Extrusion with Ultrasound Applied on Intumescent Flame-Retardant Polypropylene

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In this work, the effect of processing conditions on the production of an intumescent flame-retardant system is studied in polypropylene-based compounds. Two distinct procedures were used: ultrasonic assisted single screw (with a static mixer die) and twin screw extrusion. The flame-retardant, thermal, mechanical, morphological, and rheological properties were measured. It was found that the flame-retardant intumescent content can be diminished from 30 phr (as usually used) to 21 phr using the application of ultrasonic waves during extrusion and with the addition of chemically modified clay to obtain a V0 classification according to UL94-V standards. In addition, the processed materials presented improvements in the mechanical properties such as impact resistance (Izod Notched), strain at break and tenacity upon ultrasound application. The online application of ultrasound through a die that produces extensional flows improved greatly the dispersion and distribution of the particles of the intumescent system and the chemically modified clay in the polymer matrix. POLYM. ENG. SCI., 53:2018–2026, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Intumescent systems have been widely studied due to their effectiveness as flame-retardant additives. [1–3]. These systems have been formulated with various polymers, such as PU, EVA, SBR, PE, LDPE, PLA [4–9], with particular attention to polypropylene compounds. These works are diverse, including the synthesis of an intumescent system by reactive extrusion [10–12], the incorporation of different nanofillers in the intumescent system [13–16] and the formation of an interfacial layer containing intumescent flame-retardant compounds [17]. In addition, thermal degradation and the combustion behavior of a novel intumescent system [18] were also given attention, among others. However, to obtain these results, high flame-retardant additive concentrations are commonly used in order to achieve the flammability levels suitable for application in the electronics, electrical, and automotive industries.

The components of an intumescent system are usually: (1) carbon-based compounds, such as polyols, which contribute to the char yield, for example pentaerythritol (2). Nitrogen compounds such as organic amines or amides, for example, melamine, which acts as blow agent, and (3) inorganic acids, such as phosphoric acid in the form of ammonium salt such as ammonium polyphosphate, which is widely used. Traditionally, to obtain a UL94-V0 classification with polypropylene, the total concentration of the intumescent additives used is in the range of 30–40 wt% [19]. Notwithstanding, at these contents, the intumescent additives are not well dispersed, giving rise to poor mechanical properties [20, 21].

Chemical reactions occurring during the polymer combustion process, in the presence of intumescent systems, depend on the type, number, and proportion of each functional group and component in the system. The mechanism by which the intumescent systems act as flame retardants has been studied extensively [1, 22, 23]; these studies point out that this implies the formation of a char layer on the surface of the materials exposed to fire, produced by carbon-former compounds. Simultaneously, nitrogen compounds generate gaseous products which expand the carbon layer and act as a barrier to heat transfer, avoiding the diffusion of oxygen and thus preventing the polymer pyrolysis in volatile compounds. The third component is a phosphorous compound whose main action is to promote the charring process together with

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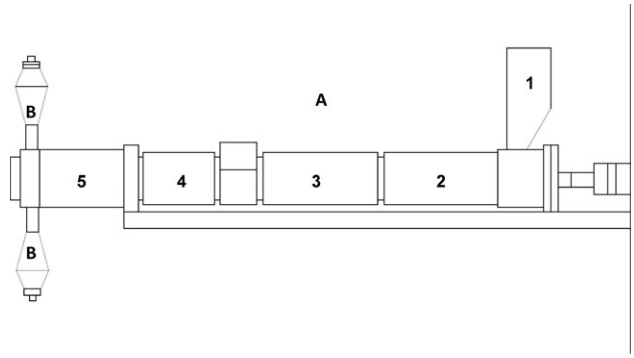

FIG. 1. Ultrasound system. Single extrusion equipment coupled with a static mixer die and ultrasonic elements lateral view. (A) Single extrusion equipment lateral view. (B) Ultrasonic elements. (1) Feeding zone; (2) heating zone 1; (3) heating zone 2; (4) heating zone 3; and (5) static mixer die.

the carbon-former compounds. Another advantage of the intumescent compounds for flame-retardant properties is the char layer formation on the surface that avoids dripping of the material and prevents fire propagation.

One of the disadvantages of the intumescent systems for flame-retardant properties is the high concentrations required to achieve the flammability levels required, which induce agglomeration and offset good dispersion and distribution of additives in the polymer matrix. A technique suggested for obtaining a good dispersion and distribution of polymer nanocomposites is the application of ultrasonic waves during extrusion. Important advantages of good distribution and dispersion of particles at the nanometric size of carbon nanotubes or various clay types have been reported [24–27].

