

*Dedicated to Professor Alexandru T. Balaban
on the occasion of his 85th anniversary*

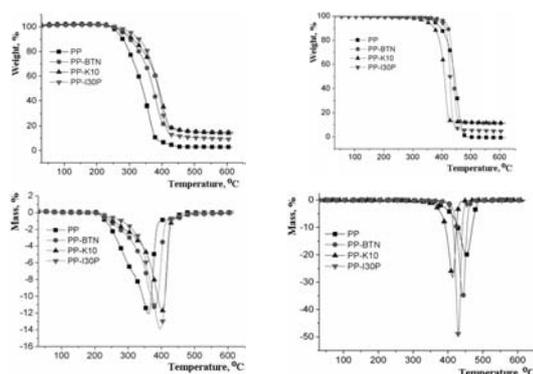
CRITICAL ASSESSMENT OF THE THERMAL AND THERMO-OXIDATIVE BEHAVIOUR OF SOME POLYPROPYLENE-CLAY COMPOSITES

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This study is a comparative evaluation of the thermal stability, as well as the thermal and thermo-oxidative stress, in a series of composites obtained using a commercial polypropylene (PP) and three different clays: a native bentonite from Valea Chioarului, Maramureș, Roumania (BTN); a sodium montmorillonite (K10); a montmorillonite organically modified with octadecylamine (I.30P). The influence of the clays on the thermal behaviour of composites was studied and the experimental data confirmed the increasing thermal stability of all samples. The discrepancies that appeared among samples of different series were attributed to the complex phenomena that occur at the polymer-clay interface, strongly correlated with the properties of the clay and the degree of intercalation/exfoliation.



INTRODUCTION

Polypropylene (PP) is one of the most common thermoplastic polymers, known for its good thermal stability, chemical resistance and environmental inertness, low moisture uptake and excellent dielectric properties, relatively low price of production. Due to its attractive combination of low density, high stiffness and toughness, and heat distortion temperature above 100°C, PP proved an extraordinary versatility that recommended it for a wide variety of applications ranging from molded parts to films and fibers used electronics, automotive

industry, textiles, structural or packaging materials, etc.^{1,2} Being readily processable using the existent technologies, PP is also fit for recovery and up-cycling. With an expected annual growth of about 6% (approx. 69.1 million tones were globally manufactured in 2013), PP remains one of the fastest growing polymers over the years along with the constantly expanding area of applications.^{3,4}

When PP is used to obtain polymer-clay nanocomposites, the new materials exhibited remarkable enhancement of properties upon the addition of only 3-5 wt % clay. The typical enhanced characteristics include tensile and

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flexural strength, heat deflection, thermal stability, flame retardancy, barrier properties toward gases and liquids, etc., which make these composites a great promise for industrial applications.⁵⁻⁸

Clays – mainly represented by montmorillonite (MMT), most commonly used in polymer-clay nanocomposites⁹ – are composed of tactoids containing stacks of nanometric platelets; assuming a density of 2.65 g/cm³, then the upper limit of the surface area per gram for fully exfoliated clays is about 750m²/g (5-10 times higher than ordinary mineral fillers).⁴

The unique combination of properties of PP and clays is favouring the interfacial interactions that generate a specific morphology depending on the intercalation/exfoliation ratio. Upon complete exfoliation, the interfacial contact is maximized and the bulk properties are significantly changed.

Another factor that favoured the development of PP-clay nanocomposites is their processability by conventional melt-mixing technology, during which all components are subjected to high temperatures and shear stress, further processing and service time adding supplementary stress. If the processing temperature is higher than the thermal stability of the components, decomposition occurs and the interface between the filler and the matrix is effectively altered. A substantial amount of research was devoted to study the thermal stability and thermal degradation of polymer-clay nanocomposites, but some questions still remained unanswered.¹⁰⁻¹² Noticeable advances were also made in designing novel formulations that included thermally stable organic modifiers fit not only to compatibilize the polymer-clay compounds, but also to help them act synergistically.

The thermal stability of polymer-clay nanocomposites (PCNs) is still an active field of research that constantly offers new insights,^{5, 12-15} given the possibility to achieve information on the extent of the material degradation which can be used to assess the effect of clays on thermal properties of the system. These experimental results may also give some indirect data about the morphology and amount of exfoliated nanoclay in the PCNs.

