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Valorization of Recycled LDPE by MMT Nanocomposite

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Abstract

The present work aims to add value to recycled low-density polyethylene (LDPEr) by adding 1 and 3 wt.% of nanoclay montmorillonite (MMT). The characterizations were performed by Fourier transform infrared spectroscopy, melt flow index, uniaxial tensile and impact tests, thermal gravimetric analysis, contact angle measurement, water sorption and eco-efficiency analyses. The MMT incorporation increases mechanical strength, thermal stability, and sorption, especially for recycled matrix. Moreover, eco-efficiency analysis shows that the recycled composites presented 15% of efficiency increase in comparison to virgin composites. LDPEr reinforced with MMT emerges as an eco-friendly material which can be applied for green composite.

Keywords: *Polymer Recycling, Recycled LDPE, Nanocomposite, MMT, Eco-efficiency.*

1. Introduction

The increase of waste disposal and the growth of non-renewable resource extraction highlight the need for developing clean, renewable, and sustainable materials. Among solid wastes, in particular, plastics are increasing more rapidly, especially from packaging.[1]

Every Brazilian citizen produces an annual average of 383.2 kg of municipal solid waste (MSW), and there is a little recycling of this total. However, the Belgium, for example, has another scenario with the production of 466 kg of MSW and presents high recycling rate, around 80%.[2] This situation is approximately observed in the USA, the UK, and GCC countries.[3,4] In Brazil the MSW is divided in plastic, metal, paper and glass. According to Al-Maaded et al. these plastic contents are about 14% of the total MSW volume; only 1–2% of this is recycled.[5]

Many of the polymers produced are used for packaging application, and they are most of the accumulated materials in the local disposals.[6] The primary polymer employed in films and packaging is low density polyethylene (LDPE), and it represents only 1.1% of the total volume that is recycled.[7-8] The difficulty of separation from other types of polymers for recycling can be overcome by using methods such as depolymerization, incineration and the production of blends.[9-10]

The LDPE is used both virgin and recycled.[11] Lee et al. employed the LDPE to obtain wood plastic composites and emphasized the importance of the processing the polymeric matrix.[12] However, in order to get better properties of the composites, the authors show the importance of using reinforcing fillers and considering their interface which affects the distribution, dispersion, and adhesion of fillers.[13] The high exfoliation of clays and the difference of structural organization are some of the particular points observed in the literature.[14]

Nanoclays in Brazil, such as bentonites, are presented in significant quantities in the soil making it more feasible to their use. The incorporation of low levels of it provides a greater mechanical and thermal properties, barrier to gases and low opacity of LDPE films.[15] The organophilization processes of nanoclays, such as montmorillonite (MMT), improve the clay exfoliation and consequently polymer chain intercalation. Virgin LDPE is highly nonpolar and hard for the MMT exfoliation process. When the LDPE is reprocessed it may be degraded and the polymer chain is reduced, which increase the melt flow and create new radicals that allow the nanoclay's incorporation. This paper aims to prepare and compare the use of recycled and virgin LDPE by adding MMT (1 and 3 wt.%). The materials prepared were characterized by Fourier transform infrared spectroscopy (FTIR), melt flow index (MFI), uniaxial tensile and impact tests, thermal gravimetric analysis (TGA), contact angle measurement and water sorption analysis. The purpose is to develop an environmental friendly composite and high value application.

2. Experimental

The virgin low density polyethylene (LDPEv) was supplied by Braskem (SP-BR) name TX 7003 (0.922g/cm^3 and MFI 0.27g/10min). The recycled low density polyethylene (LDPEr) was obtained from a cutting of Cobrevale Ind. Com. Ltda. and processed by Plast Thalin Ind. Com. The montmorillonite nanoclay (Cloisite 30B) (MMT) was supplied by Buntech Tec. Ins. (SP-BR) and modified with quaternary ammonium ion (90 meq/100 g nanoclay).