In this work, the processing of flame-retardant intumescent materials with L-lysine-grafted clays is analyzed. A single screw and twin screw extrusion processes were considered. The single screw process included a static mixer die that induces extensional flows coupled to an ultrasound system. The resulting mechanical, thermal, rheological, morphological, and flame-retardant properties are directly related to the degree of dispersion of both the intumescent flame-retardant additives and clay particles. It is revealed, to our knowledge for the first time, that the application of ultrasonic waves in the actual extrusion operation is a pre-requisite to adequately disperse the particles of the intumescent flame-retardant system and the clay in the polymer matrix to achieve a synergistic effect on the flame-retardant properties of the polymer.

EXPERIMENTAL

Materials

These include medium-impact polypropylene copolymer (PP) with a melt index of 4 g/10 min from Indelpro (Mexico); sodium bentonite clay (BEN) Actisil 220FF, with 55 meq/100g ionic interchange capacity from Süd-Chemie; pentaerythritol (PENTA) with purity of 94–95%, melting point of 260°C; melamine, with purity of 99.8%; and ammonium polyphosphate (APP) Exolit AP422, from Clariant, with phosphorous content of 31–32% wt and with decomposition temperature higher than 275°C. L-Lysine mono-chlorohydrated aminoacid (Lys) and industrial-grade maleic anhydride (MAH).

Equipment

The PP-based composite materials, the intumescent system and bentonite clay were processed in a twin screw counter-rotating extruder (Leistritz Micro 27) with $L/D = 32$ and diameter of 27 mm; alternatively, a single screw

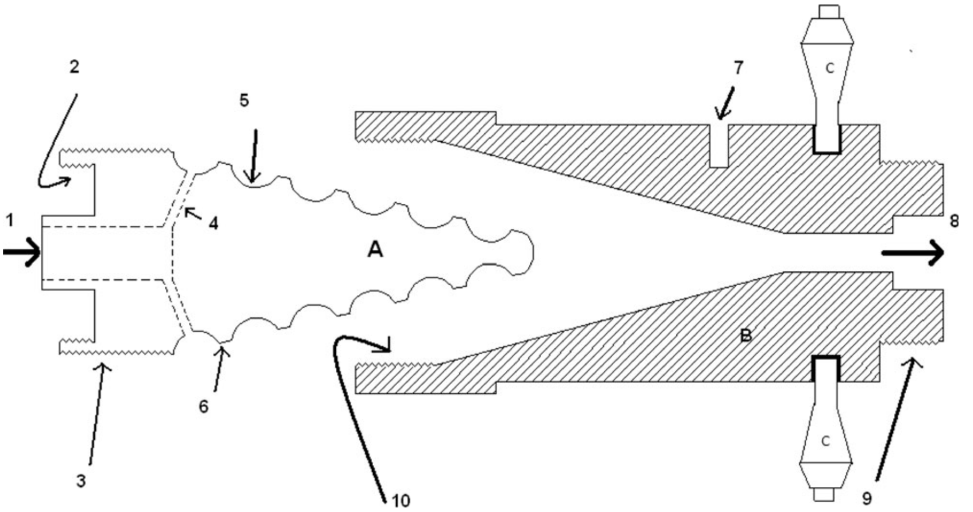

FIG. 2. Static mixer die lateral view. (A) Polymer melt feed helical cone. (B) Static mixer exterior part Cone angle matches part A. (C) Ultrasonic elements. (1) Static mixer to extruder coupling section. (2) Cone base internal screw section. (3) External screw section to part B. (4) Polymer melt feed channels. (5) Feed cone clearance. (6) Feed cone flight. (7) Thermocouple fit. (8) Polymer melt out. (9) Screw section to couple die. (10) Screw section to cone.

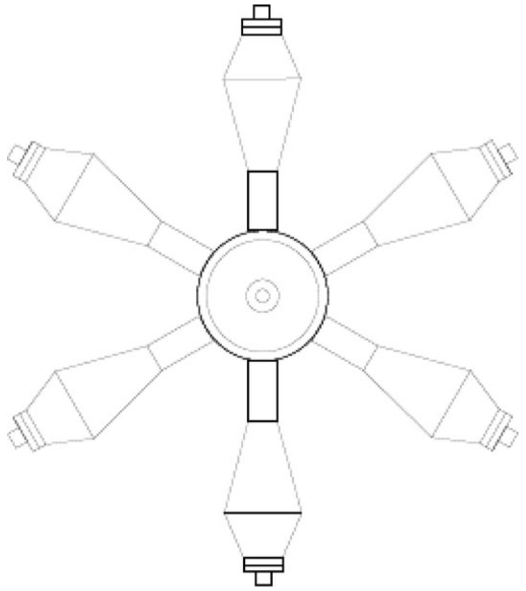

FIG. 3. Ultrasonic elements coupled to static mixer die. Frontal view.

