

Research Article

Effect of Particle Size of Additives on the Flammability and Mechanical Properties of Intumescent Flame Retarded Polypropylene Compounds

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The effect of particle size reduction of the components of a common intumescent flame retardant system, consisting of pentaerythritol (PER) and ammonium polyphosphate (APP) in a weight ratio of 1 to 2, was investigated on the flammability and mechanical performance of flame retarded polypropylene (PP) compounds. Additives of reduced particle size were obtained by ball milling. In the case of PER, the significant reduction of particle size resulted in inferior flame retardant and mechanical performance, while the systems containing milled APP noticeably outperformed the reference intumescent system containing as-received additives. The beneficial effect of the particle size reduction of APP is explained by the better distribution of the particles in the polymer matrix and by the modified degradation mechanism which results in the formation of an effectively protecting carbonaceous foam accompanied with improved mechanical resistance. Nevertheless, 10% higher tensile strength was measured for the flame retarded PP compound when as-received APP was substituted by milled APP.

1. Introduction

In parallel with the continually increasing use of plastics, the issue of fire safety has come to the forefront. Flame retardancy of polymers has become essential in many application fields such as transportation, construction, and electrical industries [1–4].

Among the commercially available halogen-free flame retardants, the so called intumescent flame retardant (IFR) systems have gained increasing interest due to their low toxicity and smoke production in fire accidents. The fire retardant mechanism of IFRs involves the formation of an expanded charred foam layer on the polymer surface, which acts as a heat insulator, limiting the heat transfer from the heat source to the polymer and the mass transfer from the polymer [5–7]. In general, the intumescent formulations are composed of three main ingredients: acid source, char forming agent, and blowing agent [8]. A typical example in the case of polypropylene (PP) is the ammonium polyphosphate (APP)/pentaerythritol (PER) system [9]. Xia et al. [10]

comprehensively investigated the effect of weight ratio of APP to PER on the carbonaceous foam deriving from PP/IFR system and revealed the ratio of 2:1 to be optimal in terms of flame retardant performance. Generally, 20–35 wt% of IFR is used in PP [11], in which loading level necessarily causes noticeable deterioration in the mechanical performance of the polymer [12–14]. Many experiments, including surface modification [14] and compatibilisation [13], have been conducted to diminish the loss in mechanical properties of an intumescent flame retarded polypropylene system; however, the particle size effect has only been barely investigated. Subasinghe and Bhattacharyya [15] studied the flammability, degradation, and mechanical performance of PP/kenaf fibre composites filled with three different types of APP at 20 wt% loading and found that the APP having the smallest particle size increases the mechanical strength of the char residue and, therefore, it performs better under sustained combustion compared to others.

In this work, the particle size of commercially available APP and PER was reduced by ball milling in order to

study the effect of particle size on the morphology, thermal degradation, flammability, and mechanical properties of intumescent flame retarded polypropylene compounds.

2. Materials and Methods

2.1. Materials. Polypropylene (PP, Moplen HP500N grade, homopolymer, MFI = 12 g/10 min at 230°C/2.16 kg) was purchased from LyondellBasell Industries N.V. (London, UK); JLS APP type ammonium polyphosphate (APP) was kindly supplied by Hangzhou JLS Flame Retardants Chemical Co., Ltd. (Hangzhou, China). Pentaerythritol (PER) was received from Wako Pure Chemical Industries Ltd. (Osaka, Japan).

2.2. Methods

2.2.1. Milling Experiments. According to SEM analyses, the characteristic average particle sizes of as-received APP and PER are about 15 μm and 200 μm , respectively. The PER crystals turned out to be easily grindable, while the reduction of the particle size of APP proved to be rather challenging. Several experiments were carried out using a ball milling machine equipped with 250 mL pots made of stainless steel to determine the optimal milling conditions to obtain APP of noticeably reduced particle size. In each experiment 2 \times 9 g APP was milled by keeping the ball to powder weight ratio at 20 and by setting the milling machine to maximum power. The effect of milling time and ball diameters (5, 8, and 11 mm) on the morphology of APP particles was comprehensively studied. Accordingly, a milling time of 72 min and the use of 5 and 11 mm balls in a weight ratio of 2 to 1 were selected to produce APP of reduced particle size in larger amounts.

