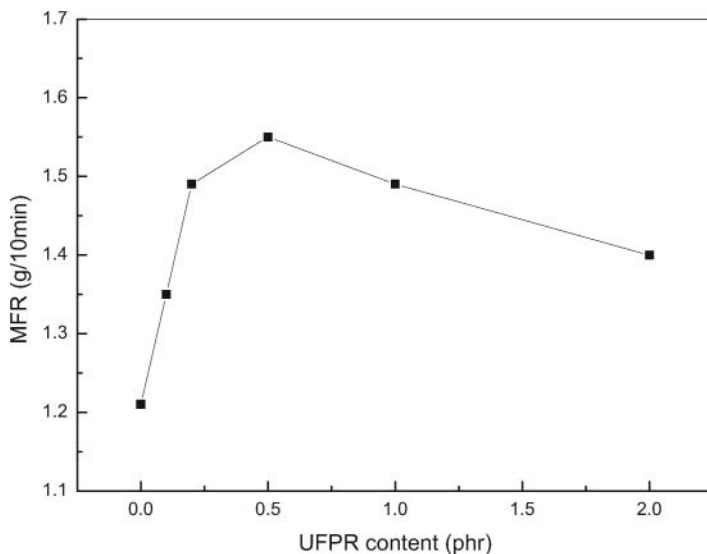
**Figure 2.** The strain–stress curves of PP/IFR/UFPR composites with different UFPR contents.



**Figure 3.** The elongation at break and yield strength of PP/IFR/UFPR composites with different UFPR contents.

### ***Thermal Behavior***

TG curves of PP/IFR/UFPR composites are shown in Fig. 1, and the relevant data are summarized in Table 3. Table 3 illustrates that the onset weight loss temperatures and the maximum weight loss temperatures for the UFPR composites are similar to IFR-PP and, the residue weights are lower than IFR-PP at 400°C, 500°C, and 700°C with increasing UFPR content. Moreover, the TG curves of the composites with different UFPR contents



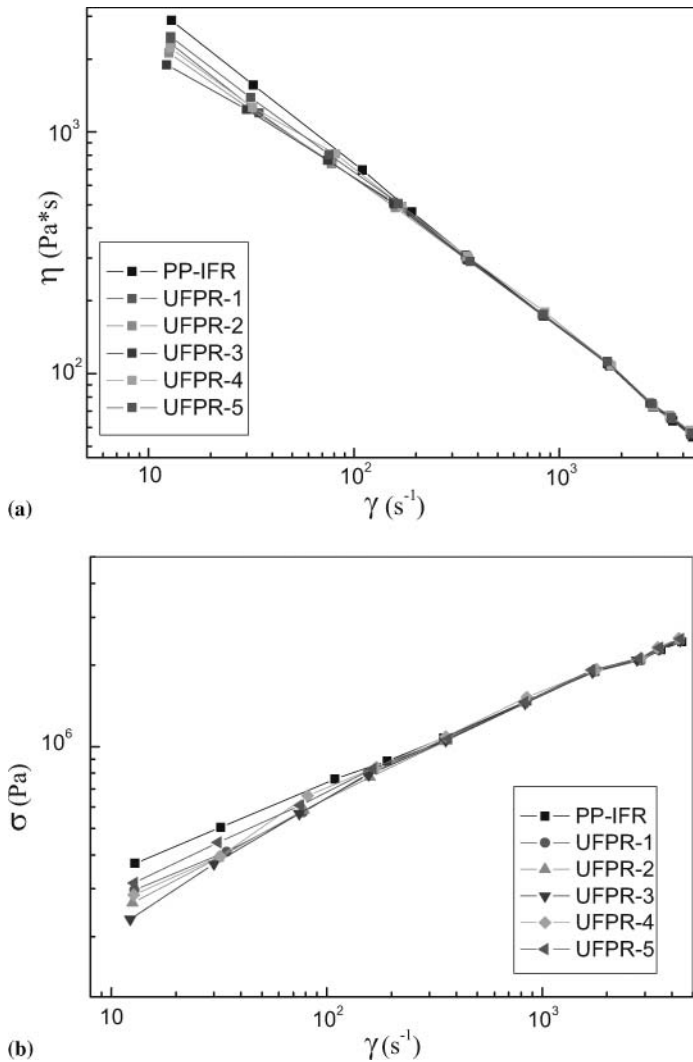
**Figure 4.** MFR of the PP/IFR/UFPR composites with different UFPR contents.

show that they had a little higher weight loss rate with more UFPR addition, and the IFR-PP composite had the highest residual char weight in terms of the main weight loss area.

