

POLYPROPYLENE NANOCOMPOSITES BY MELT PROCESSING*

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Abstract

In this paper the clay treatments for production of polypropylene nanocomposites by melt intercalation method are used. Polymer-clay composites have been prepared by melt blending an organo-nanoline with linear polymers in a disk-screw extruder. Nano-structure of produced composites and the interactions between atomic groups and polymer chains is demonstrated by X-ray diffraction. The physical-mechanical properties of prepared composites with different percents of clay are measured and compared, too. The obtained results show that treated clay increase mechanical properties of prepared composites.

1. Introduction

Polymer clay nanocomposites are a new class of materials which show improved properties at very low loading levels of filler comparing to conventional particulate composites of thermoplastic materials. Usually introducing of well dispersed nano-particles in thermoplastic matrices can improve the most important physical and mechanical properties of polymer matrices.

In 1997, Toyota Group has demonstrated that incorporation of small amount of clay particles (2-6wt %) into a thermoplastic polymeric matrix can generate enhanced properties such as thermal and UV resistance, low permeability towards gazes and to some extent improved mechanical properties. Since then, thousands of papers have been published on the subject. The majority of the papers, if not all, use chemical or mechanical approaches to reach exfoliation (delamination and dispersion of individual clay lamellae inside the polymeric matrix). Such exfoliation is claimed to impart the polymer nanocomposites with enhanced mechanical properties. The second, well known claim is that high shear stresses are required

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to destroy the clay galleries and to exfoliate the clay lamellae. The third claim is that an initial intercalated structure is needed to allow polymeric chains to penetrate the galleries and to exert local stresses that would exfoliate the structure under mechanical shearing [1-4]. Polypropylene (PP) and its copolymers are some of the most interesting thermoplastic materials due to their low price and balanced properties. However, due to low polarity of PP, it is difficult to get the exfoliated and homogenous dispersion of the silicate layer at the nanometer level in the polymer. This is mainly due to the fact that the silicate clay layers have polar hydroxyl groups and are compatible only with polymers containing polar function groups. Consequently the matrix modification with polar group is necessary prior to modified clay introduction in order to achieve nanometric dispersion of the clay.