2.2.2. Sample Preparation. Flame retarded polypropylene mixtures were prepared with 24 wt% additive contents. APP and PER, in a weight ratio of 2 to 1, were homogenized with PP in a Brabender Plasti Corder PL 2000 (Brabender GmbH & Co. KG, Duisburg, Germany) type internal mixer at a temperature of 170°C and with a rotor speed of 30 rpm, for 5 min. The blends were then hot pressed to form 4 mm thick sheets in a Collin P200E type laboratory hot press (Dr. Collin GmbH, Ebersberg, Germany) set to 180°C.

2.2.3. Characterization Methods. Scanning electron microscopic (SEM) images were obtained with a JEOL JSM-5500 LV type apparatus (JEOL Ltd., Akishima, Tokyo, Japan) using an accelerating voltage of 5 keV in the case of the additives and 15 keV in the case of the flame retarded PP compounds. All the samples were coated with gold-palladium alloy before examination to prevent charge build-up on the surface.

Infrared spectra (4000–400 cm^{-1}) were recorded using a Bruker (Bruker Corporation, Billerica, MA, USA) Tensor 37 type Fourier transform infrared (FT-IR) spectrometer equipped with DTGS detector with a resolution of 4 cm^{-1} . Before testing, the powder of samples was mixed with potassium bromide (KBr) powder and cold-pressed into a suitable disk for FT-IR measurement.

A TA Instruments (New Castle, NH, USA) Q5000 type instrument was used for *thermogravimetric analyses* (TGA).

TGA measurements were carried out at a heating rate of 10°C/min under 25 mL/min nitrogen gas flow, covering a temperature range of 25–700°C. About 15–20 mg of sample was used in each test.

The flame retardant performance of the prepared samples was characterized by *limiting oxygen index* (LOI) measurements according to the ASTM D 2863 standard. The LOI value is the lowest oxygen to nitrogen volumetric ratio, expressed as a percentage, where specimen combustion is still self-supporting.

Standard *UL-94 flammability tests* (ASTM D 635 and ASTM D 3801) were also performed on the composite specimens. UL-94 classification is used to determine dripping and flame spreading rates.

Mass loss type cone calorimeter tests were carried out by an instrument delivered by Fire Testing Technology Ltd. (East Grinstead, West Sussex, United Kingdom) using the ASTM E 906 standard method. Specimens (100 mm \times 100 mm \times 4 mm) were exposed to a constant heat flux of 50 kW/m^2 and ignited. Heat release values and mass reduction were continuously recorded during burning.

An AR2000 Rheometer (TA Instruments, New Castle, NH, USA) with special adjustment was used for structural and *mechanical characterization of chars* obtained from disk shaped specimen (diameter = 25 mm) after burning at 500°C under the cone heater. Compression tests were carried out with a constant squeeze rate of 30 mm/s while the changes in the normal force were recorded. The diameter of the squeezing upper plate was 25 mm and the initial gap was 20 mm in all cases. As the heights of the examined chars were different, the registered normal force values were plotted against the percentage of deformation of the corresponding chars.

Comparative static tensile tests were performed on rectangular specimens of 10 mm \times 100 mm (width \times length) using a Zwick Z020 universal testing machine (Zwick GmbH & Co. KG, Ulm, Germany) with a crosshead speed of 5 mm/min (according to the ISO 527-4:1997 standard).

Static 3-point bending tests were performed on rectangular specimens of 20 mm \times 80 mm using a Zwick Z020 universal testing machine according to the ASTM D 790 standard. The crosshead speed was 5 mm/min and the span length was 64 mm.

3. Results and Discussion

3.1. Characterization of As-Received and Milled Flame Retardant Additives. Typical SEM images of APP and PER additives before and after milling are shown in Figure 1. As a result of milling, the average particle size of APP was reduced from 15 μm to 8 μm (2.5 wt% of stearic acid was added to separate the aggregates and make single particles visible during SEM examination), while in the case of PER mostly submicronic particles were obtained.