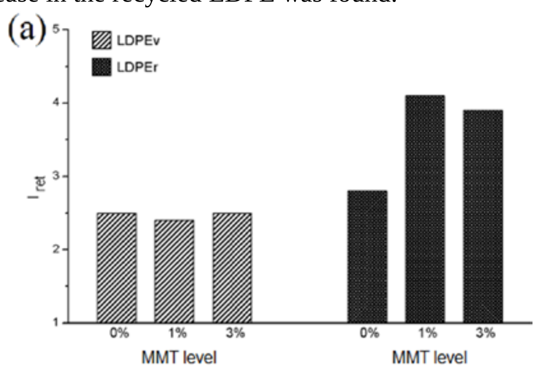
The mixtures containing LDPE (virgin or recycled) with MMT (0, 1 and 3 wt.%) were prepared using K-Mixer homogenizer (MH - 50hIR) (MH Equip. Ltda.) at 3800 rpm at 215°C. The chemical groups were characterized by Fourier transform infrared spectroscopy (FTIR), in a

Thermo Nicolet Nexus 4700 spectrophotometer with 64 scans (400 to 4000 cm^{-1}).[16] The melt flow index (MFI) test was performed in a plastometer CEAST modular line (ASTM D1238). The elastic modulus (E), ultimate tensile strength (σ_{max}) and elongation at break (ε_{max}) were determined using a universal testing machine (Instron 5900) (Instron S/A Ind. e Com. Ltda.) at 50 mm/min with 500kgf (ASTM D638). Charpy impact test (I) was performed using an Impact Izod SE-01-Shanta Eng. and Charpy XJC25D with 2.7 J (ASTM D256). Thermal degradation behavior was performed in a TGA Q500 by TA Instruments with N_2 from 20°C to 180°C at 10°C/min. Contact angle (CA) assay was performed using a Dynamic tensiometer (DCAT) with water and according to the Young-Laplace equation.[17] The sorption coefficient (D) was obtained by monitoring the absorbed mass, in water (168h) according to second Fick's law.[18]

3. Results and Discussion

3.1 Fourier transform infrared spectroscopy (FTIR)

Figure 1 (a) shows the crosslinking density changes (Iret) and (b) carbonyl formation (I_{carb}). FTIR spectrum of virgin and recycled LDPE present peaks of $-CH_2-$ groups (720 cm^{-1}), attempting to analyses changes in crosslinking density and the degree of oxidation of polyolefin according to carbonyl formation (1720 cm^{-1}).[16] In the regions of 720 cm^{-1} none significant variation was observed for the virgin matrix composites [Figure 1 (a)], however, an increase in the recycled LDPE was found.



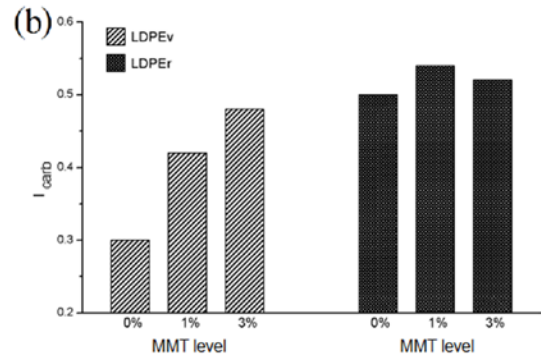


Fig. 1 (a) Crosslinking density formation and (b) carbonyl formation.

Figure 1 (a) shows a slight change in the virgin LDPE index (I_{ret}), however a greater crosslinking density was observed for LDPEr. These results are promoted by recycling process and may outcome to higher Young's modulus. Figure 1 (b) presents an increase of the degree of carbonyl index for the virgin sample by adding MMT. The recycled polymer does not change this parameter. This higher intensity of carbonyl absorbance was also observed in another study.[19]

3.2 Melt flow index (MFI)

Figure 2 shows low MFI values for the virgin LDPE and higher values for LDPEr, as it was expected. These results suggest the presence of smaller chains for the recycled polymer due to chain scission, which could oil and allow the melt flow and better MMT exfoliation.[20]

