

## **Synthesis and evaluation of physical-chemical properties of a composite based on poly (acrylic acid) and Nanocellulose Crystalline (NCC) for reinforcing polyesters matrix such as PET**

\* Mancera-García Karen M.<sup>1)</sup> and Escobar-Barrios Vladimir A.<sup>2)</sup>

<sup>1), 2)</sup> *Environmental Science Division, Instituto Potosino de Investigación Científica y Tecnológica, Camino a la presa San José 2055, Lomas 4ª Sección. San Luis Potosí, CP. 78216, SLP, México*

<sup>1)</sup> *karen.mancera@ipicyt.edu.mx*

### **ABSTRACT**

The nanocellulose crystalline (NCC) could reinforce polymer matrix, but its dispersion into polymeric material is difficult. Therefore, in order to enhance its dispersion into polymers or polymer blends, it is proposed to synthesize a composite able to interact with the NCC during synthesis. The new nanocomposite is based on nanocellulose crystalline (NCC) and poly (acrylic acid) (PAA). The effect of this composite on the physical and chemical properties of recycled PET was evaluated by several spectroscopic, thermal and electron microscopy techniques (FTIR, Raman, XRD, DSC, SEM and TEM). The resulting material showed different physical and thermal properties regarding the material without NCC. Thus, the synthesized composite effectively reinforced the plastic matrix, which enhanced the mechanical and thermal properties of recycled PET.

### **1. INTRODUCTION**

In the area of reinforcement materials of composites, some interesting nanofillers include clay, silica, metal nanoparticles, carbon nanotubes, and crystalline nanocellulose (NCC) (Hsu 2011), which is today, due to its properties, a particularly attractive class of nanomaterials (Peng, 2011). The NCC is a crystalline material with shape of bars of about 100 to 600 nm long and 3 to 20 nm in diameter. Its size and crystallinity depends on the source of cellulose used. Most often, these types of nanocrystals are obtained from cellulose fibers by controlled acidic hydrolysis of cellulose fibers. In addition, because of its nanometer-size, it has excellent stability, high surface area and excellent mechanical and optical properties. Along with these properties, other advantages including high reactivity, natural abundance, no toxicity and biodegradability have been remarked (Moon, 2011).

The effect of NCC within polymer matrices has been confirmed (Junior de Menezes, 2009); however, its adequate dispersion is reduced because its hydrophilic character; being necessary to modify its surface, which increases the cost of production of this material. According to research conducted by Mancera and Escobar (2012), a

---

<sup>1)</sup> Doctorate Student

<sup>2)</sup> Professor

compatibilizer for plastic blends based on an interpenetrating polymer network (IPN) using poly (acrylic acid) and a thermoplastic elastomer was synthesized. It had a significant effect on the morphology of the studied polymer blends improving their interfacial adhesion and increasing the mechanical and thermal properties that exceeded the commercial compatibilizer effect.

In a study carried out by Yang (2012) a new series of nanocomposite hydrogels based on nanocrystalline cellulose (NCC) and poly (acrylic acid) (PAA) were synthesized in situ by polymerization by free radicals in an aqueous medium, the results indicated that gel is formed as a monomer (acrylic acid, AA) grafted NCC surface where PAA chains intertwined flexible generated NCC-PAA gels. The NCC-PAA gels exhibited good mechanical properties such as a large percentage of elongation (> 1100 %) and high tensile strength (> 350 kPa) properties.

## **2. PROPOSED REINFORCER MATERIAL**

Due to the favorable interaction of NCC with PAA, a new compatibilizer can be synthesized based on interpenetrating polymer networks with the addition of NCC, thereby enhancing the dispersion in NCC polymeric matrices through extrusion, providing greater mechanical and thermal properties to the resulting materials. In this work, dispersion and maximum content of NCC in the IPN (90% PAA and 10% elastomer thermoplastic) were evaluated in terms of their morphology and thermal properties. The contribution of this work is relevant since we have synthesized a new composite capable of providing compatibility features and reinforcing the plastic blends from recycling.

### *2.1 Composite of poly (acrylic acid) and Nanocellulose Crystalline (NCC) in form of interpenetrating polymer network (IPN) with and elastomer thermoplastic (TPE).*

In order to obtain a homogeneous composite, the previous addition of NCC to the reaction medium (water) into the reactor prior to adding the remaining components for the reaction, was carried out.

The thermal behavior was evaluated by differential scanning calorimetry for the materials, IPN with different NCC concentrations (0, 1, 5, 10 and 20 % w/w) and PAA. In this sense, the materials with NCC, compared with the matrix (PAA), showed an increment about 10 °C in melting peak belonging to PAA.