2. Materials and methods

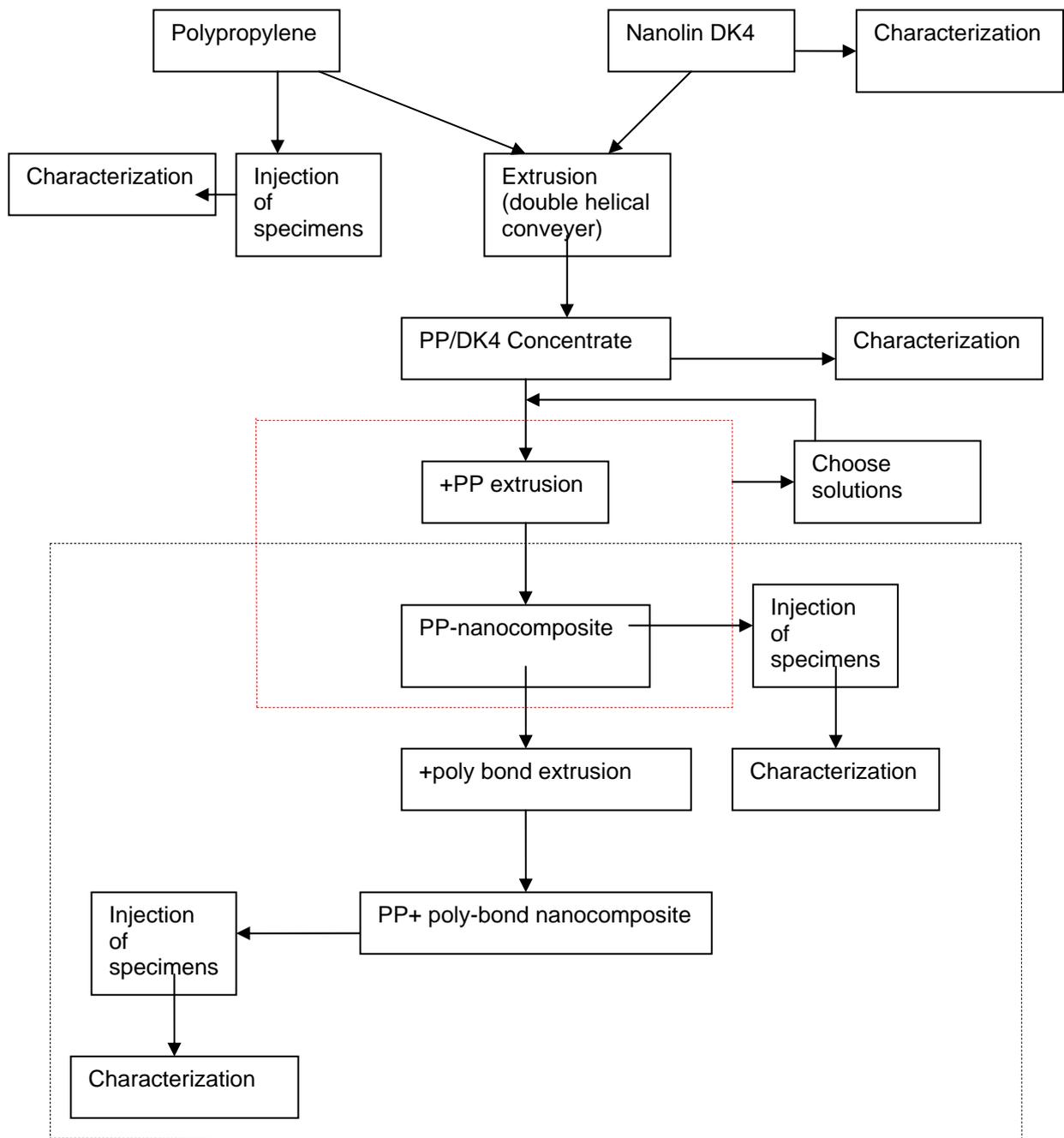
2.1. Preparation of polyolefine nanocomposites

The experiments carried out were focused on obtaining the polypropylene nanocomposite samples. In all the experiments the polypropylene (PP J700) with flow rate in melt of 13.92g/10min ($8.58\text{cm}^3/10\text{min}$) and NANOLIN DK4 were used. The series of NANOLIN DK introduced by ZHEJIANG FENGHONG CLAY CHEMICALS CO. LTD [1] are made of ultra fine pure smectite. The dimensions of NANOLIN DK nanoclay usually range between 1- 100 nm. It can be completely dispersed, the average size of the dispersed layers being around 25 nm, while the L/D ratio ranges between 100 and 1000. These nanoclays can be added to different types of polymers. There are a number of types of clays produced by ZHEJIANG FENGHONG CLAY CHEMICALS CO. LTD and among them the DK4 was chosen for the experiments, with the following characteristics: 110- 120 meq/100g, interlayer distance (d-001) 3.5 nm, color- white, organic compound of smectite. Scheme I shows the stages of the technological processes. Here we have marked the segments of experiments which were repeated for different percentage mixtures of concentrate and polypropylene necessary to obtain the samples with final nanoclay contents of 2, 4 and 6%, respectively. We have worked according to this pattern and, as the result of the characterization of the obtained samples from the standpoint of the physical- chemical properties, the variant with ~7% nanoclay in nanocomposite was chosen.