extruder with $L/D = 24$ and diameter of 2.54 mm (see Fig. 1) was coupled to a static mixer die producing extensional flows (see Fig. 2) assisted by a set of six ultrasonic elements of 50 W each to generate ultrasonic waves (see Fig. 3, patent under revision). The injection molding operation was carried out in a Demag–Ergotech 50-200 (L/D =20) injection molding machine.

Processing Method

The following stages were included in the materials preparation:

1. Grafting of MAH on PP via twin screw extrusion to produce PP-*g*-MAH was done according to Shi et al. [28]: PP polymer was dried and added with 1.0 phr of MAH and 0.2 g of BPO. The grafting reaction was carried out by reactive extrusion in a twin screw conical counter-rotating extruder with temperature profile of 160°C at the feeder zone, 180–190°C at the mix zone, 200°C at die, and 70 rpm screw speed. Residence time was 60 sec. BPO and MAH were reagent-grade products and used without further purification. The grafted amount of MAH on polymer was determined by high-resolution thermogravimetry technique (TGA-HR) throughout measurements of loss of weight between both pristine polymer and polymer-*g*-MAH at 160°C under nitrogen flow of 40 ml/minute, to determine non-grafted MAH decomposition percentage. The material produced with this procedure, PP-*g*-MAH, had a MAH- grafted content of 0.43 % weight. PP-*g*-MAH is used as compatibilizer between BEN-Lysine and pristine PP.
2. Chemical modification of the bentonite clay via ionic interchange reaction was carried out using L-lysine amino-acid to produce BEN-Lys, where clay surface is grafted with a moiety ending in a carboxylic functional group able to react with anhydride groups [29–31].
3. Once PP-*g*-MAH and BEN-Lys were obtained, material formulations were made according to Table 1, using the twin-screw extruder with screw speed of 200 RPM and maximum temperature of 205°C.
4. The materials produced in part 3 were processed in the single screw extruder using 30 RPM screw speed and 215°C maximum temperature applying ultrasound waves to promote dispersion and distribution of additives particles in the blend. The ultrasonic waves were applied with a frequency of 40 kHz, 100 V amplitude, and 300 W power. These processing parameters were determined according to frequency and amplitude sweeps previously done on PP (results not shown).
5. Samples for mechanical and flammability tests of the materials formulated in section "Results and Discussion" were produced by injection-molding.

Materials Characterization

Flame-retardant properties were evaluated according to ASTM D635 (IEC60695-11) in horizontal position and ASTM D3801 (IEC 707-9 e ISO 1210) in vertical position. Sample dimensions were 125 × 13 × 3 mm; they were maintained at 23°C and 50% humidity during 48 h prior to analysis. Mechanical properties were measured in an Instron-5565 machine with speed of 50 mm/min according to ASTM D638. Impact resistance tests were

TABLE 1. Materials description.

		Components				
ID	Extrusion process	PP-g-MAH (phr)	BEN-Lys (phr)	APP (phr)	Penta (phr)	Melamine (phr)
PP		0	0	0	0	0
30 FR/TS	Twin screw	0	0	10	10	10
21 FR/TS	Twin screw	0	0	7	7	7
21 FR-1 BEN/TS	Twin screw	2	1	7	7	7
21 FR-3 BEN/TS	Twin screw	6	3	7	7	7
30 FR/SS-US	Single screw-Ultrasound	0	0	10	10	10
21 FR/SS-US	Single screw-Ultrasound	0	0	7	7	7
21 FR-1 BEN/SS-US	Single screw-Ultrasound	2	1	7	7	7
21 FR-3 BEN/SS-US	Single screw-Ultrasound	6	3	7	7	7

made according to ASTM D256 (Izod-notched) in an Atlas CS-137C impactometer with sample dimensions of 64 × 12.7 × 12.7 mm. Thermogravimetric analysis (TGA) was carried out in a TA-Instruments 2950 calorimeter with heating rate of 10°C/min under nitrogen atmosphere. Rheological tests were performed in a stress-controlled TA-G2 rheometer using the parallel-plates fixture with 25 mm diameter and a heating chamber (TA-Extended Temperature System). Micrographs were taken in a field-emission scanning electron microscope (SEM) Jeol JSM-7600F.