On the one hand, fire testing and thermal behavior show the UFPR had no synergistic effect with IFR. On the other hand, if UFPR was treated as part of the polymer matrix in the composite, fire retardance and thermal behavior would drop due to the decrease in IFR content. Nevertheless, the fire retardance did not decrease significantly and thermal behavior had little variation.

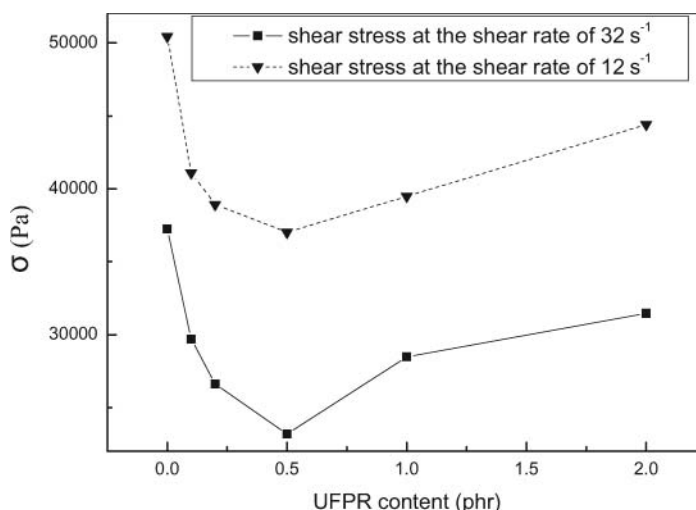
**Mechanical Properties**

Figure 2 shows the stress–strain curves of the composites with different contents of UFPR, and the yield strength and elongation at break of different composites are shown in Fig. 3.



**Figure 5.** The capillary rheology curves of the PP/IFR/UFPR composites with different UFPR contents: (a) the viscosity–shear rate curve and (b) the shear stress–shear rate curve.





**Figure 6.** Shear stress of the PP/IFR/UFPR composites with different UFPR contents under two shear rates.

As shown in Fig. 3, addition of the IFR significantly decreased the elongation at break of PP; it was less than 70%. Compared to the PP/IFR composite, the elongation at break of the composites was increased by adding UFPR. As the content of UFPR increased, the elongation at break of the composites increased and then decreased, reaching the maximum when the content of UFPR was 0.5 phr, at which level it was about 80% more than that of the PP/IFR composite. However, when the UFPR content was more than 0.5 phr, the elongation at break still remained at a much higher level, about 95% and 90% with the addition of 1 phr and 2 phr UFPR, respectively. It is suggested that a small amount of UFPR could effectively improve the adhesion between the matrix and the IFR filler and mend the interface defect that was caused by the IFR filler during the tensile process. Excessive addition of UFPR had a bad effect on the elongation at break, possibly because it agglomerated in the matrix PP and caused new interface defects during the tensile process. But the elongation at break of the composites did not decrease so much when the UFPR content was increased only too little because of the adhesion of UFPR.