The concentrate was obtained on a laboratory extruder with two co-rotating helical conveyers type APV Baker, England, working at temperatures between 183- 226°C on the heating zones, using as starting material the J 700 type polypropylene with fluidity index 13.92g/10min, and Nanolin DK4 nanoclay. A polypropylene- DK4 nanolin concentrate was

obtained with the 50/50 mass ratio, which was later used to obtain samples of polypropylene nanocomposite on the micro- pilot installation of compounding by extrusion (*Research Institute for Synthetic Fibres-Savinesti*) of a pre-established quantity, such that finally the theoretical content of nanoclay in composite was 2, 4, and 6%. For all the experiments, the same formula was respected, as well as the same temperature zones on the extruder heating zones, namely between 200- 230°C. Even if the experimental conditions were similar, several samples of nanocomposite were obtained, with nanolin concentration between 1.5 and 7.8%. Considering the obtained data, the resulted samples were mixed on the extruder such that finally samples with DK4 nanolin loading of 2.31, 3.95 and 6.98% were produced. The target of the experiments, as well as the main purpose of the work, was to obtain polyolephyne nanocomposites with improved properties that should represent the basis of starting materials for the preparation of techno-polymers for different fields of application. In order to characterize the obtained specimens, both usual techniques for polymer characterization and techniques to determine the structure, nanomer dispersion degree, etc, were used. The flow rate on warm material (MRF) was determined on a Koka Flow Tester Shimadzu (for volume flow rate) and on an apparatus made at *Research Institute for Synthetic Fibres (RISF)-Savinesti* according to the standards for mass flow index. The flow rate is an important property for plastics processing. The dispersion of a nanomer in a polymer can change its flow properties, this involving also alterations of the processing parameters. Knowing the flow rate gives the users the necessary information for a correct processing of nanocomposites. As it has already been mentioned, the experiments were carried out with polypropylene for injection with a flow rate of 13.92g/10min. For the polypropylene nanocomposite with 6.98% DK4 nanolin load, a flow rate of 14.69g/10min was obtained. With the view to perform the resistance tests (stretch and bending) for each of the obtained samples, specimens were injected with the injection machine IMATEX- MP- TI- 100/50, in order to choose the ones considered as having the best behavior. The resistance tests were carried out at RISF Savinesti on a dynamometer FPZ 10Heckert and a Charpy pendulum. One must specify that these tests were carried out on specimens injected on the same injection machine. In order to obtain specimens of the adequate quality, the processes occurring in the injection machine were considered, such as:

- Typological peculiarities of the olefine polymers for injection (melt viscosity, melting interval, specific heat, crystallization).
- The thermo-technological process (injection time, post-processing time, injection pressure, polymer mass temperature, mould temperature)
- Internal contractions and tensions in the injection products.



Scheme I. Experiment working stages

Table I presents the mechanical properties of the polypropylene nanocomposites and polypropylene, according to the results obtained from the tests carried out at RISF.

Table I. Mechanical Properties

Sample	Content of nanolin DK 4, wt %	Tensile strength, (MPa)	Elongation at break (%)	Elasticity Modules Strength (MPa)	Elasticity Modules at flexion (MPa)	Soc Charpy (KJ/m ²)
PP J700	0	28.67	13.43	1850.76	1814.44	6.30
Nano-PP	2.31	29.33	10.25	1997.12	2018.87	6.38
Nano-PP	3.95	29.77	7.7	2079.58	2049.94	6.96
Nano-PP	6.98	30.55	8.6	2171.74	2074.32	7.64
Increase, %		6.15	-35.9	14.78	12.53	17.54

The Figs. 4a-4d shows the obtained results at ICEFSF-Savinesti on mechanical properties of nano PP composite for the next concentrations of nanoline DK4 :2.312, 3.95 and 6.98 %.

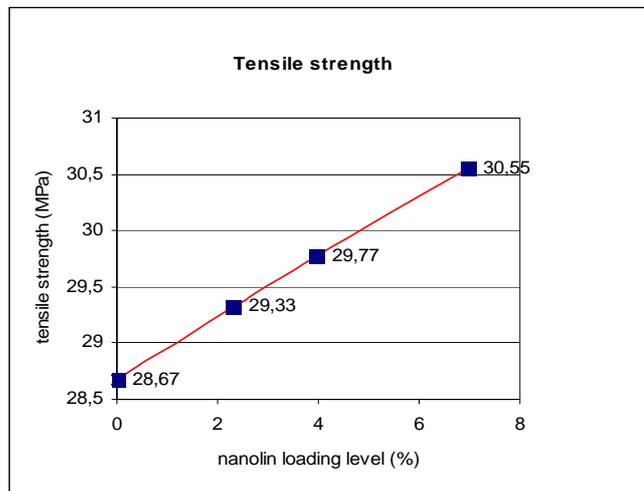


Fig. 4a. Variation of the tensile strength.