The chemical structures of the as-received and milled additives were examined and compared using FTIR spectroscopy. In the case of PER, no changes were observable in the IR spectra, while in the case of APP after milling a new absorption peak appeared at 681 cm^{-1} (Figure 2). According

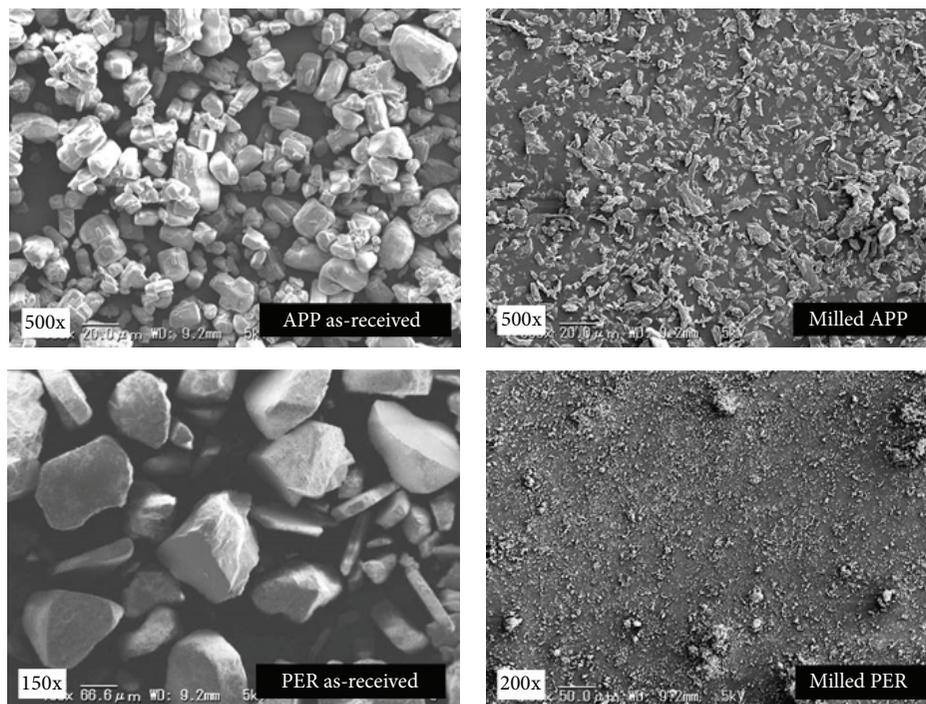


FIGURE 1: SEM micrographs of APP and PER additives before and after milling.

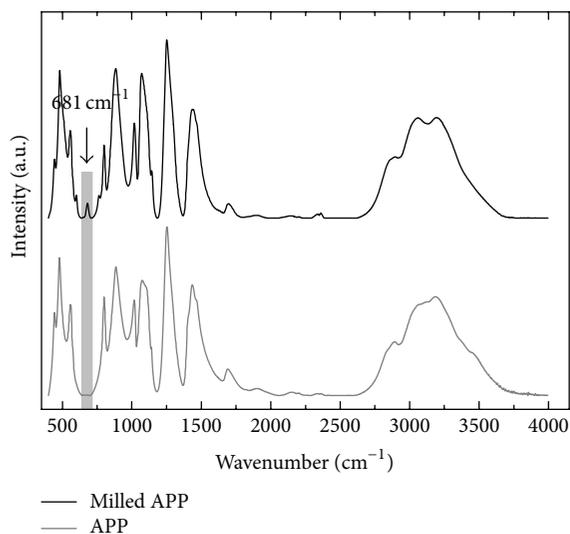


FIGURE 2: FTIR spectra of as-received and milled APP.

to the study of Yi and Yang [16] this peak indicates the presence of a lattice defect within the crystalline structure of APP, which may have been caused during high energy milling. However, TGA measurements did not indicate any differences between the thermal stability of the as-received and the milled additives.

3.2. Characterization of PP Compounds Flame Retarded with Intumescent Systems of Different Particle Size. Four types of flame retarded compositions with 24 wt% additive content were prepared by varying the use of as-received (APP and

PER) and milled particles (mAPP and mPER). In accordance with the results of Xia et al. [10], the weight ratio of APP to PER was kept constant at 2 to 1. The flame retarded PP compounds were examined by TGA, flammability and foam stability tests, mechanical tests, and SEM analysis.