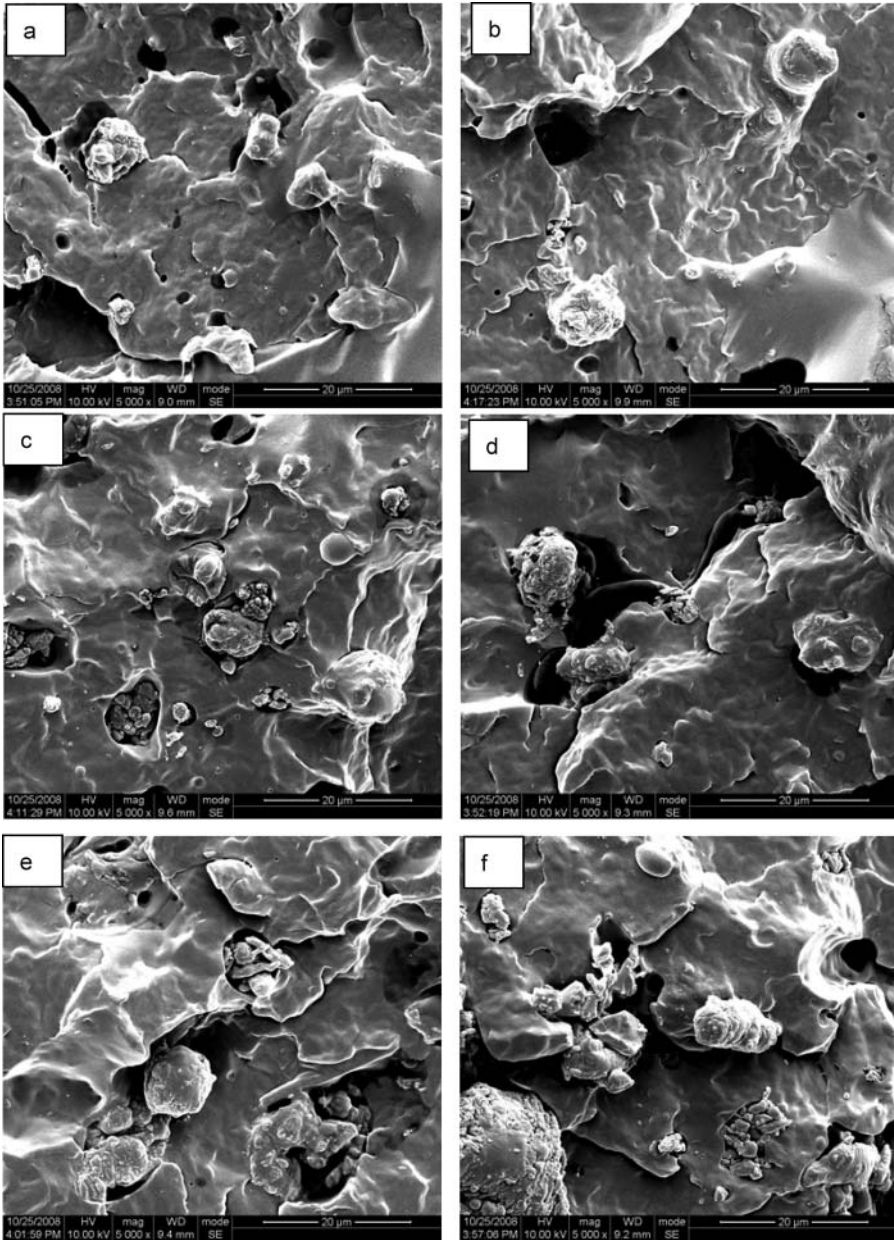
In addition, it can be seen from Figs. 2 and 3 that the yield strength of the composites appreciably decreased with increasing content of UFPR. It may be related to the lower yield strength of UFPR than that of the PP matrix.

### ***Melt Flow Behavior***

MFR of the PP/IFR/UFPR composites are shown in Fig. 4 and the capillary rheology curves are shown in Fig. 5.

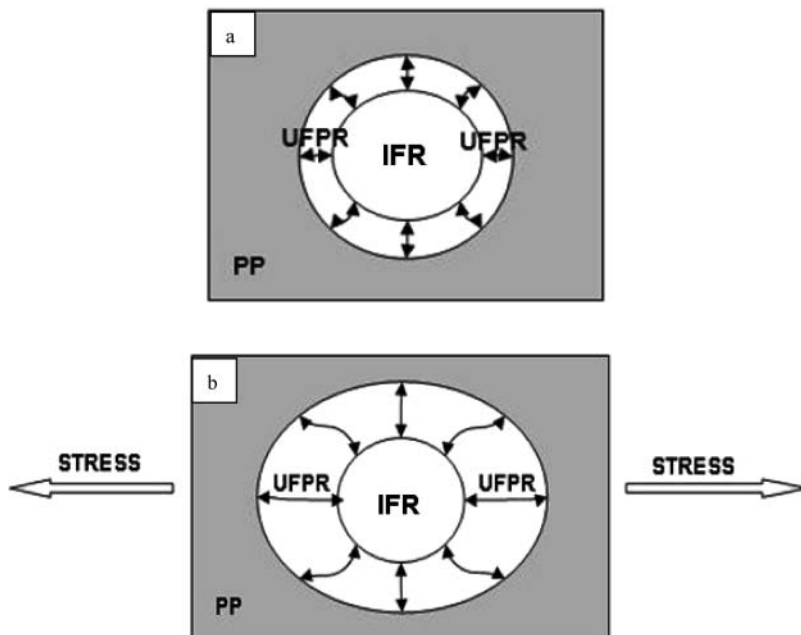
In Fig. 4, the MFR of the samples increased with increasing UFPR content from 0 to 0.5 phr and then decreased with adding more than 0.5 phr of UFPR. It is suggested that UFPR improved the fluidity of the composites when the UFPR content was less than 0.5 phr. However, as a rubber, UFPR flowed slower than the polyolefin that decreases the flowability of the composite gradually with increasing content.