In order to see the diffraction pattern of the IPN with the addition of NCC, with various concentrations, the X-ray diffraction analysis was carried out. The pure IPN was compared with IPN having different contents of NCC. As shown in Fig. 1, the crystallinity of the IPN is maintained despite the NCC concentration, although from values equal to or greater than 5% NCC content, and increase in the intensity of the peak located at approximately 22.5 ° and the other at 33.6 ° C was observed, which is characteristic of the NCC.

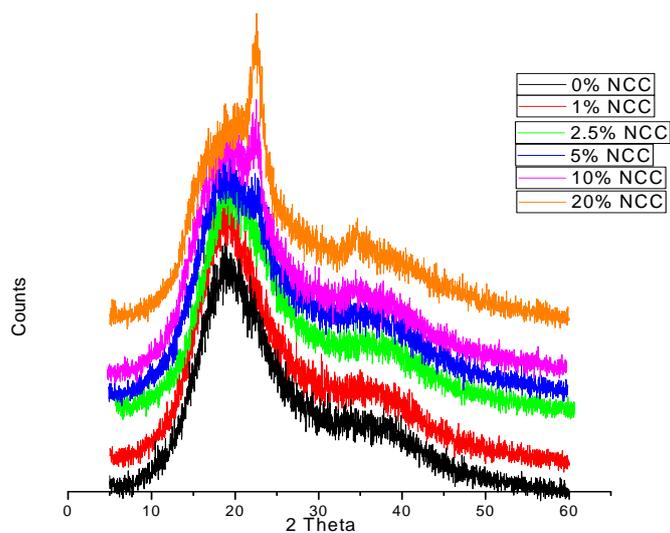


Fig. 1 X-ray spectra from different samples of composites and pure IPN.

Morphological analysis was performed by scanning electron microscopy, for various samples of IPN modified with NCC. The results show a significant change in the morphology of the sample, since the surface of the IPN with NCC begins to be more porous as the NCC concentration increases, compared with the IPN without NCC (see Fig. 2).

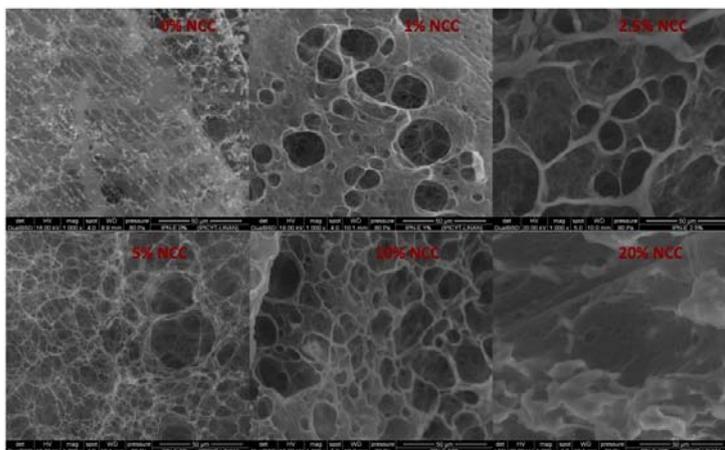


Fig. 2 Scanning electron microscopy and composites.

## 2.2 IPN with NCC in the polymer blends of PET/PE

To evaluate the behavior of IPN with NCC, we select the IPN with more quantity of NCC (20%) in blends of PET/PE (75/25). The concentration the IPN into the polymer blend was 1 and 5% wt. Also, blends at such concentrations of commercial compatibilizer (PE-g-MAH) were obtained, which were named as MC1 and MC2, for 1 and 5 %, respectively.

In Fig. 3, it can be seen that samples containing the synthesized nanocomposite IPN-NCC exhibit a significant increase in the tensile strength, between 8.7 and 12.0 % higher than the specimen non-compatible. This behavior is due to an increased stiffness of the material generated by the formation of domains between LDPE with SEPS, because they are chemically akin forming more homogenous dispersion due to interactions between the compatibilizer and the blend but also the number of interaction between PAA, NCC and PET, by their functional groups, was reduced, then the plasticizer effect was slighter.

Blends with commercial compatibilizer (MC1 and MC2 samples), for PET matrix, have a lower performance compared to the compatibilized blends with IPN, due to the greater number of functional groups in the PAA that can interact with PET, and compared with the small amount of MAH (1 % w/w) present in the commercial compatibilizer. Thus, the quantity of functional groups present in compatibilizer is important to improve the interfacial adhesion between the plastics to be blended. Also, it is important to have specific functional groups akin to both type of plastics, this was achieved with the new compatibilizer.