3.2.1. Thermal Degradation. The four types of flame retarded PP compounds were examined by TGA under a nitrogen atmosphere. The obtained TG curves are presented in Figure 3. As it can be seen, up to 700°C the neat PP has completely volatilised, while about 5 wt% residue remained from each flame retarded compound at the end of the heating program. The main decomposition of the flame retarded compounds occurred at 30°C higher temperature than that of neat PP. The decomposition of the mAPP containing compounds started at slightly lower temperature (220°C) than that of the unmilled APP-containing PP compounds (235°C). Nevertheless, major differences were observed between the values of weight loss in the first degradation stage, occurring in the temperature range of 220–300°C, where a series of esterification reactions between APP and PER take place. It is proposed that the size and distribution (i.e. “availability”) of the flame retardant components has an influence on the generation pathways and on the amount and composition of phosphorus degradation products derived from pyrolysis of organic phosphates, which, according to the study of Xia et al. [10], also noticeably affect the characteristics of the solidified carbonaceous foam. The degradation steps above 500°C indicate the volatilisation of phosphorus degradation products (carbonaceous char is stable at this temperature range). Therefore, phosphorus-rich chars are presumed to be formed from the IFR systems, excluding the composition

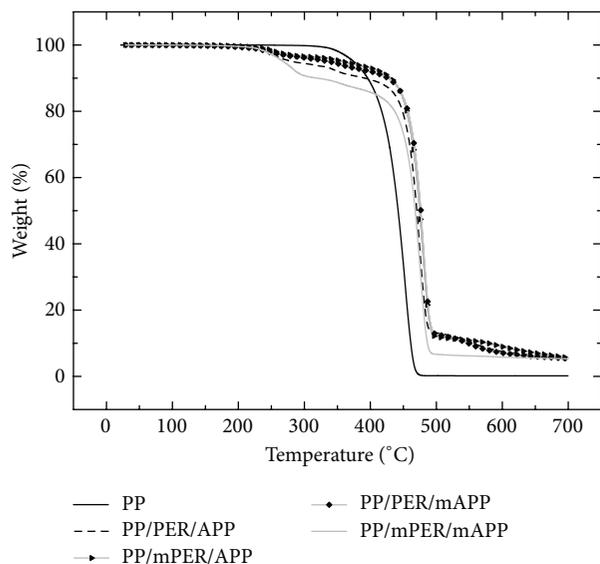


FIGURE 3: TG curves of neat PP and four intumescent flame retarded PP mixtures containing as-received and milled additives.

where both flame retardant components were of reduced particle size (PP/mPER/mAPP). Based on the TGA results, different carbonaceous foam structures were expected to be formed during the fire tests.

3.2.2. Flammability Characteristics. The flammability characteristics of the flame retarded PP compounds were evaluated based on UL94 test, LOI measurements, and cone calorimeter tests. The measured LOI values and the UL94 ratings are summarized in Table 1. It was concluded that the particle size of the additives influences the flame retarded effectiveness of the intumescent system. At the additive loading of 24 wt%, the flame retarded PP compounds show self-extinguishing behaviour and meet the requirements of the UL94 V-0 classification. This was not the case for the PP/mPER/APP sample, which due to flaming drips has been classified as V-2 rating. Also, compared to the LOI value of 28 vol% of the PP compound containing as-received additives (PP/PER/APP) the LOI decreased when milled PER (mPER) was used. The addition of milled APP (mAPP) somewhat compensated for the deteriorating effect of mPER (PP/mPER/mAPP: UL-94 V-0 rating, LOI: 27 vol%), and the same LOI value of 28 vol% was measured when mAPP was present in combination with unmilled PER (PP/PER/mAPP). It was concluded that while the reduction of the particle size of PER results in deterioration of the flammability properties of intumescent flame retarded PP compounds, the use of APP of reduced particle size proved to be advantageous.

Based on the mass loss calorimetric test results similar conclusions may be drawn. The heat release rate curves recorded during cone calorimeter tests and the corresponding evaluated experimental data are presented in Figure 4 and Table 2, respectively. Compared to the intumescent flame retardant system containing only as-received additives (PP/PER/APP), better flame retarding performance

TABLE 1: LOI and UL94 results of the flame retarded PP compounds.

	LOI (vol%)	UL-94 (rating)
PP/PER/APP	28	V-0
PP/mPER/APP	26	V-2
PP/PER/mAPP	28	V-0
PP/mPER/mAPP	27	V-0