The present study is a critical assessment of the thermal stability, as well as the thermal and thermo-oxidative stress, in a series of composites based on a commercial polypropylene (PP) and three different clays (montmorillonite), as follows: a native bentonite (BTN) from Valea Chioarului, Maramureş, Roumania; a sodium montmorillonite (K10) and a montmorillonite organically modified with octadecylamine (I.30P).

RESULTS AND DISCUSSION

Composites formulation and their sample codes are presented in Table 1.

Given the TG and DSC data recorded for successive steps in the decomposition process of these samples, it was possible to determine the main characteristic thermal parameters for each reaction step.

DSC measurements for PP were in good concordance with literature data. The endothermic peak corresponding to the PP melting was followed by another exothermic peak that corresponds to the formation of hydroperoxidic groups in the presence of oxygen.¹⁶ This behaviour is supported by a slight increase in the PP weight evidenced in TG and DTG records.¹⁷ In the following thermal oxidation stage, the hydroperoxides underwent decomposition reactions, yielding in volatiles.

Corroborated literature data confirmed not only the formation and decomposition of peroxides during the oxidation of PP at low temperatures (50-90°C), but their nature as well, evidencing the presence of two types of peroxides: some fast-decomposing and others slow-decomposing peroxides. When both species are formed in the system, the PP oxidation rate is controlled by the fast decomposing peroxides.¹⁸

The results of TG analysis performed in air (Table 2) and in nitrogen (Table 3) indicated a slightly different behaviour, obviously due to the different mechanisms of the thermal and thermo-oxidative degradation, which is influenced by the nature and characteristics of clays, properties of the polymer matrix, and of hybrids as well.

Table 1

Nanocomposite sample codes and their formulation

Sample code	Clay	Clay particle size, µm	Composition, %	
			PP	Clay
PP	—	—	100	—
PP-BTN	Bentonite	9-20	95	5
PP-K10	Montmorillonite K10	5-10	95	5
PP-I.30P	Nanomer I.30P	15-25	95	5

Table 2

Thermal parameters of the TG analysis in air

Sample code	T_m , °C	T_{onset} , °C	T_{10} , °C	T_{20} , °C	T_{max} , °C	ΔW , %	Char yield, %
PP	170.3	277	285	304	367	97.22	2.88
PP-BTN	167.0	280	304	332	383	85.00	15.00
PP-K10	165.8	339	341	343	403	86.00	14.00
PP-I.30P	167.4	337	338	363	405	90.75	9.25

Table 3

Thermal parameters of the TG analysis in nitrogen

Sample code	T_m , °C	T_{onset} , °C	T_{10} , °C	T_{20} , °C	T_{max} , °C	ΔW , %	Char yield, %
PP	170.8	411	397	418	452	99.30	0.70
PP-BTN	169.2	422	424	432	443	89.00	11.00
PP-K10	166.3	378	386	394	415	88.64	11.36
PP-I.30P	167.9	421	421	428	437	95.37	4.63

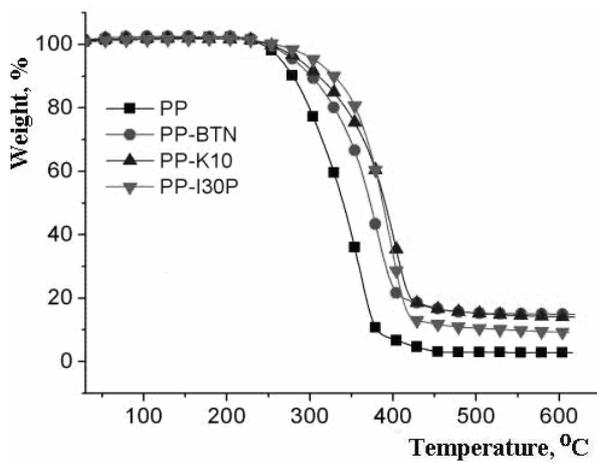


Fig. 1 – TGA thermograms in air for PP and corresponding nanocomposites.

