Preparation and Physical Characterization of Nanocomposites of PLA / Layered Silicates

I. Restrepo, S. Solorzano

Abstract—This work was focused in to study the compatibility, dispersion and exfoliation of modified nanoclays in biodegradable polymers and evaluate its effect on the physical, mechanical and thermal properties on the biodegradable matrix used. The formulations have been developed with polylactic acid (PLA) and organically modified montmorillonite-type commercial nanoclays (Cloisite 15, Cloisite 20, and Cloisite 30B) in the presence of a plasticizer agent, specifically Polyethylene Glycol of low molecular weight. Different compositions were evaluated, in order to identify the influence of each nanoclayin the polymeric matrix. The mixtures were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), X-ray diffraction (DRX), transmission electron microscopy (TEM) and Tensile Test. These tests have allowed understanding the behavior of each of the mixtures developed.

Keywords—Biopolymers, Nanoclays, polylacticacid (PLA), polymer blends.

I. INTRODUCTION

POLY (lactic acid) is a commercially available bio-based material that could become in a good option for different applications due to its good clarity, high strength and good processability. One of the limitations in some application is the low glass transition temperature ~58°C [1], one way for to alter the Tg is through the addition of plasticizers which increase the molecular mobility. Polyethylene glycol (PEG) of low molecular weight plasticizers is one of the most studied and most effective plasticizing of the PLA [2]. Besides, adding montmorillonite organically modified commercial available (15, 20, 30B) can be used to improve the mechanical and barrier properties of the PLA [3]

II. SELECTION OF MATERIALS

A first selection of materials includes the PLA (Ingeo 3251D from Nature Works) as biodegradable polymer matrix and montmorillonite-type commercial nanoclays organically modified, (Cloisite® 15, 20, and 30B) plus the PEG additive, Carbowax PEG 400 with a molecular weight of 400 g/mol.

The equipment selected to carry out the mixture was a torque rheometer type Brabender. The PLA is a thermoplastic aliphatic polyester derived from a natural source like corn starch, tapioca or sugarcane. The mechanical and thermal properties are similar to other non-biodegradable polymers like poly ethylene terephthalate (PET) and present good processability and low environmental impact.

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III. APPLIED METHODOLOGY

Mixtures were carried out in different compositions (see Table I), for which the procedure was as follows:

- 2 hours drying at 40°C of the pristine PLA
- Nanoclay/PEG pre-mixture in a beaker
- The previous mixture or nanoclay/PEG is added to PLA in torque rheometer, processing at 60 rpm -120°C – 8 minutes, in order to process it by melt-blending method.

IV. CHARACTERIZATION

With the purpose of studying the, dispersion and exfoliation of nanoclay in the PLA matrix and evaluating its effect on the mechanical and thermal properties on the biodegradable matrix, the following characterization was carried out (see Table I).

TABLE I
TECHNIQUES, EQUIPMENT AND CONDITIONS OF CHARACTERIZATION FOR MIXTURES

Technique	Equipment	Conditions
TGA	Trademark NETZSCH Model TG 209F3	Heating cycle from 35 to 600 ° C - rate of 10 ° C / min, the samples were analyzed in aluminum crucibles
DSC	Trademark NETZSCH model DSC 204F1	Heating cycle from 25 a 350 °C - rate of 10°C/min, the samples were analyzed in aluminum crucibles
DRX	Diffractometer Bruker Endeavor model D4/MAX-B	40 kV y 40 mA and scanning 2θ was of 1,7 a 30° step of 0,02° and counting time of 0,6° by minute
Mechanical properties	Universal testing machine, Trademark Karg Industrietechnik model Smar tens 005	According to standard ASTM-D 638, samples type V were fabricated using a mini injection equipment type HaakeMinijet II, and injection conditions were 350 bar de pressure and130°C of temperature and then conditioned under 25°C and 65% HR for 7 days.The tensile test was performed under estándar ASTM 638D using a cross head speed of (1mm/min).
TEM	High resolution microscope (HRTEM) trademark FEI model Tecnai G2 F20 S-Twin, equipped with an electron gun of 2 (Å) of diameter	operated at a tension of 120 kV and extraction voltage of 3400 V

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TABLE II
COMPOSITION OF MIXTURES

Sample N°	PLA (wt. %)	Cloisite 30B (wt. %)	PEG (wt. %)
1	100	0	0
2	99	0	1
3	98	0	2
4	97	0	3
5	97	3	0
8	94	3	3
12	92	5	3
Sample N°	PLA (wt. %)	Cloisite 20A (wt. %)	PEG (wt. %)
17	97	3	0
20	94	3	3
21	92	3	5
22	92	5	3
Sample N°	PLA (wt. %)	Cloisita 15 (wt.%)	PEG (wt. %)
23	97	3	0
26	94	3	3
27	92	3	5
28	92	5	3

A. Differential Scanning Calorimetry(DSC)
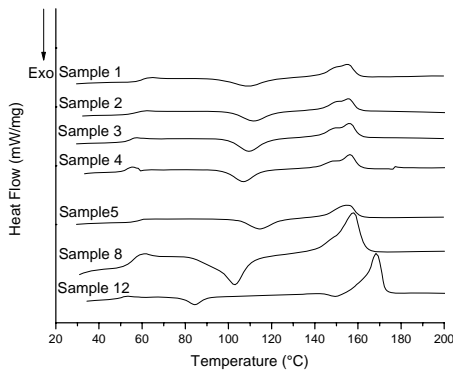
Fig. 1 DSC Thermograms for the nanocomposites containing
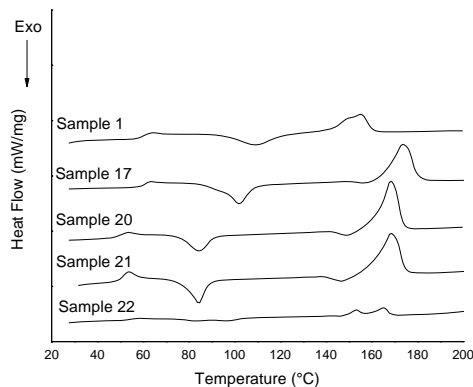Cloisite 30B