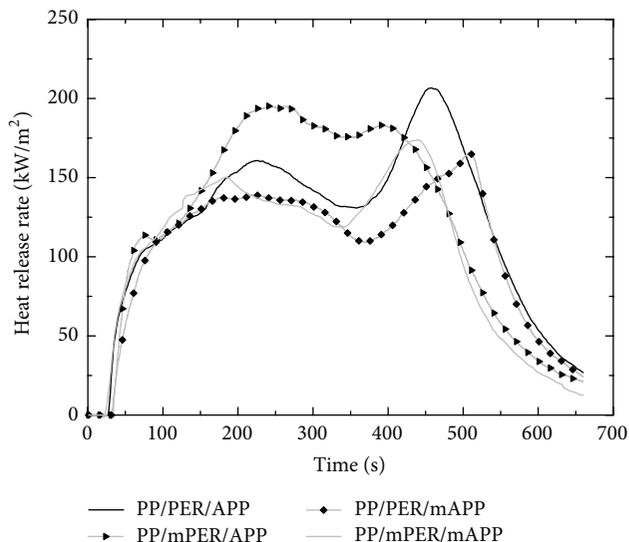


FIGURE 4: Heat release rate curves of intumescent flame retarded PP compounds.

was obtained when milled APP was used; about 15–20% reductions both in peak of heat release rate (pkHRR) and total heat release (THR) were achieved and noticeably higher amounts of charred residues were obtained. In contrast, the application of milled PER in combination with as-received APP resulted in a different HRR curve shape and significantly earlier appearance of pkHRR. The dissimilar behaviour of the four types of flame retarded compounds can be explained by the different degradation mechanisms (as also observed from the TGA results) and char forming processes of the examined intumescent flame retardant systems, which are apparently remarkably affected by the size and distribution of the reacting components.

To investigate the structure of the formed charred foams, compression tests were performed in a rheometer with plate-plate geometry [17]. In Figure 5, the recorded normal force values were plotted against the deformation percentages, typical for each charred residues. The first linearly increasing section of the curves represents the mechanical resistance of the chars until the first crack is initiated. When considering the initial slope of the curves, it is noticeable that the stiffness of the char corresponding to the PP/PER/mAPP sample is much higher than that of the other chars, which show rather flexible behaviour. Based on the flammability test results (UL94, LOI, and cone calorimeter tests) the mechanically most resistant foam structure provides the best

TABLE 2: Summary of the mass loss calorimetric test results.

	TTI (s)	pkHRR (kW/m ²)	pkHRR _{time} (s)	tHR (MJ/m ²)	Residual mass (%)
PP/PER/APP	22	207	458	77.8	8.0
PP/mPER/APP	27	195	242	77.4	10.7
PP/PER/mAPP	24	165	508	67.7	11.0
PP/mPER/mAPP	21	174	441	65.2	13.7

TTI: time to ignition; pkHRR: peak of heat release rate; pkHRR_{time}: time of peak of heat release rate; tHR: total heat released.

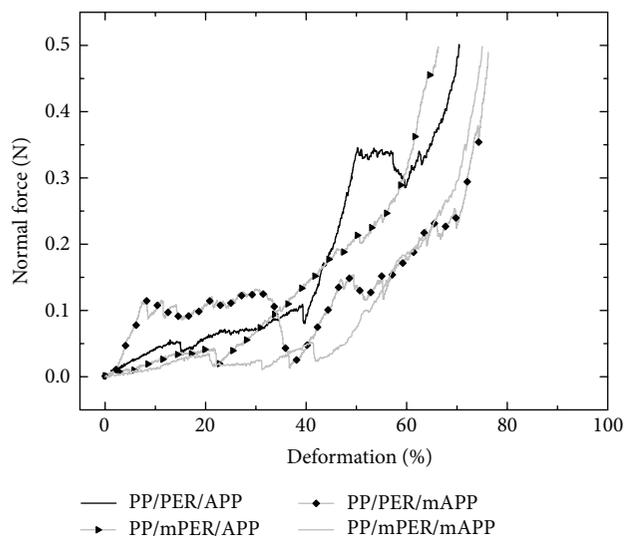


FIGURE 5: Compression test of charred foams obtained after combustion under cone heater.

flame retardant performance. Subasinghe and Bhattacharyya ascribed the enhanced flame retardant efficiency of APP of smaller particle size also to the formation of a stable char structure [15].