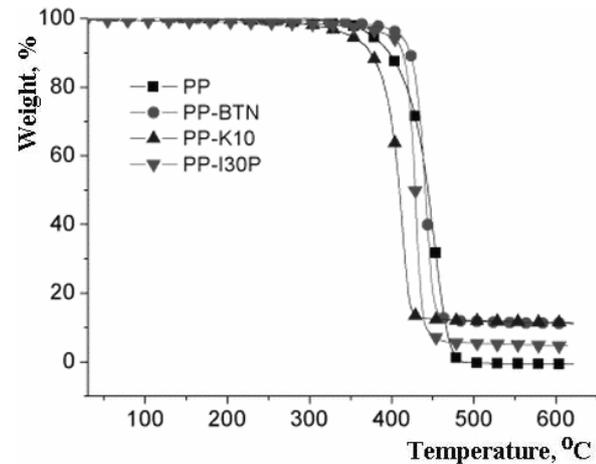


Fig. 2 – TGA thermograms in nitrogen for PP and corresponding nanocomposites.

The melting temperatures (T_m) in air and in nitrogen do not show major disparities for the composites when compared with the neat PP. Decreases are lower with 2.9–4.5°C in air, and with 1.6–4.5°C in nitrogen. The amount of clay (5 wt-%) is sufficiently low not to significantly affect the melting temperatures of the matrix.¹⁹

The slight decrease of T_m can be caused by the presence of some impurities, in the case of PP-BTN hybrids, or the organic modifier used for I.30P nanoclay, namely octadecylamine (ODA) (decomposition temperature 300°C), in the case of PP-I.30P samples.²⁰

TGA thermograms in air and nitrogen for neat PP and nanocomposite samples are presented in Figures 1 and 2.

It can be observed that the degradation in air or nitrogen of PP-clay composites corresponds to the single stage process similar to the neat polymer,

with well defined initial and final degradation temperatures. This process is confirmed not only by TG curves, but also by the presence of a single peak of degradation observed in the DTG thermograms (the first derivative plots), showed in Figs. 3 and 4.

With respect to the T_{onset} values, it was observed that, in air, the PP-BTN sample is the first one to degrade. In the case of the PP-K10 and PP-I.30P (Fig. 1), the samples were more stable than PP under thermo-oxidative degradation conditions. The significant higher difference ($\approx 60^\circ\text{C}$) as compared to PP indicates that oxygen diffusion in composites is seriously impeded by the dispersion of clay tactoids and platelets inside PP matrix. An increase in the T_{10} and T_{20} in air was recorded, too. T_{max} in air for PP-clay samples showed a similar trend: the additions of 5% clay resulted in an increase by 16, 36 and 38°C respectively.

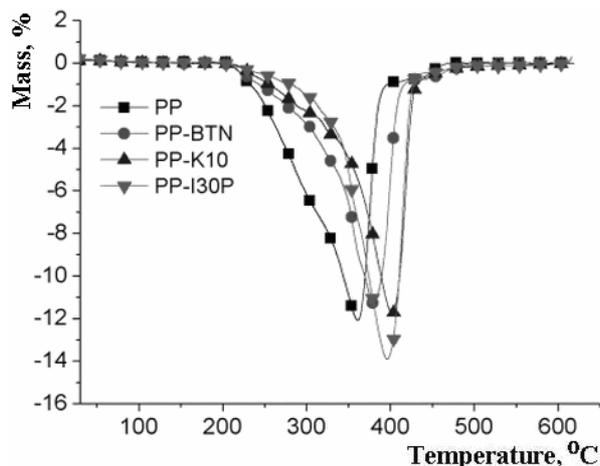


Fig. 3 – DTG thermograms in air for PP and corresponding nanocomposites.

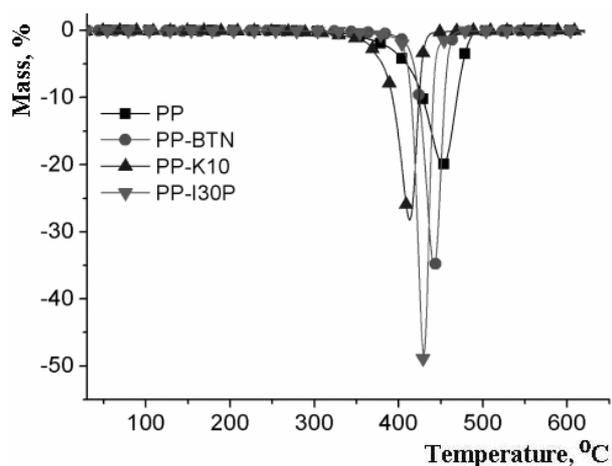


Fig. 4 – DTG thermograms in nitrogen for PP and corresponding nanocomposites.