RESULTS AND DISCUSSION

Table 1 discloses the formulations used in this study. Samples are classified according to the following procedure: for example, in 21 FR-1 BEN/SS-US, 21 FR means 21 phr (parts per hundred resin) of intumescent flame-retardant additives, 1 BEN means 1 phr of bentonite clay-lysine, SS-US stands for single screw ultrasound extrusion process. In the other cases, TS means processing under twin screw extrusion.

Morphology

Figure 4a shows the SEM micrograph for the 30 FR/TS system. Agglomerates of sizes up to 30 microns of the intumescent additive particles are observed, illustrating the problem to achieve an adequate level of dispersion and distribution of the additives when high concentrations are employed, even though a high screw speed is used (200 RPM). In Figure 4b, the micrograph of the 30 FR/SS-US system shows a much better dispersion and distribution of the intumescent additives, with a particle size of 1–4 microns. This implies a system with improved particle dispersion and distribution and consequently much more exposed area of the particles of the dispersed phase. This effect was achieved in all materials with the ultrasound process. For example, micrographs for the systems 21 FR/TS and 21 FR/SS-US, Figure 4c,d, respectively, reveal a decrease in particle size of the intumescent additive from 10 microns to a size of <3 microns. In the case of the composite materials 21 FR-1BEN/TS and 21FR-1BEN/SS-US, also better particle dispersion is observed using the ultrasound process. In the micrograph corresponding to the material obtained through twin-screw extrusion (Fig. 4e), additive particles of size around 20 microns are observed, while in the micrograph shown in Figure 4f, using the single screw with ultrasound process, the largest size amounts to only one micron. This remarkable decrease in the particle size is directly related to the process implemented here.

Thermal Properties

Figure 5 shows the weight loss-temperature of the materials produced in the two processes considered (twin screw and single screw with ultrasound). The first process produces materials with higher decomposition temperatures; however they present two decomposition steps, the first one is observed between 220–300°C with a weight loss of 5–7% approximately. This first decomposition step is independent of the clay and additives content and it is possibly caused by loss of low molecular weight compounds in the agglomerates of the intumescent additives.

With respect to the products obtained through the second process (with ultrasound), Figure 5 reveals clearly the effect of the clay content on the decomposition temperature; this temperature increases with BEN-Lys content, indicating that at 21 phr concentration of intumescent additives (FR), the clay imparts better thermal stability. This behavior could be possibly attributed to the barrier effect due to the presence of clay particles dispersed in the polymer matrix [32] by the action of the ultrasound device. For higher additive contents (30 phr) the material does not present enhanced decomposition temperatures with respect to those with 21 phr FR. Considering the pristine polymer, the composite materials produced by both processes present lower decomposition temperatures; however at the end of the decomposition process, the pristine polymer does not present residues formation, in contrast to the composite materials. This shows clearly the effect of the intumescent additives on PP, as they produce residues found at the end of the decomposition process.

Table 2 presents decomposition temperatures at 10, 50, and 90% weight loss and % residues formation at 600°C under twin screw extrusion and single screw with ultrasound. For the first process (twin screw), at 10% weight loss, the 30 FR/TS, and 21 FR/SS-US materials show similar decomposition temperatures (371 and 373°C, respectively) indicating independence of the FR concentration. On the other hand, the clay addition shows a negative effect on the decomposition temperature in the 21 FR-1 BEN/TS and 21 FR-3 BEN/TS materials throughout the 10, 50, and 90% weight loss since the materials decompose faster. This effect may be related to the incomplete exfoliation of the clay tactoids which do not participate in the formation of the char layer. The residues formation at 600°C is larger with increasing concentrations of the intumescent additives and clay. According to these results, the composite material 30 FR/TS obtained through the twin-screw extrusion presents the highest thermal stability. A lower additive concentration is not convenient to improve the thermal stability with this process.