In Fig. 5, the capillary rheology curves of the composites seem to have some differences at low shear rates but coincide very well at the higher shear rates. Using the values at the



**Figure 7.** The SEM micrographs of the PP/IFR/UFPR composites: (a) IPR-PP, (b) UFPR-1, (c) UFPR-2, (d) UFPR-3, (e) UFPR-4 and (f) UFPR-5.

first and the second shear rate point in Fig. 5b, it is shown that the minimums for the shear stress appeared for the addition of 0.5 phr UFPR in Fig. 6. The result of MFR and capillary rheology curves shows that the flowability of the composite with adding 0.5 phr UFPR was the highest at the low shear rates. On the other hand, the UFPR cannot accelerate or block the composite flow at high shear rate.



**Figure 8.** The spring model of UFPR in the PP/IFR/UFPR composites.

### *Microstructure of the Composites*

SEM micrographs of the PP/IFR/UFPR composites are shown in Fig. 7. In Fig. 7a, the IFR particles appeared on the fractured surface and the adhesion of PP matrix and IFR was poor. This is the reason that caused the decrease of the elongation at break of PP/IFR composite. In addition, the surface of the IFR filler particles looks relatively smooth. The cracks may have initiated on the binding sites between the filler and the matrix and broke easily when the force acted on the matrix.

Comparing Figs. 7b–7f with 8a, you shall see the surface of IFR filler was covered with some small particles. After measuring the diameter, it is considered that these particles should be the particles and aggregates of UFPR. In contrast to Fig. 8a, the other SEM micrographs show the IFR particles were covered by UFPR and imbedded in the PP matrix. In Fig. 8b, for instance, there is an obvious boundary between the IFR particles and PP matrix; the micrograph shows the surface of the IFR particles were encapsulated with a “UFPR shell”. The shell structure was formed by UFPR aggregates and, combined with the PP matrix and IFR fillers, increased the elongation at break and flowability when UFPR content was less than 0.5 phr. However, with increasing addition of UFPR, the number and size of UFPR aggregates increased and broke the binding sites between matrix and IFR fillers. Therefore, the composites elongation at break and flowability decreased after adding more UFPR than 0.5 phr.

Because of the formation of the “UFPR shell”, cracks did not propagate immediately when they initiated in the fracture surface of the composites in the tensile tests. As shown by the model in Fig. 8, the shell is like a spring connecting the matrix and the IFR fillers. The elongation at break of the PP/IFR/UFPR composite was improved because of the elongation and combination of the rubber.

The model can also explain the reason that MFR was highest and the shear stress had a minimum at low shear rate when the UFPR content was 0.5 phr. At low shear rate, IFR hindered molecular motion of the PP matrix but the UFPR particles connected the matrix and IFR fillers to make them a whole body and move together. However at high shear rates, the PP matrix has better flowability, sheared thinning, and it flowed through the filler easily when there was nothing connecting them; the UFPR did not react to connect the matrix and IFR fillers. Therefore, the curves coincide with each other at the high shear rates. Moreover, with increasing UFPR content, the UFPR aggregates increased and hindered the flow of PP melt in a similar manner as IFR.

## Conclusions

It is shown that the addition of UFPR decreased the fire retardance and thermal behavior of PP/IFR/UFPR composites slightly. Nonetheless, adding UFPR content of less than 2 phr permitted PP/IFR/UFPR composite to still pass UL94 V-0 (3.2 mm) and UL94 V-1 (1.6 mm) and caused the TG curves to have only a small drop in the main weight loss area. When the content of UFPR was less than 1 phr, the fire retardance of the composites did not decrease and the LOI value of the composites remained 32.

Addition of UFPR can improve the mechanical properties flowability of PP/IFR/UFPR composites. The elongation at break and melt flowability at low shear rates were better than that of PP/IFR composites, and had the highest values when the UFPR content was 0.5 phr. However, the values decreased when the UFPR content was more than 0.5 phr. A spring model can explain the reason that the mechanical properties and flowability of the composites were the highest when adding 0.5 phr UFPR.

## Acknowledgements

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