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# Nanocompounds: Better Formulations for Recycled Polyethylene

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**Summary:** To improve the properties of recycled PE for pipe applications, additions of nanoclay and adhesion promoter were done. The presence of the nanoclay Cloisite 93A and the polyethylene grafted with maleic anhydride in the compounds have promoted the thermal properties. The possible exfoliation/intercalation of the PE in the nanoclay layers increases the barrier properties and reduced permeation to oxidation agents. The melt flow index, the glass transition temperature and the initial decomposition temperature (TG) have decreased. The XRD analysis has presented increase of interplanar distance in the nanoclay layers. The FTIR analysis has showed a decrease in the oxidation peaks intensity. These results are indicators of nanocomposite/microcomposite formation.

**Keywords:** adhesion; clay; nanocomposite; polyethylene; recyclate

## Introduction

New structural materials can be obtained through blending of different polymers. Their performance depends on the properties of components, their content and morphology.[1] At the same time, a new class of materials has aroused the interest of research in various fields of application: polymer nanocomposites. A great variety of inorganic and hybrid compounds are nowadays available allowing the synthetic materials to be obtained with improved mechanical and thermal properties compared with the pure organic polymer. New properties arise from the synergy between organic and inorganic components. By the other side, the reuse of recycled polymers in engineering applications, as plastic pipes for drainage and sewerage, is desirable due to the environmental and economic concerns.[2] In this work a set of blends containing recycled PE, PE T100N, a nanoclay (montmorillonite MMT) and an adhesion promoter (compatibilizer) were compounded by extrusion. They are analyzed by thermal, mechanical, spectroscopic and diffraction methods and techniques. Mass flow index was also measured.

## Experimental Part

The HDPE used was supplied by REPSOL (PE T100N) with a density of 0,96. Two recyclates RPE1 and RPE3 were supplied by AMBIENTE industry with densities, respectively, 0.97 and 0.96. The additives used were a nanoclay (C) Cloisite 93 A, having a ternary ammonium chemistry based surface modification and a maleic anhydride grafted polyethylene (G). All the samples were, previously, conditioned during 24 h at 23 °C with a relative humidity of 50%. Nanocompounds were prepared in a Prism Eurolab twin screw extruder at temperature of 190–210 °C, at speed of 300 rpm, in two different formulas: one contains 3 phr of nanoclay and 10 phr of adhesion promoter and other with only the nanoclay in the same proportion, both in PE T100N and two PE recyclate matrices, in plastic bags before extrusion. The thermal analysis was performed by differential scanning calorimetry and thermo-

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gravimetry at 10°/min in inert atmosphere, using a DSC NETZCH 200 F3 Maia and a SETARAM TG 92-1750 in the range 23 to 300 °C and 25 to 550 °C respectively. FTIR analysis was conducted with a Thermo scientific Nicolet Magna-IR 550 Series II, in the range 4000 to 400 cm$^{-1}$. Mass flow indexes were obtained at 190 °C/5kg with an Extrusion Plastometer DTS. Mechanical results were obtained using a DMA TA Instrument Q800 with a 3-pointbending clamp, with a frequency of 1 Hz and an amplitude of 15 μm, at a rate of 3 °C/min, in the temperature range −150 °C to 90 °C. XRD was performed using a PHILIP EXPERT, with a cobalt radiation K$\alpha$, $\lambda = 1.79$ Å, at a rate of 0.05° $2\theta$/s, between 3 and 74° $2\theta$, with a voltage and filament current of 35 kV and 45 mA, respectively. The films were prepared by compression moulding at 170 °C until uniform thickness.