At higher additive content (30 FR/SS-US), the materials produced through the single screw process with ultrasound present lower decomposition temperature than those obtained with 21 phr FR at 10, 50, and 90% weight. For example, at 10% weight loss, the decomposition temperature of the 21 FR/SS-US material increases 14°C, while the material 21 FR-3 BEN/SS-US increases 36°C. Results show that the ultrasound process allows decreasing the concentration of intumescent additives from 30 to 21 phr

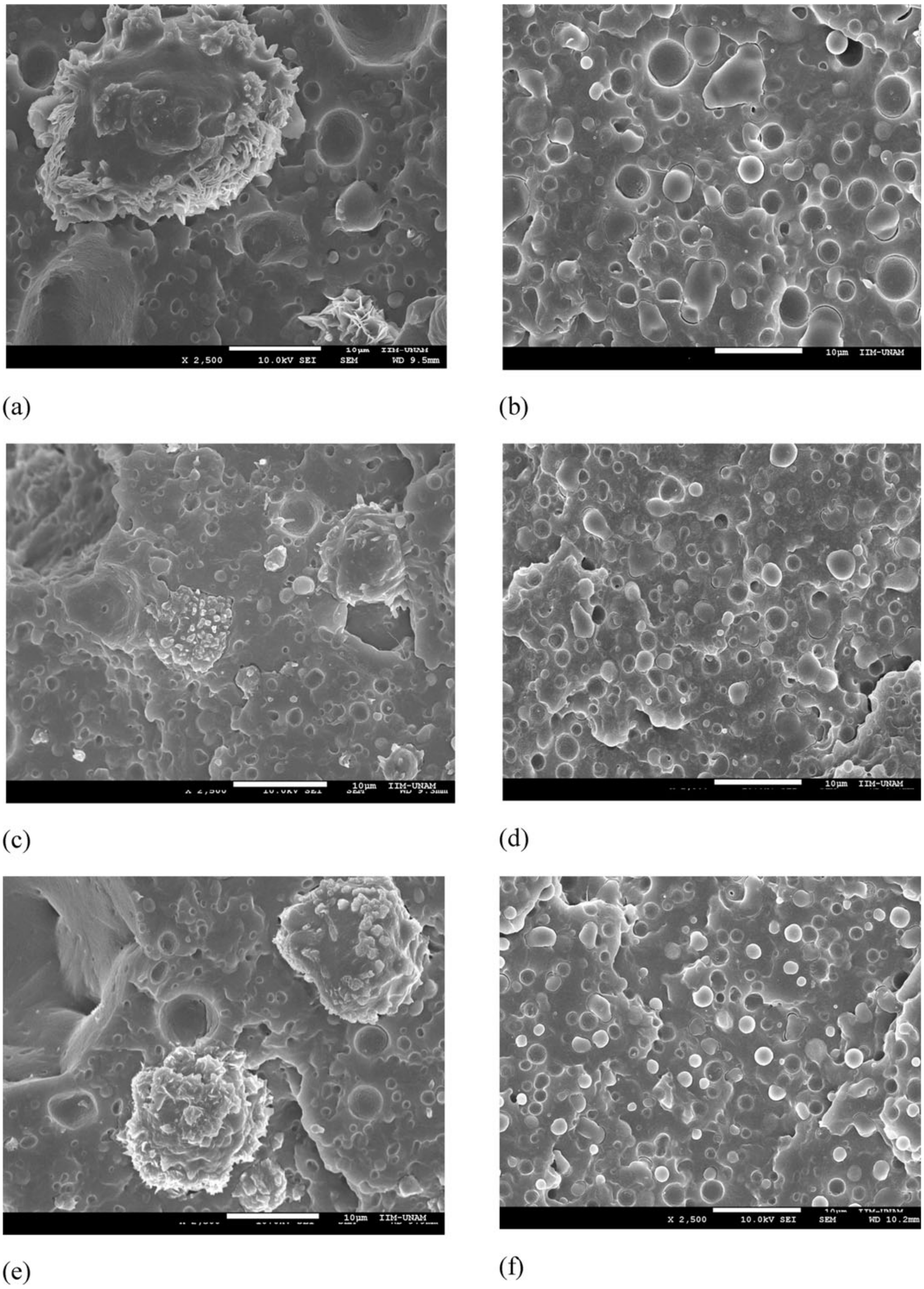

FIG. 4. SEM micrographs of a fractured surface: (a) 30 FR/TS, (b) 30 FR/SS-US, (c) 21 FR/TS, (d) 21 FR/SS-US, (e) 21FR-1BEN/TS y, and (f) 21 FR-1 BEN/SS-US. 2500X.

FR improving the thermal stability, in contrast to the materials obtained through the twin-screw extrusion.