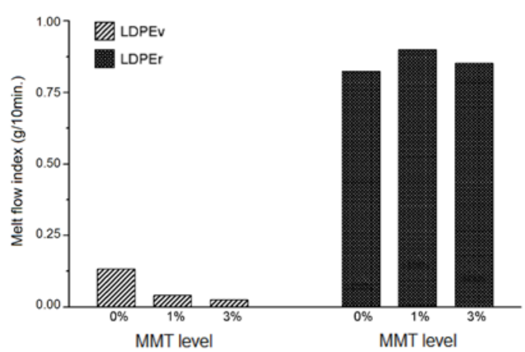


Fig. 2 MFI values for virgin and recycled LDPE and their composites with MMT (1 and 3 wt.%).

Virgin LDPE shows a reduction in the melt flow. According to Zhu et al. the MMT incorporation justifies a mobility restriction. The results suggest that in the LDPEr composites the effect of the polymer chain scission prevails.[21]

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3.3 Tensile and Impact Testing

Table 1 shows the elastic modulus (*E*) results, ultimate tensile strength (σ_{max}), elongation at break (ε_{max}) and Izod Impact resistance (I) for virgin and recycled LDPE. According to Table 1, the addition of MMT provided an increase in the the values of E, and I. However, there is a decrease of σmax and ε_{max}. This behavior was more significant for recycled LDPE which can be explained due to the better dispersion and exfoliation of the nanoclay.[22]

Table 1: Mechanical results of *E*, σ_{max}, ε_{max} and I for the virgin and recycled LDPE and their composites with MMT (1 and 3 wt.%).

	MMT (wt.%)	*E* (MPa)	σ_{max} (MPa)	ε_{max} (%)	Impact (I) (kJ/m^2)
LDPEv	0	128.1 ± 8.3	15.7 ± 0.9	725.2 ± 77.6	261.4 ± 11.2
	1	130.6 ± 11.8	14.1 ± 1.0	663.3 ± 59.7	268.8 ± 16.7
	3	158.9 ± 7.2	12.1 ± 2.2	455.5 ± 188.2	298.9 ± 14.0
LDPEr	0	236.3 ± 18.5	18.7 ± 1.0	984.1 ± 39.9	407.5 ± 26.5
	1	258.9 ± 14.2	13.8 ± 2.0	763.2 ± 82.4	415.1 ± 19.9
	3	280.8 ± 12.1	13.9 ± 1.6	740.7 ± 113.1	464.9 ± 24.2

The impact strength results show an increase of the impact property while the nanoclay content increases. This increase was most significant when incorporated 3 wt.% of MMT. According to Canevarolo Jr. et al., the main parameter to quantify the impact resistance is the energy of impact; the results described a high ductility for the matrix LDPEr.[23] According to Wetzel et al., the disorder of exfoliated silicates could reduce the propagation of micro-cracks, which promotes high impact strength.[24]

3.4 Thermal gravimetric analysis (TGA)

Figure 3 (a) and (b) show derivative (DTG) curves and crystalline melting temperature values (Tm) both obtained by TGA, respectively.