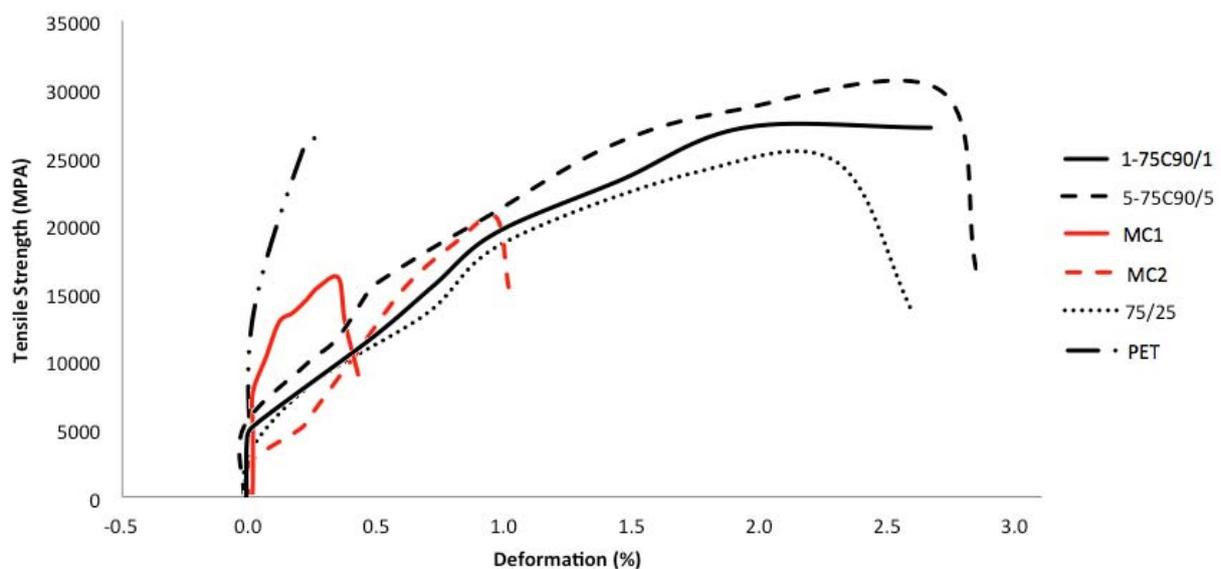


Fig. 3 Tensile strength behavior of blends of PET (75/25) with IPN, commercial material and pure PET.

### 3. CONCLUSIONS

It is possible to add up to 20 % w/w of NCC into polymeric matrix like poly (acrylic acid). The presence of NCC modifies the thermal behavior of poly(acrylic acid) giving a more rigid material due to interactions between functional groups present in both materials.

In addition, the obtained IPN, with different concentrations of NCC, showed different thermal behavior, giving a melting temperature shift for the PAA, which is indicative of the interaction between NCC and PAA.

The PAA of the compatibilizer interacts with PET giving a better material, from the mechanical point of view, since a good dispersion of the discontinuous phase into the continuous one was achieved. Depending on the PAA content in the compatibilizer such dispersion can change.

Higher Young's modulus and tensile strength were obtained with the IPN-NCC nanocomposite regarding commercial compatibilizer and non-compatibilized blends. Thus, the IPN-NCC-modified materials exhibit higher toughness, which could be related with the reinforced effect of the NCC that also promotes dispersion of the compatibilizer into the polymeric matrix.

## REFERENCES

- Hsu L., Weder C., Rowan S.J., J. (2011) "Stimuli-Responsive, Mechanically-Adaptive Polymer Nanocomposites". *Mater.Chem.*, 21, 2812-2822.
- Junior de Menezes, A.; Siqueira, G.; Curvelo, A. A.S.; Dufresne, A. 2009. "Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites." *Polymer*. 50: 4552–4563.
- Mancera Garcia K. M., Thesis of Master of Science. Síntesis de uncompatibilizante parapoliéster y polioléfinas, con base en redes interpenetradas poliméricas. Instituto Potosino de Investigación Científica y Tecnológico, A. C. San Luis Potosi SLP (México), 12 septiembre 2012.
- Moon R.J., Martini A., Nairn J., Simonsen J., Youngblood Cellulose nanomaterials review: structure, properties and nanocomposites. *J., Chem. Soc. Rev.* (2011) 40, 3971-3994.
- Peng B.L., Dhar N., Liu H.L., Tam K.C., (2011) "Chemistry and applications of nanocrystalline cellulose and its derivatives: A nanotechnology perspective". *The Can. J. Chem. Eng.*, 89, 1191–1206.
- Yang, J.; Han, C.R.; Duan, J. F.; Ma, M. G.; Zhang, X. M, Xu, F.; Sun, R. C.; Xie, X.M. 2012. "Studies on the properties and formation mechanism of flexible nanocomposite hydrogels from cellulose nanocrystals and poly (acrylic acid)." *Journal of Materials Chemistry*. 22: 22467-22480.