Flame-Retardant Properties

Table 3 discloses results on the evaluation of flame-retardant properties of the compounds according to the UL94 procedures, horizontal, and vertical position. Materials produced with 30 phr FR under the twin screw and single screw extrusion with ultrasound present a V0 classification, these results confirm the effectiveness of the intumescent additive as flame retardant at this load (30 phr) which corresponds to that traditionally used [13, 19]. Those materials produced with lower additive contents (21 phr FR) under twin screw extrusion are less effective as flame retardants, since the products present similar

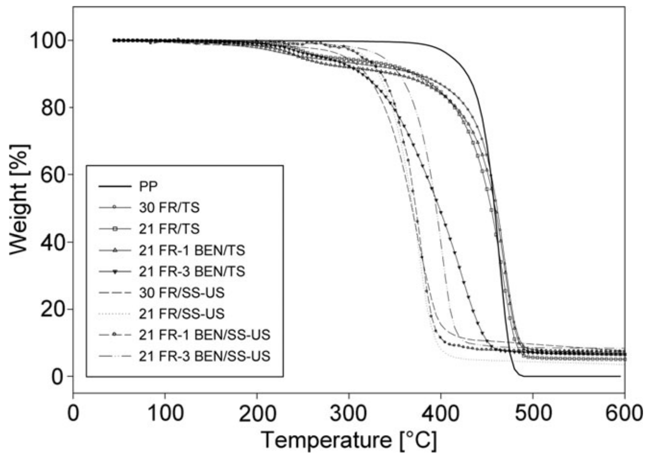

FIG. 5. Thermogravimetric analysis.

burning rate values than those of the pristine PP. The material 21 FR/TS shows a burning rate of 23.1 mm/min and no substantial effect is observed with addition of clay, since the material 21 FR-1 BEN/TS shows 21.1 mm/min, and the 21 FR-3 BEN/TS material shows 24.3 mm/min. These results are attributed to inadequate intumescent additive and clay particle dispersion and distribution, diminishing the effect of the additives upon the desired fire-retardant properties [33–36].

Materials produced following single screw extrusion with ultrasound present a remarkable improvement on the flame-retardant properties of PP. The material 21 FR/SS-US shows a burning rate of 21.2 mm/min, similar to that obtained using the twin screw process (23.1 mm/min) revealing no influence of ultrasound. However, when 1 phr clay and PP-*g*-MAH are added to the same formulation (21 FR), a material with UL94-V0 rating is obtained. The extrusion with ultrasound achieves this remarkable result (UL94-V0 rating) even when the intumescent additive concentration is decreased from 30 to 21 phr (17% w/w). This result derives from improved dispersion of both the additives and clay particles, exhibiting a synergy that leads to optimum formation of the char layer acting as a barrier to heat transfer during the combustion process. Moreover, a reaction of the clay with phosphates has been reported elsewhere to stabilize the intumescent char [19] improving its performance. Larger concentrations of the clay (3 phr) offset these advantages, increasing burning rate (26.2 mm/min); this effect has been observed in other systems [37] and it has been attributed to the lack of adequate dispersion of the nanometric-size particles in the polymer matrix.

Rheological Properties

Figure 6 shows the shear viscosity as a function of shear rate of the pristine PP and the materials obtained using the two processes (twin screw and single screw with ultrasound). A substantial effect of the extrusion process exists on the viscosity behavior under shear of the products. Shear affects largely the systems where particle degree of dispersion is comparatively low, where particle–matrix interactions reveal lack of adhesion and compatibility; in fact, as shown in the micrographs, agglomerates are present and influence the flow behavior, notably for shear rates larger than 0.1 s^{-1}. On the other hand, the single-screw process with ultrasound produces smaller-size particles which are better dispersed, exposing larger surface area revealing increasing particle-matrix interactions. This system consequently shows a lower effect of shear on the system structure. The viscosity in this case is less shear-thinning, confirming previous findings on the system microstructure.

TABLE 2. Decomposition temperature and residues formation.

ID	10% Loss weight *T*(°C)	50% Loss weight *T*(°C)	90% Loss weight *T*(°C)	Residue (600°C) (%)
PP	428	458	473	0.00
30 FR/TS	373	461	486	6.96
21 FR/TS	371	454	481	5.09
21 FR-1 BEN/TS	349	459	485	6.43
21 FR-3 BEN/TS	314	398	451	6.60
30 FR/SS-US	318	368	479	7.52
21 FR/SS-US	332	369	395	3.45
21 FR-1 BEN/SS-US	337	372	404	7.35
21 FR-3 BEN/SS-US	354	395	428	8.35

In Figure 7, the complex viscosity is plotted with respect to temperature for pristine PP and 21 FR/TS and 21 FR-1 BEN/SS-US materials. Usually, changes in the complex viscosity with temperature reflect microstructure modification due to increasing thermal energy in the system. With increasing temperature, the structure is softened and the viscosity falls, down to a minimum after which the viscosity rises due to char yield [38]. A shift in the minima to lower temperatures from that of pristine PP is observed in the intumescent additive mixtures, around 40°C. Although the minima in the compounds occurs at about same temperature (around 335–340°C) the viscosity of compounds produced using the twin screw extrusion process show a larger drop, revealing a softer structure than that of the materials produced with the second pro-

TABLE 3. Flame-retardant properties according to UL94 tests.