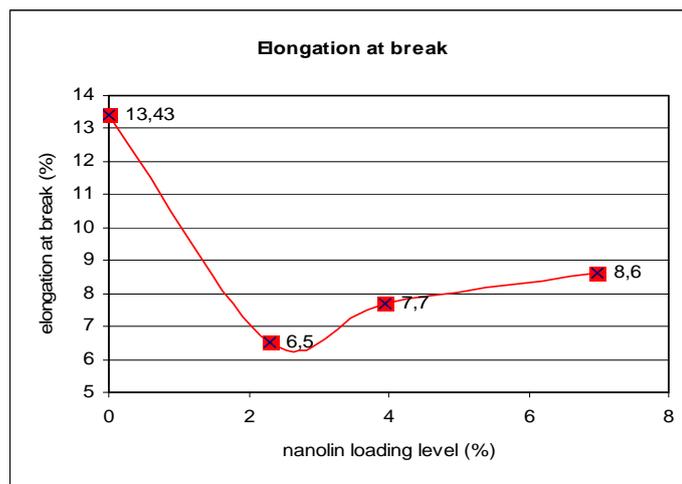


Fig. 4b Variation of the elongation at flexion

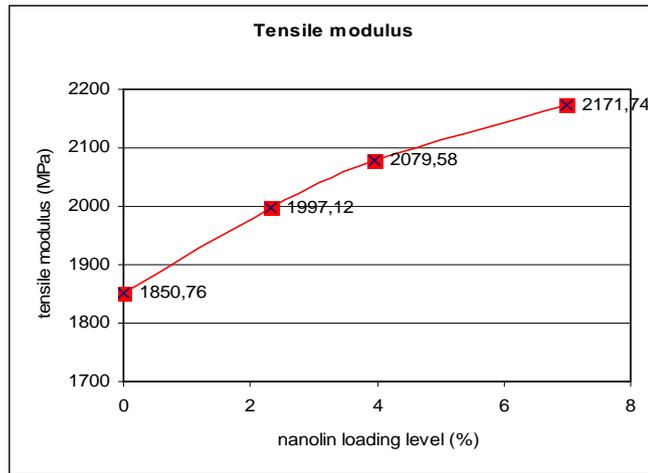


Fig. 4c. Variation of the Tensile Modulus

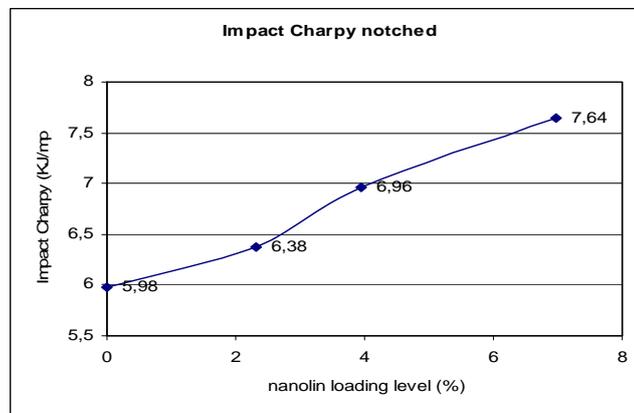


Fig. 4d. Variation of the impact Charpy.