A quantitative comparison, for each series in terms of T_{onset} , T_{10} , T_{20} , evidenced that all samples analyzed in air displayed an enhanced thermal stability within a range of 3–60°C, but in nitrogen, samples with K10 showed a lower thermal stability. This behaviour may be explained considering the fine granulation of K10 (Table 1), which, corroborated with the absence of a surfactant or a coupling agent, indicated that in these samples the clay has a rather poor dispersion and particles are agglomerated.²¹

The thermal and thermo-oxidative degradation mechanism

The thermo-oxidative degradation of PP in air begins at a much lower temperature than in nitrogen (as shown in Table 3), following a chain of reactions presented in Scheme 1, as suggested in literature.^{22,23}

The structure of PP consists of a high number of tertiary carbon atoms which are highly susceptible to undergo thermo-oxidative reactions. First weight losses were noticed in the interval 227–247°C, but the volatile emission rate is significant above 300°C.²³ The presence of oxygen in the environment strongly influenced both the rate and mechanism of decomposition. Although it was initially suggested that the oxidation mechanism is evolving through hydrocarbon oxidation, it was experimentally proven that, in fact, the process is controlled by the decomposition of peracids formed during the oxidative degradation of the primary decomposition products.¹⁸

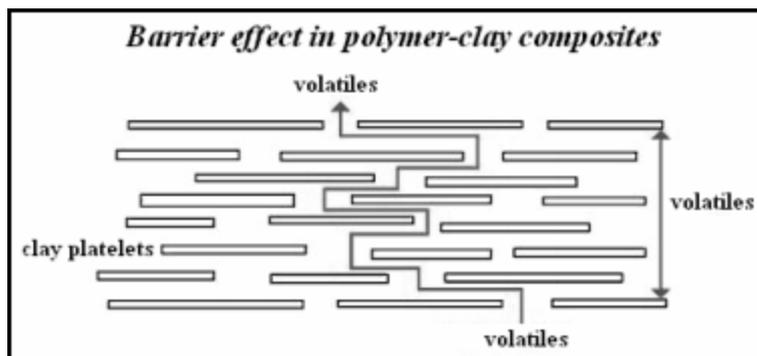
Below 200°C, the mechanism A prevails: the oxygen addition occurs at the carbon radical

formed within the polymer chain by hydrogen abstraction. On the other hand, above 200–250°C, the hydrogen abstraction becomes more likely as in mechanism B resulting in an oxidative dehydrogenation. As the temperature increases, the concentration of the chain end radicals (radicals II) increases because β scission of radicals I (process C) becomes competitive with either oxygen addition (A) or hydrogen abstraction (B). The direct thermal scission of carbon-carbon bonds becomes possible above 300°C (Figure 1) and might not be relevant any longer to thermal oxidation of PP because the polymer is massively volatilised at that temperature.²⁴

In inert atmosphere (nitrogen), the thermal degradation is expected to evolve without thermo-oxidative reactions or with reduced oxidative stress due to the limited presence of residual amounts of oxygen trapped inside the material. Therefore, the thermal degradation in PP and its corresponding composites should proceed in a similar manner and, therefore, differences in the degradation onset temperatures are much smaller (Table 3).

In nitrogen, the PP thermally degrades to volatile products above 350°C through a radical chain process propagated by carbon centered radicals resulted from carbon-carbon bonds scission,²⁵ as suggested in Scheme 2.

The thermal degradation mechanism may involve a random chain scission at the weak bonds along the polymer backbone that produces large amounts of hydrocarbon volatile products. The degradation highly depends on the particles wettability by the matrix, which is a clear indication of their compatibility, and extent of their interfacial interaction.²⁶ Given the data from Tables 2 and 3, an



Scheme 3 – The barrier effect in polymer-clay composites (tortuosity or labyrinth effect).