ID	Flammability	
	UL94-V Rating	UL94-HB (mm/min)
PP	No rating	26.5
30 FR/TS	V0	0
21 FR/TS	No rating	23.1
21 FR-1 BEN/TS	No rating	21.1
21 FR-3 BEN/TS	No rating	24.2
30 FR/SS-US	V0	0
21 FR/SS-US	No rating	21.2
21 FR-1 BEN/SS-US	V0	0
21 FR-3 BEN/SS-US	No rating	26.2

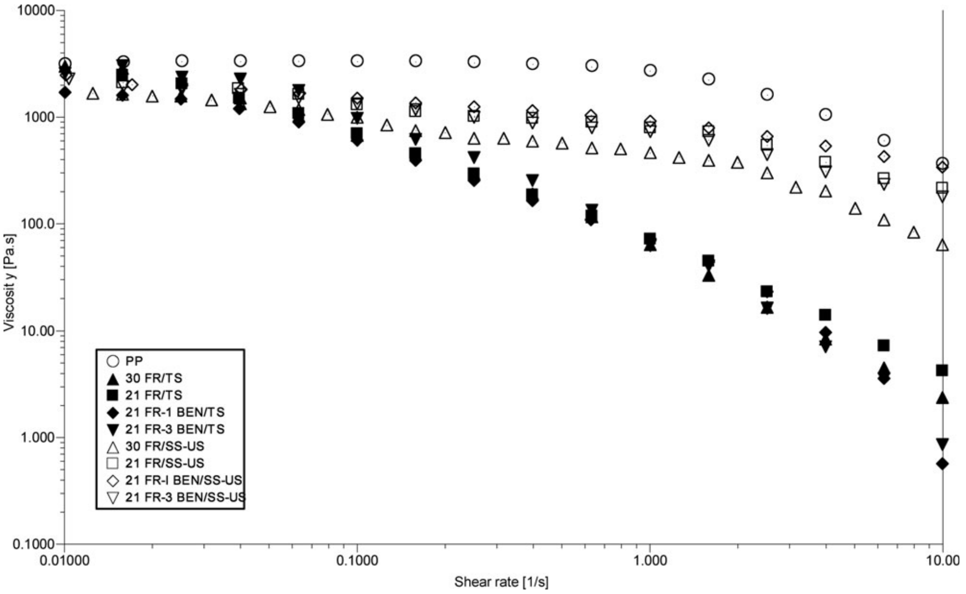

FIG. 6. Viscosity versus shear rate flow curves of pure PP and composite materials prepared by twin screw and single screw with ultrasound. 215°C test temperature.

cess with ultrasound. The structure of the former materials is even better preserved than that of pure PP, for which only a small complex viscosity rise is observed at temperatures higher than 375°C.

Mechanical Properties

In Table 4, impact resistance (Izod Notched), Young modulus, tension strength, strain at break, and tenacity properties of the systems under study are disclosed. In the composite materials the property that increases with respect to the pristine PP values is the Young modulus due to the high additive load. Larger impact resistance is obtained in the extrusion process with ultrasound. For example, comparing material impact resistance of the compounds with 21 phr FR, this property increases from 65 to 124 J/m if ultrasound is used. This property is closely related to the dispersion of particles in the polymer matrix, where fracture propagation is inhibited in better dispersed systems, where particle size is small.

The strain at break and tenacity increase in the process with ultrasound. Materials produced with 30 FR present enhancements from 17 to 34% in the strain at break and from 3 to 7 MPa in tenacity. In the case of the materials 21 FR-1 BEN, the increase in the strain at break occurs from 39 to 115%; in tenacity occurs from 8 to 22 MPa.