3.2.3. Mechanical Properties. It was proposed that the particle sizes of the additives used may also influence the mechanical properties of the obtained flame retarded compounds. The mechanical performance of the four types of intumescent flame retarded compounds was evaluated based on static tensile and 3-point bending tests. The tensile and flexural strength and modulus values of the flame retarded PP compounds are compared in Figure 6. SEM pictures taken from the fracture surfaces are presented in Figure 7, which help the observed differences in the mechanical properties to be understood. Compared to the tensile strength measured for the neat PP (31.5 MPa), about 30% loss in tensile strength was measured when the as-received additives were introduced at 24 wt% loading (PP/PER/APP). It was found that compared to the mechanical performance of the PP/PER/APP sample the use of milled PER caused deterioration of both the tensile and the flexural strength, which is mainly attributed to the aggregate formation of the submicronic, that is, high surface energy and hydrophilic particles in the hydrophobic polymer matrix (see Figure 7). In contrast, the substitution of as-received APP with milled APP provided increased

tensile and flexural strength to the flame retarded polymer compound. On average 10% higher strength was achieved only by reducing the average particle size of APP by half. The highest strength values were measured when both additives were of reduced particle size (PP/mAPP/mPER). Also, the most homogeneous additive distribution was observed for this sample (Figure 7). As expected, the stiffness of PP (tensile modulus: 1.3 GPa, flexural modulus: 1.7 GPa) increased with the addition of the flame retardants. When smaller particles were embedded the magnitude of the increase in stiffness lessened (Figure 6); however, the tensile and flexural moduli of the effectively flame retarded systems still outperform those of neat PP.

4. Conclusions

It was concluded that the particle size of the flame retardant additives has a significant impact on both the flammability and mechanical performance of intumescent flame retarded compounds. Depending on the particle size (ratio) and the distribution of the two flame retardant components (PER and APP) in the polymer matrix their reaction pathway and degradation mechanism may change; therefore, carbonaceous chars of different composition and structure can be obtained from the PER/APP system, significantly differing in flame retarding performance. The introduction of PER of significantly reduced particle size proved to be disadvantageous in terms of both flammability and mechanical properties, which was mainly attributed to the inadequate distribution of the submicronic (i.e., high surface energy) hydrophilic particles prone to aggregate in PP. On the other hand, noticeable improvement in the flame retardant effectiveness of the intumescent system was observed when the as-received APP was substituted by milled APP particles. 20% reduction was achieved both in pkHRR and in tHR, and higher amounts of char remained after exposure in the cone calorimeter. Compression testing of the charred foams revealed improved mechanical resistance for this PP/PER/mAPP system, which more than likely contributes to the improved flame retardancy. According to SEM investigations, the distribution of milled APP in the polymer matrix was proper. These better dispersed particles caused less deterioration in the tensile strength of the flame retarded PP; 10% higher tensile strength was measured compared to the as-received IFR system. It is proposed that further reduction of the particle size of APP may further improve the flammability and mechanical performance of the intumescent flame retarded PP system. However, the particle size reduction of the additives should be