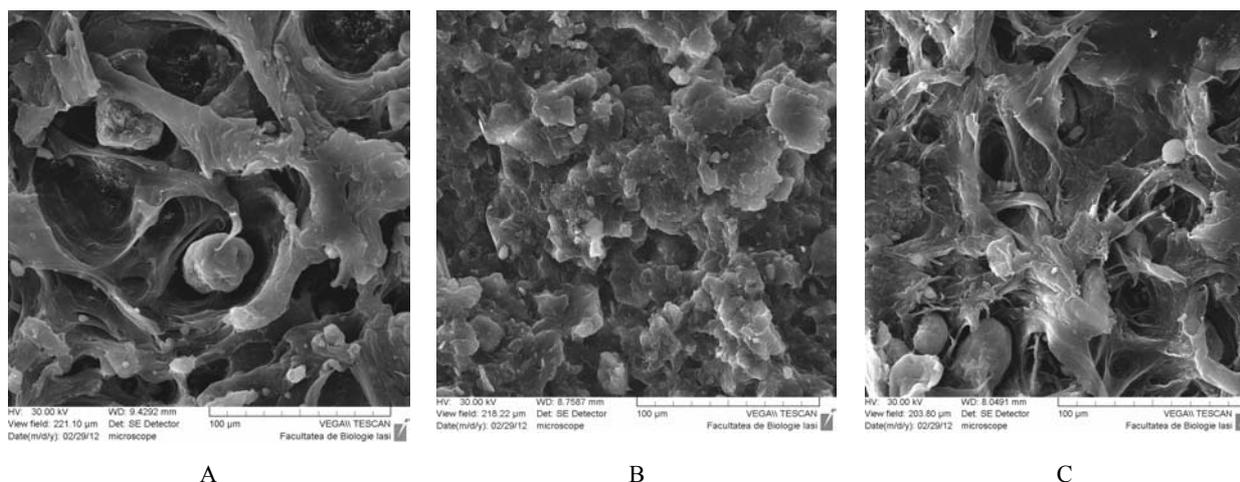


Fig. 5 – SEM micrographs of PP-clay samples (x100): A – PP-BTN; B – PP-K10; C – PP-I.30P.

However, all data recorded in nitrogen were slightly lower than expected, probably due to the residual oxygen trapped inside the samples bulk, which is favouring the thermo-oxidative degradation processes. Taking into consideration that a cavitation phenomenon was proved to occur in PP during melt mixing,^{28,29} these data suggested that PP-clay nanocomposites may also undergo a cavitation phenomenon, not only the neat PP. The occurrence of cavitation depends on the relationship between the strength of amorphous phase for break and strength of crystalline phase for initiation of crystals slips.²⁸ The cavitation process may be controlled by altering the crystalline/amorphous ratio. It was found that the occurrence of cavitation depends also on the temperature and rate of deformation.²⁹

On these grounds, a morphology study was further performed and the micrographs obtained by SEM are presented in Fig. 5.

As noticeable, all samples displayed cavities, but their density and dimensions varied (hence, the amount of residual oxygen trapped inside was different) in correlation with the nature of clay and

its compatibility toward PP matrix, as well as the dispersion and degree of intercalation/exfoliation.

Correlating thermal data (Table 3) with SEM information, the peculiar behaviour of K10 composite samples in nitrogen might be explained as follows: the cavitation of PP occurred in all composites; K10 has the finest granulation and, in the absence of a coupling agent/compatibilizer, it agglomerates to a higher extent than BTN and I.30P; therefore, the PP-K10 samples contained a higher number of small cavities (as evident in Fig. 5B), containing clay agglomerates and residual oxygen. This morphology can accumulate a higher amount of oxygen than the others, which yielded in supplemental oxidative stress and, subsequently, a lower thermal stability of PP-K10 in nitrogen.

EXPERIMENTAL

Materials

The polymer used as matrix in this study was a commercial PP (iPP, isotactic index 95%) (Malen-PF 401, Petrochemia Plock S.A., Poland). Its main characteristics are: melting temperature (T_m) 170°C; decomposition temperature

250-430°C, Vicat softening point 148°C; melt flow index (2.16 kg/230°C) 2.4-3.2 g/10min; volatile matter 0.3%wt.

Na-Bentonite was provided by S.C. Mateo S.R.L., collected from Valea Chioarului (Maramureş, Roumania). Main characteristics: specific surface area 25-30 m²/g; apparent specific weight 260-300 g/L; particle size 9-20 µm.

Montmorillonite K10 is a sodium montmorillonite (Sigma Aldrich Co., USA). Main characteristics: surface area 220-270 m²/g; bulk density 300-370g/L; particle size 5-10 µm.