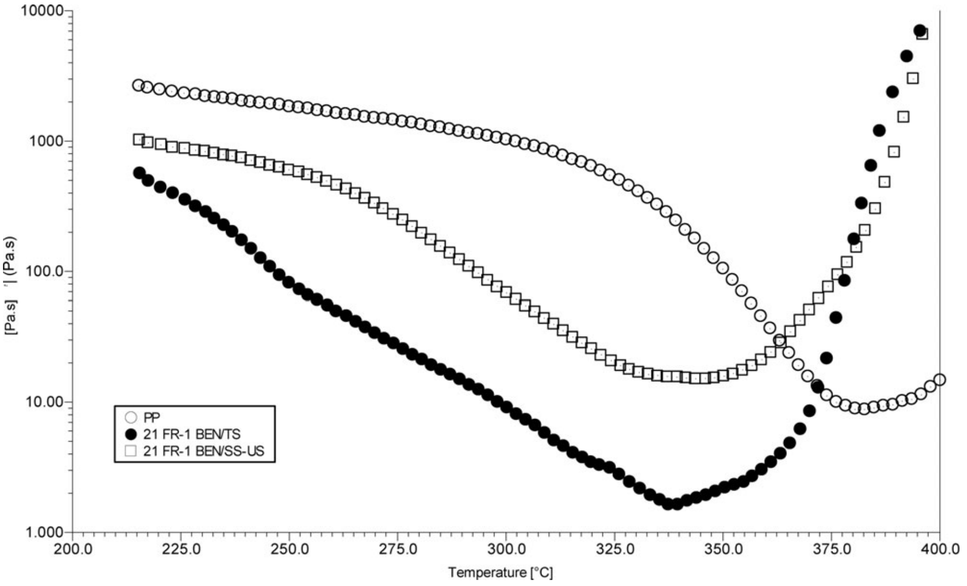

FIG. 7. Complex viscosity versus temperature curves of pure PP and composite materials: 21FR-1 BEN/TS and 21FR-1 BEN/SS-US. 10°/min heating rate, 1.0 rad/s angular frequency.

TABLE 4. Mechanical properties.

ID	Izod impact resistance (J/m)	Young's modulus (MPa)	Tensile strength (MPa)	Straint at break (%)	Tenacity (MPa)
PP	175	751	29	163	33
30 FR/TS	73	946	25	17	3
21 FR/TS	65	935	27	98	19
21 FR-1 BEN/TS	67	989	27	39	8
21 FR-3 BEN/TS	70	1025	26	105	20
30 FR/SS-US	84	1019	27	34	7
21 FR/SS-US	124	909	25	95	18
21 FR-1 BEN/SS-US	89	950	26	115	22
21 FR-3 BEN/SS-US	85	931	25	103	20

Intumescent and clay particles sufficiently dispersed give these enhanced results.

CONCLUSIONS

In this work, the flame-retardant properties of materials produced using two extrusion processes to obtain intumescent flame-retardant polypropylene compounds with modified clays were studied in detail. The process involving the single screw extruder with a static mixer die which produces extensional flows assisted by ultrasonic waves was evaluated. Remarkable improvements in particle dispersion are revealed, with average particle sizes around one micron, in such a way that lower concentrations of additives can be used (from the usual 30 to 21 phr) to obtain a V0 rating according to the UL94-V. Better thermal stability and mechanical properties brought about by the system structure are achieved with 1 phr BEN-Lys and 2 phr de PP-*g*-MAH contents. The use of a special (static mixer die) online ultrasonic device has been proved to be able to produce optimized flame-retardant materials.

ACKNOWLEDGMENTS

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NOMENCLATURE

APP Ammonium polyphosphate.

BEN bentonite clay.

BEN-Lys betonite clay modified with L-lysine amino acid.

30 FR/TS 30 per hundred resin of flame retardant extruded by twin screw.

21 FR/TS 21 per hundred resin of flame retardant extruded by twin screw.

21 FR-1 BEN/TS 21 per hundred resin of flame retardant and 1 phr of betonite clay modified with L-lysine amino acid extruded by twin screw.

21 FR-3 BEN/TS 21 per hundred resin of flame retardant and 3 phr of betonite clay modified with L-lysine amino acid extruded by twin screw.

30 FR/SS-US 30 per hundred resin of flame retardant extruded by single screw with ultrasound.

21 FR/SS-US 21 per hundred resin of flame retardant extruded by single screw with ultrasound.

21 FR-1 BEN/SS-US 21 per hundred resin of flame retardant and 1 phr of betonite clay modified with L-lysine amino acid extruded by single screw with ultrasound.

21 FR-3 BEN/SS-US 30 per hundred resin of flame retardant and 3 phr of modified betonite clay with L-lysine amino acid extruded by single screw with ultrasound.

Lys L-lysine amino acid.

MAH Maleic anhydride.

PENTA Pentaerythritol.

phr Parts per hundred resin.

PP Polypropylene copolymer.

PP-*g*-MAH Polypropylene grafted with maleic anhydride.

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