## Results and Discussion

The incorporation of a nanoclay and nanoclay with adhesion promoter has induced some changes in the behavior of PE samples. The results are presented in the Table 1. The oxidation induction time (isothermal OIT) increased at both temperatures for all nanocompounds. The thermal stability found in the samples with nanoclay is related to the decrease of the oxygen molecules diffusion into the nanocomposite. The nanoclay particles have a barrier effect to the entry of this oxidizing agent, increasing resistance to oxidative degradation. The increase in the isothermal OIT of the blends containing nanoclay and adhesion promoter suggests an enhanced effect of barrier, showing effective protection by the nanoclay layers. The compatibilizer improved the adhesion of the nanoclay particles in the PE matrix. The dynamical OIT showed similar results: the recyclate nanocompounds temperature increased with the presence of nanoclay and was improved with the addition of adhesion promoter.

All the samples showed a decrease in the initial decomposition temperature (IDT) with the presence of the nanoclay. With the addition of nanoclay and adhesion promoter, the temperature increased but remained below or at the temperature of the recyclate. In this case the nanoclay and the adhesion promoter possibly have that effect, leading to a decrease of the thermal stability. The organoclay had a catalytic effect which has caused premature degradation of the polymer matrix (antagonism).[3] This result is due to the low thermal stability of the ammonium salts when processed at temperatures above 200 °C.[4] According to Leite et al. (2010)[5] the ammonium salt leaves acidic protons in the clay surface. These protons have a catalytic effect in the initial decomposition in the organophilic nanoclay.[6,7] The glass transition temperature has decreased with the presence of the nanoclay, suggesting a plasticizer effect. The melt flow index decreased in the nanocompounds. The

***Table 1.***
Properties values of the PE samples.

| Samples | OIT (200 °C) | OIT (160 °C) | OIT | IDT (TG) | MFI (190/5) | DRX | Tg |
|---|---|---|---|---|---|---|---|
| | min | min | °C | °C | g/10min | $2\theta$ | °C |
| PE | 78 | – | 248 | 409 | 0.4 | – | −116 |
| PE + C | 83 | – | 251 | 395 | 0.4 | 4.50 | n.m. |
| PE + C + G | 88 | – | 251 | 399 | 0.4 | 4.20 | n.m. |
| RPE1 | 1 | 22 | 200 | 397 | 2.0 | – | −128 |
| RPE1 + C | n.m. | n.m. | 201 | 390 | 1.9 | 6.00 | −131 |
| RPE1 + C + G | 2 | 37 | 203 | 397 | 1.9 | 5.85 | −128 |
| RPE3 | 0 | 17 | 194 | 409 | 2.5 | – | −124 |
| RPE3 + C | n.m. | 22 | 199 | 384 | 1.5 | 4.15;6.75 | n.m. |
| RPE3 + C + G | 2 | 61 | 208 | 389 | 1.5 | 4.05;6.55 | n.m. |

n.m.: not measured; C: nanoclay; G: adhesion promoter.

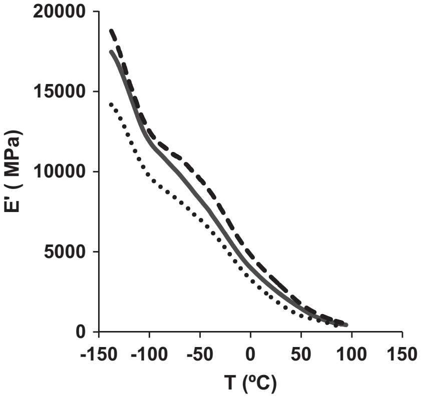

***Figure 1.***
Storage modulus E' in function of temperature of RPE1 samples in the range −150 °C to 90 °C; – = RPE1, – – = RPE1 + C, •• = RPE1+C+G.