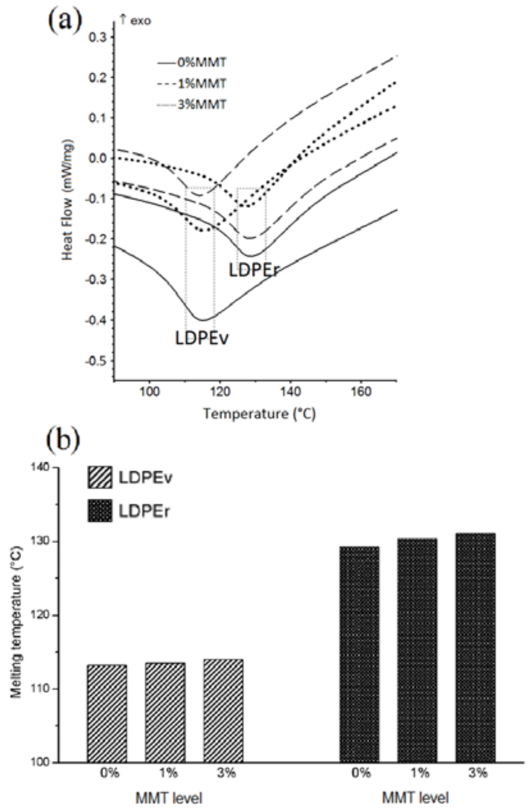

Fig. 3 (a) Principal part of the DTG curves of the samples. (b) Crystalline melting temperature (T_m) for virgin and recycled LDPE and their composites with MMT (1 and 3 wt.%).

In Figure 3 (a) it is possible to observe a slight mass loss up to 180°C, which is below the onset degradation temperature of the LDPE. Cardenas et al. had similar results in TGA. They observed a little mass loss before the polymer degradation, which is attributed to a dehydration of the material. The results showed higher thermal stability for recycled matrix than the virgin polymer, independent on load contents and hydration level.[25]
The results presented in Figure 3 (b) show an increase in the thermal stability of composites, probably because of MMT incorporation. According to the literature, the nano-silicate from MMT clay acts as a retardant for the transport of volatiles generated during sample heating. This effect appears similarly in the gas barrier thin films.[26]

3.5 Contact Angle (CA)

Figure 4 presents and illustrates the contact angle values (ɵ) from matrices and their composites prepared with virgin and recycled resins. This Figure also shows the wettability of their respective surfaces.

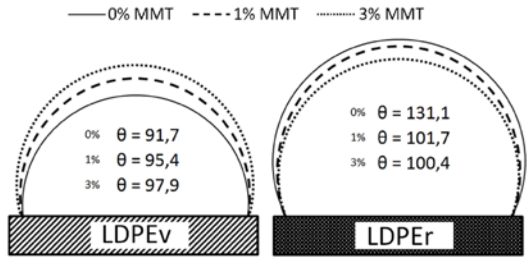

Fig. 4 CA results for the virgin and recycled LDPE and their composites with MMT (1 and 3 wt.%).

In general, the polyolefins have predominantly non-polar character with contact angles (ɵ) > 90° in water/polymer system.[30] Figure 4 shows the contact angle values and the profile of the water drop on surfaces. The same Figure shows that the LDPEv has a shorter contact angle than LDPEr. A possible explanation is that the recycled material contains mixtures of other polyethylenes, which increase the disorder of the polymer chains causing an increase in surface tension and therefore increasing the value of ɵ.[27] The LDPEv composites have increased ɵ due to first reprocessing (K-Mixer) while the recycled composites have decreased ɵ due to the hydrophilic change of MMT. This behavior also shows the increase of hydrophilic clay dispersion, such as MMT, and promotes a reduction in hydrophobicity.[28]

3.6 Sorption Testing (D)

Figure 5 shows the results of the water sorption test for the composite LDPE virgin and recycled and their composition after 168 hours.

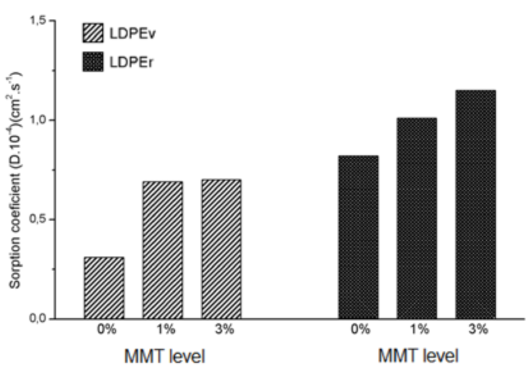

Fig. 5 Sorption results for virgin and recycled LDPE and their composites with MMT (1 and 3 wt.%).