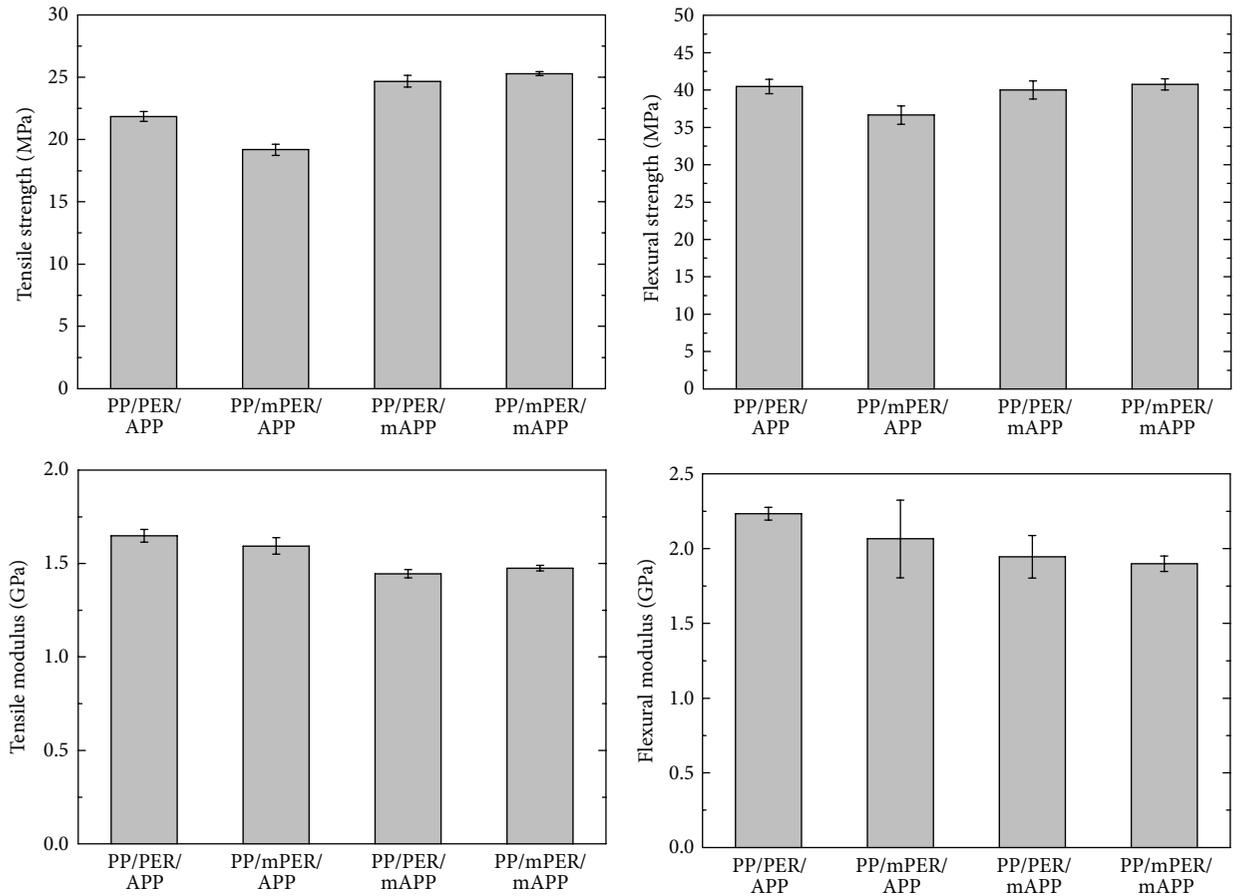


FIGURE 6: Comparison of the tensile and flexural strength and modulus of the intumescent flame retarded PP compounds.

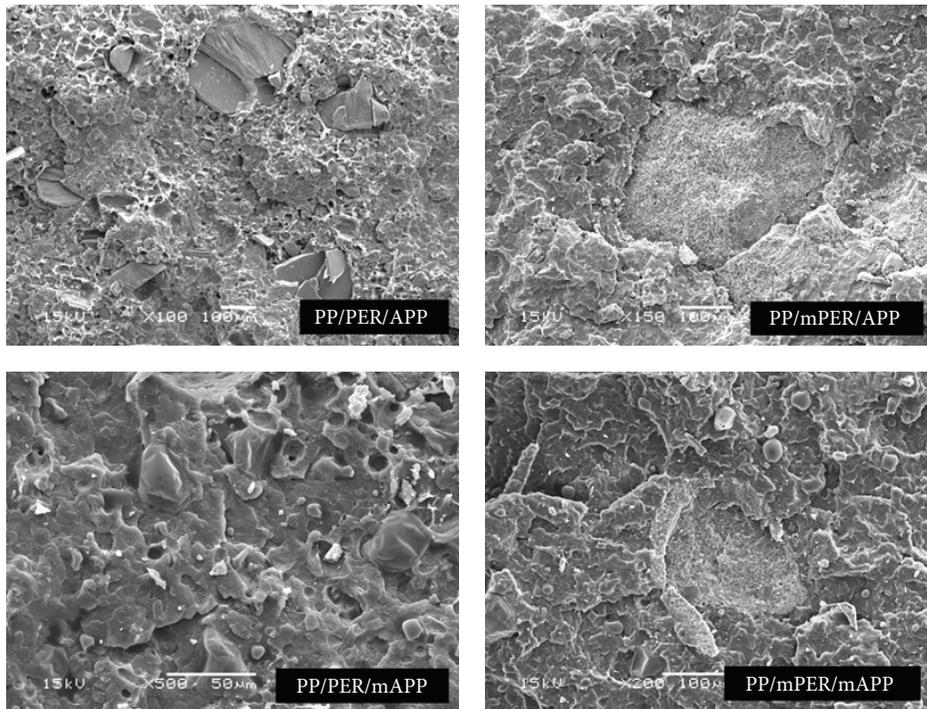


FIGURE 7: SEM images taken of the fracture surfaces of the intumescent flame retarded PP compounds.

optimized by taking also into account the deteriorating effect of proneness to aggragation.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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