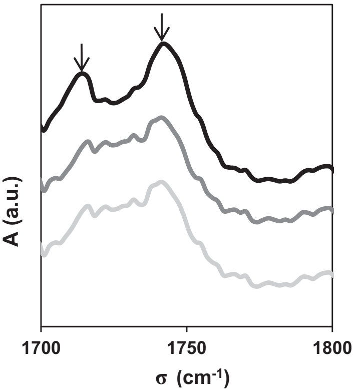

***Figure 2.***
Absorbance A in function of wavenumber α of RPE1 samples in the range 1700–1800 cm$^{-1}$; – = RPE1, – = RPE1+C, – = RPE1+C+G.

presence of the nanoclay has resulted in stiffness of the matrix polymer chains, hindering their movement and decreasing the flow inside the plastometer cylinder. In the DMA analysis (Figure 1) the recyclate RPE1 have presented an increase of the storage modulus, E', with the nanoclay addition, in the range of temperature studied, indicating a mechanical reinforcement, due to good dispersion of nanoclay. However, the presence of the adhesion promoter in the mixture, have caused a decrease of E'. This result is due, possibly, to the formation of clusters and lead to different behaviors. The nanocompounds of the recyclate RPE3 have showed a decrease in the storage modulus E'. The blends preparation method probably has influenced the results, leading to different degree of dispersion of the nanoclay powder. By the other hand, the nanoclay and adhesion promoter ratio must be optimized.

In the FTIR analysis (Figure 2), the recyclate nanocompounds have showed peaks at 1713 cm$^{-1}$ (C = O carboxylic acid) and at 1742 cm$^{-1}$ (C = O ester) with lower intensity than the recyclate peaks at the same wavenumber. The presence of hydrogen in the nanoclay modifies the surface, possibly through hydrogen bonds with the oxygen.

In the XRD analysis (Figures 3 and 4), the samples with nanoclay and compatibilizer have showed the nanoclay peaks at lower values of the 2θ angles than the values obtained to the same peak of the samples only with nanoclay, suggesting the increase of interplanar distance in the nanoclay layers.

These results indicate the formation of a nanocomposite or a microcomposite. It is recommended a study of the ratio of compatibilizer to organoclay in these nanocompounds. This parameter fully con-

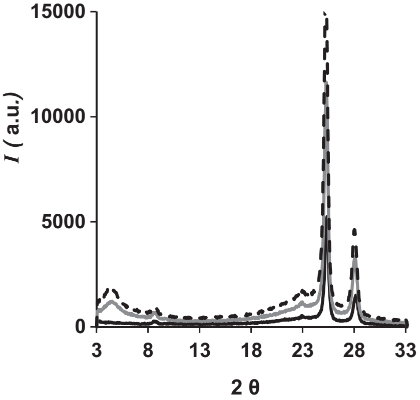

***Figure 3.***
Intensity I in function of 2θ angles of PE T100N samples; – = PE T100N, – = PE T100N+C, – = PE T100N+C+G.

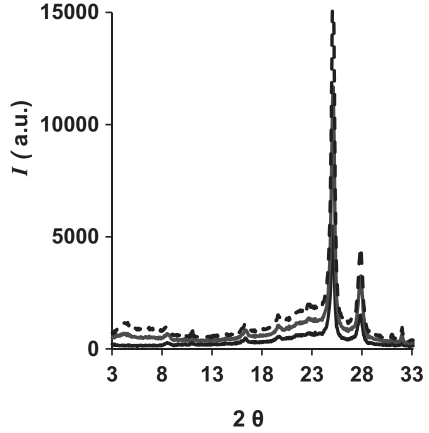

***Figure 4.***
Intensity $I$ in function of 2θ angles of RPE3 samples; – = RPE3, – = RPE3+C, – – = RPE3+C+G.

trols the final structure of the micro- or nano-composites.[8]

## Conclusion

The addition of nanoclay and polyethylene grafted with maleic anhydride to PE T100N and recyclates has improved the thermal properties. The possible exfoliation/intercalation of the PE in the nanoclay layers creates a path that increases barrier properties. The result is the reduction of the permeation to oxidation agents through the polymeric matrix, which improves the resistance to oxidative degradation. The initial temperature decomposition have decreased or remained equal to the original samples. The melt flow index decreased, the intensity of the FTIR oxidation peaks has been reduced and the XRD angles have displaced to lower values. These results are indications of a nanocomposite/microcomposite formation. The ratio of nanoclay and the adhesion promoter is a key feature and it is advisable to optimize their content.

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