Figure 5 shows that the recycled matrix has higher sorption coefficient than the virgin polymer. This behavior can be attributed to the increased mobility of the recycled polymer chains, probably because it has smaller chains. For both, the adding MMT causes an increase in this property.[29] Pavlidou et al. have found similar results with the addition of MMT. They showed that the occupation of the empty volume by water molecules is facilitated by the charge to polar structure. [30]

It is also possible to attribute higher sorption coefficient values (D) to the recycled resin samples, which had a greater variation in size of the polymeric chains and greater clutter. Zhang et al. show that the highest rates of water absorption get to an increase cracks and an acceleration of materials degradation. Móczó et al. showed previously that the penetration of water into LDPE matrix is an initial step in the process of erosion.[31-32] It is important to observe that the samples had greater mass loss, near the MMT content, after the sorption experiment (Δm). In previous studies, Macedo and Rosa evaluated the thermal degradation of LDPE-MMT composites, and PLA-MMT composites, they observed an intensification of mass loss justified by sorption process.[33]

3.7 Eco-efficiency analyze

Due to the variety of tests and results of this work, the authors propose a weighed analysis of these discussed properties based on eco-efficiency analysis methods.[34] The authors considered the two pure materials of study (virgin and recycled LDPE) and their composites with MMT 3 wt.% seeking a more eco-friendly material. Figure 6 shows the result of the composites.

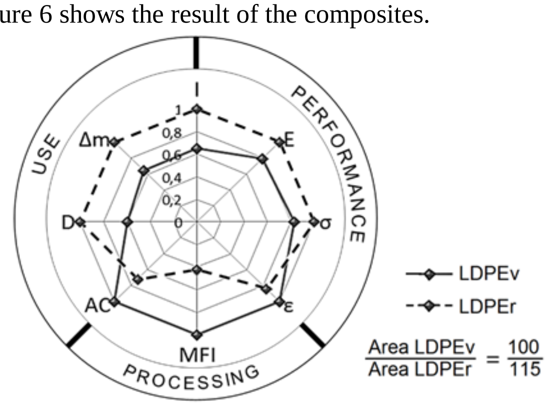

Fig. 6 Environmental "fingerprint" of the results from the virgin and recycled LDPE composites with MMT (3 wt.%).

Figure 6 demonstrates that the LDPEr is 15% more viable than the virgin resin. The total area corresponding to the application for the recycled material was higher than LDPEv.

The differences in behavior of virgin and recycled matrix composites have been previously studied.[11-14] It is known that the presence of smaller chains is important for the better dispersion strengthening as well as for the presence of chemical groups to a stronger interface.[21] Thus Figure 7 represents the base of a proposed model for the virgin and recycled LDPE composites behavior with MMT.

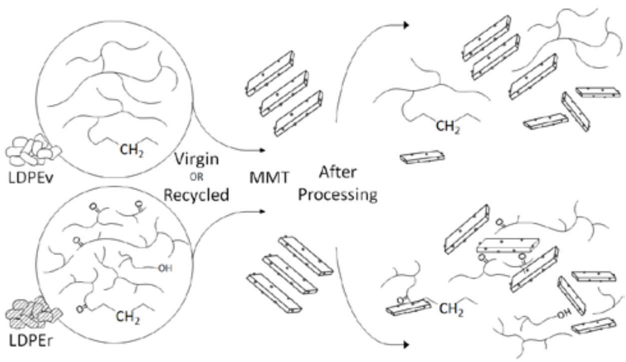

Fig.7 Proposed model for the virgin and recycled LDPE composites behavior with MMT.

4. Conclusions

The incorporation of nanofiller (MMT) in virgin and recycled LDPE matrix increased the elastic modulus, the Izod Impact resistance, the thermal stability and the water absorption of LDPE. The increase in properties was more significant in LDPEr. This can be an advantage in biodegradation processes of these composites. The life cycle analysis suggests that the composite with LDPEr is more eco-friendly and can be applicable in new films and packaging.

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