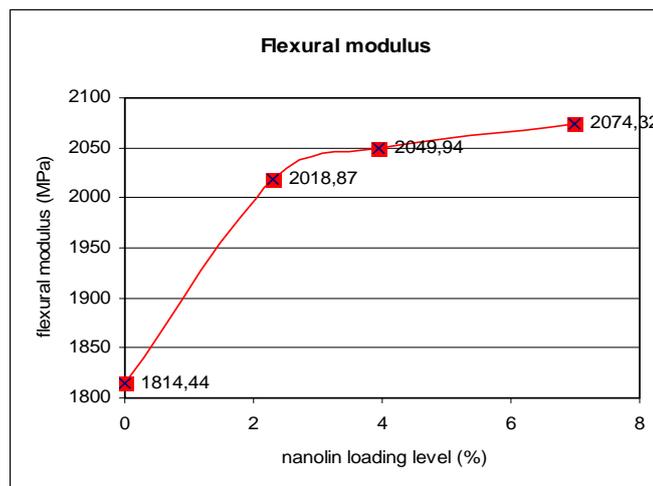


Fig. 5. Variation of the elasticity modules at flexion

The mechanical tests for PP J700 and nano PP composite show an increase of elasticity modules strength with 14.78 %, and with 12.53 % for elasticity modules at flexion,

respectively. The increase of soc Charpy was about 17.54 % and this means an increase of the rigidity of the nanocomposite comparatively to propylene. Increasing the rigidity leads to a better thermo-stability and to the contraction reduction at the injection processing. After the analyses done, starting from the idea that a good compatibility between the nano clay and the polymer matrix leads to a well-defined compact structure, we performed more experiments. As presented in the experimental model, compounding on the extruder with a polypropilenic nanocomposite snec (previously obtained by means of ~ 7% nanolin DK4) with a coupling agent based on polypropylene (poly-bond-PP greffed with maleic anhydride) we have obtained polypropilenic nanocomposite with a fluidity index of 17.23 / 10 min, which shows significant increase in resistance, as the analyses show. The coupling agent concentration was chosen such as the nanolin DK4 charging would not be significantly modified. Table II compares the mechanical properties for PP J700, nano PP and nano PP poly-bond. This increasing in the properties can be the result of a good compatibilization between the polymer matrix and the nanoclay, also confirmed by the XRD analyses (Fig.6 and Fig.7).

Table II. Mechanical Properties of nano PP poly-bond

Sample	Concentration of nanoline DK4 (%)	Tensile strength, (MPa)	Elongation break (%)	Elasticity Modules Strength (MPa)	Elasticity Modules at flexion (MPa)	Soc Charpy (KJ/m ²)
PP	0	28.67	13.43	1850.76	1814.44	6.30
Nano PP	6.98	30.55	8.6	2171.74	2074.32	7.64
Nano PP+poly-bond	6.90	35.73	9.44	3465.97	2715.95	8.9
Increase (%) vs. PP		19.76	- 0.42	46.60	33.19	29.21
Increase (%) vs. nanoPP		14.5	+ 8.9	37.34	23.62	14.16

2.2 XRD Analyse

Fig. 6 shows the XRD spectra of the nanolin DK4, PP J700 and the various PP nanocomposites compounded in a single-screw extruder configured with different temperature arrangements. The organosilicate, nanolin DK4, exhibited five distinct peaks characterising its interlayer basal spacing, at 3.82, 5.62, 8.52 and 23.18° 2θ angles. The nanocomposites spectra showed evidence of exfoliation, indicated by the smoothening, disappearance of the second, third, and fifth order organosilicate reflections. In addition, intercalation of the organosilicate galleries by polymer matrix can be witnessed by the shift to lower 2θ angles of the second and third order organosilicate peaks. The variation in pattern observed for the various nanocomposites spectra would corroborate the influence of temperature configuration on the structural development of layered-silicate during the extrusion process.

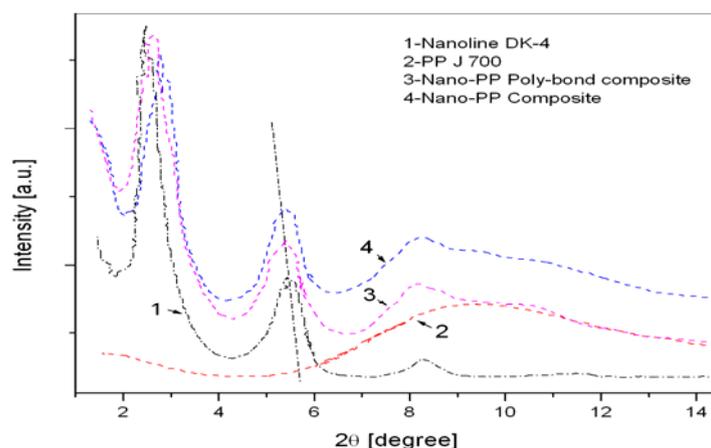


Fig. 6. XRD pattern.