Nanomer I.30P is an organically modified montmorillonite (Nanocor Inc., USA). Main characteristics: modifier octadecylamine (70-75% montmorillonite, 25-30% octadecylamine), density 1.7 g/cm³; mean dry particle size 15-20 µm.

Nanocomposites preparation

The composite samples with different clays (5%) were prepared by melt mixing in a HAAKE RHEOCORD 9000 mixer equipped with two internal roller mixers and a capacity of mixing chamber of 48.3 cm³, fill factor 0.8.

Before compounding, PP and clays were thoroughly dispersed in acetone for 1 h and dried, first in air and then at 80°C in a vacuum oven for 24 h to remove moisture and to enable uniform distribution of PP pellets and clay particles, which will subsequently influence the nanocomposites homogeneity. Samples composition is listed in Table 1. All blend components were calculated as parts per 100 parts resin (phr).

Processing parameters were chosen as to minimize possible degradation of components: the mixing temperature 190°C, the rotor speed 100 rpm, time 7 min. After processing, samples were removed from the mixer and allowed to cool down to room temperature to avoid thermal-induced defects.

Composites characterization

Thermogravimetric analysis (TG) was performed under either inert (nitrogen) or air atmosphere using a Jupiter STA 449F1 thermogravimetric analyzer (Netzsch, Germany), from room temperature up to 600°C, at a heating rate of 10°C/min. The gas flow rate was 20 ml/min independent of the sample weight that was in the range of 6-10 mg. The samples were heated in open alumina crucibles, using Al₂O₃ as reference material. Data was processed with Proteus® software.

The DSC measurements were carried out under nitrogen atmosphere by using a TA instrument from Perkin-Elmer (USA), Pyris Diamond model, which is a power-compensated type. The DSC apparatus was calibrated with Indium before experiments. Samples of about 7 mg were enclosed in Al crimped pans, and through cells was purged dry N₂ gas at flow rate of 20 ml/min.

The main thermal characteristics: T_m – melting temperature; T_{onset} – onset degradation temperature; T_{10} and T_{20} – temperature corresponding to 10% and 20%, respectively, weight loss; T_{max} – temperature of maximum rate of degradation; ΔW – weight loss in the main decomposition step; char yield – the fraction non-volatile at 600°C.

The morphology of the fracture surface of composites was investigated by a VEGA II SBH scanning electron microscope (SEM) instrument (TESCAN, Brno, Czech Republic). The samples were cryogenically fractured by immersion in liquid nitrogen for 30-50 minutes. Shortly after fracturing, the rupture surfaces were coated with a thin silver layer (of about 50 nm).

CONCLUSION

The present study is a critical assessment of the thermal stability, as well as the thermal and thermo-oxidative stress, in a series of PP-clay composites containing three different clays: a Roumanian native bentonite (BTN), a sodium montmorillonite (K10), and an organically modified montmorillonite (I.30P). The influence of the clays on the thermal behaviour of composites was proved and the experimental data confirmed the increasing thermal stability of all samples. The discrepancies that appeared among samples of different series were attributed to the complex phenomena that occur at the polymer-clay interface, strongly correlated with the properties of the clay and the degree of intercalation/exfoliation.

The TG analysis showed that samples had a distinctly different behaviour, obviously due to the different mechanisms for thermo-oxidative and thermal degradation. The weight loss curves of the nanocomposites in inert atmosphere were almost vertical which indicated a rapid decomposition process.

Enhanced thermal stability, commonly observed when clay particles are well-dispersed into the polymer matrix, was a result of the hindered diffusion of heat and volatiles (tortuosity or “the labyrinth effect”). The char formation that occurred in nanocomposites also contributed to the enhanced thermal stability, adding to the barrier effect of clay, due to the intimate contact at the clay-polymer interface.

The peculiar behaviour in nitrogen of K10-containing samples might be explained by the cavitation phenomenon of PP that favoured the residual oxygen to be trapped in the composite bulk. At the same time, K10 might generate agglomerates due to its fine granulation and the absence of a compatibilizer.

Therefore, the higher the dispersion of clay platelets (preponderantly exfoliated morphology), a higher degree of tortuosity (barrier effect), hence, the higher the thermal stability of PP-clay nanocomposites.

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