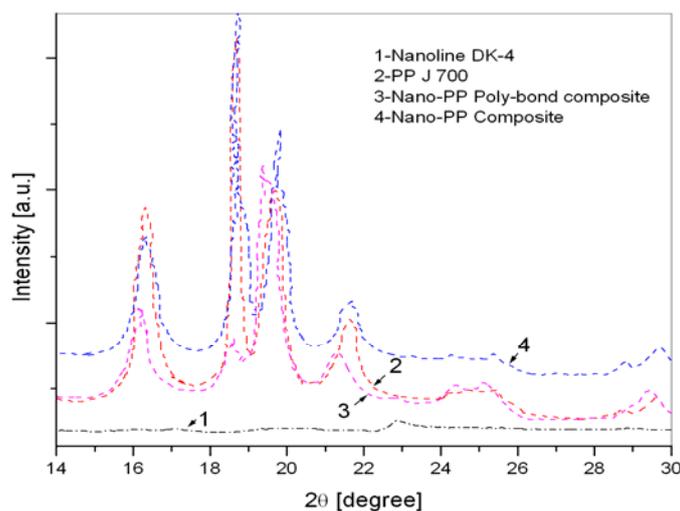


Fig.7.XRD pattern.

The nanocomposite samples in Fig. 7 exhibit a depressed peak pattern without significant shift in the 2θ angles. This pattern typically suggests effective break-up of the organosilicate into thinner layered-silicate stacks by extrusion shear stress. This phenomenon may be attributed through a top-down layer by layer peeling process proposed by Fornes et al. [5] or Kim et al. [6] would relate, to the presence of an optimum shear stress to overcome the electrostatic force between the layered-silicate interlayer. The nanocomposites showed similar peaks depression observed in [5], in addition, registered a lower 2θ angle. Their second order peak was shifted from 3.82° to below 2.72° , which represents an interlayer expansion from 1.4nm to a value greater than 2.4nm. This type of trend would generally suggest that exfoliation of layered silicate was achieved via a combination of matrix-gallery swelling followed by spontaneous interlayer delamination by the shear stress. However, the small shift recorded for the third order peaks to a larger 2θ angle suggests that the diffusion of polymer

chain into the organosilicate gallery was not effective. Furthermore, the organosilicate interlayer appeared to experience some form of structural compression, resulting in smaller gallery spacing than in its pristine form. The XRD spectra would suggest highest degree of organosilicate exfoliation were the PP J700 /compatibiliser/organosilicate blends mixed using the highest extrusion temperature. The confusingly aspect of this result is that a higher extrusion temperature generally dilutes the melt viscosity of polymer and thus reduces the shear strength required for the organosilicate delamination. On the contrary, a higher mixing temperature may also promote dilution between the PP and the compatibiliser matrix. This may enhance surface wetting of the layered-silicate. On this basis, the favorable exfoliation pattern exhibited by nano PP poly-bond may be attributed to the satisfactory mixing of the PP and compatibiliser phase which promoted the wetting and diffusion of the compatibiliser into the organosilicate gallery during the first stage mixing at 215°C. The poor intercalation may be attributed to the low processing temperature, which was not favorable for diffusion of polymer chain into the organosilicate interlayer. Therefore, layered-silicates in this group were exfoliated primarily through a physical shearing rather than a thermodynamic process.

3. Conclusions

The preparation of nanocomposites by extrusion of linear polymers with organo nanoline depends on the level of polymer's polarity. For nano polypropylene poly-bond we observed the exfoliation of organo-bentonites at this order preparation of composites. As a result, the mechanical and thermal properties were improved. The organo-nanocomposites show improved mechanical properties: both tensile strength and, surprisingly, Charpy impact were higher than the ones of the pure polymer.

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