Fig. 2 DSC Thermograms for the nanocomposites containing Cloisite
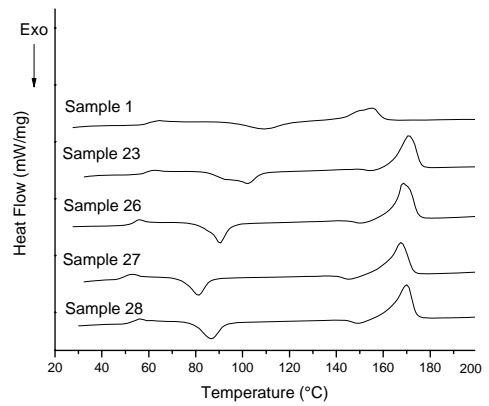20

Fig. 3 DSC Thermograms for the nanocomposites containing
Cloisite 15

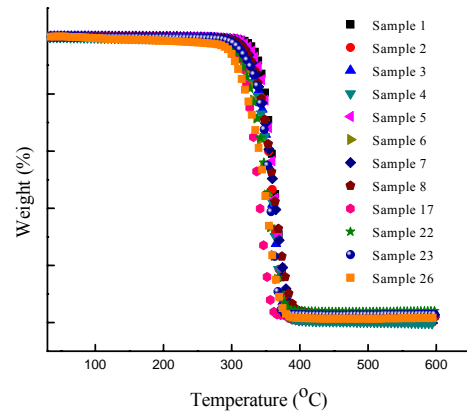*B. Thermogravimetric Analysis (TGA)*

Fig. 4 TGA thermograms of nanocomposites containing Cloisite 15,
20 and 30B

TABLE III
COMPARATIVE TEMPERATURES (5%, 50% AND MAXIMUM LOSS) OF
NANOCOMPOSITES

	T (°C)–(5%)	T (°C)-(50%)	T(°C) -deg.
Sample 1	334	359	339
Sample 2	319.5	354.5	334
Sample 3	314.9	354.9	329.9
Sample 4	308.7	353.7	328.7
Sample 5	324.2	359.2	334.2
Sample 6	316.8	346.8	326.8
Sample 7	319.6	359.6	329.6
Sample 8	318.5	358.5	328.5
Sample 17	306.8	336.8	316.8
Sample 22	307.4	347.4	317.2
Sample 23	312.7	352.7	327.7
Sample 26	294.7	344.7	304.7

From the above diagrams, the following can be highlighted:
Figs. 1, 2 and 3 show the thermal transitions of the material in
which there is no significant difference by adding clay and
polyethylene glycol (PEG) and variations are within the error
range of the equipment. Regarding the content of the
plasticizer used (PEG), when increasing its quantity in the
mixture, there is a decrease in the glass transition temperature

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and a slight increase in the melting temperature of the nanocomposite due to a possible nucleating effect of the nanoclay in PLA.

Additionally also shows that regardless of the type of clay used, the influence on the mixture of PEG is slightly lower Tg. The slight decrease in the glass transition temperature of PLA nanocompositos with an increase in the PEG content can be a result of dual rol of PEG as plasticizer and as compatibilizer in the preparation of PLA nanocompositos [4].However, such variations of the glass transition temperature and melting point not show a remarkable difference in the range studied. These results are comparable to those obtained by [2].

By observing Fig. 4 shows thermogravimetric analysis in mass loss versus temperature, finding that the material has a thermal stability up to 320oC, regardless of the presence of nanosized clays and plasticizer. Table III shows that at 5%, 50% and the degradation temperature of the Sample 26 is presenting a greater difference, however, they are within the error range of the equipment
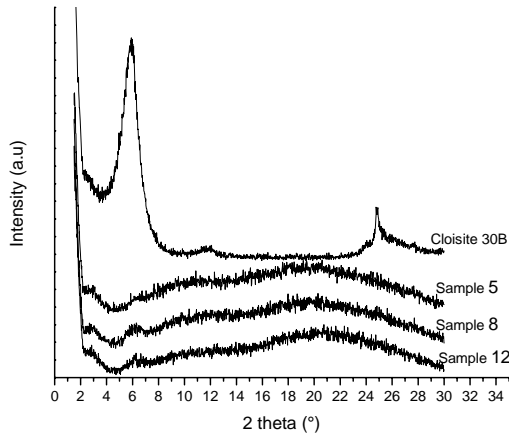
C.X-Ray Diffraction (XRD)

Fig. 5 X-ray diffractograms of Cloisite 30B and mixtures containing Cloisite 30B
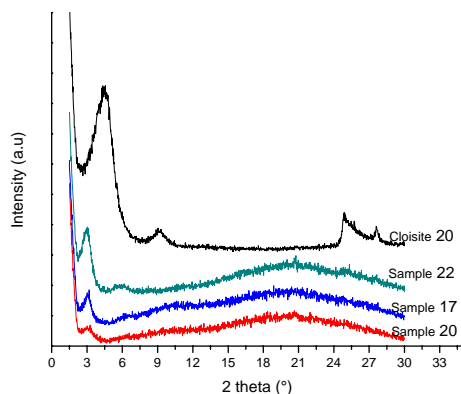

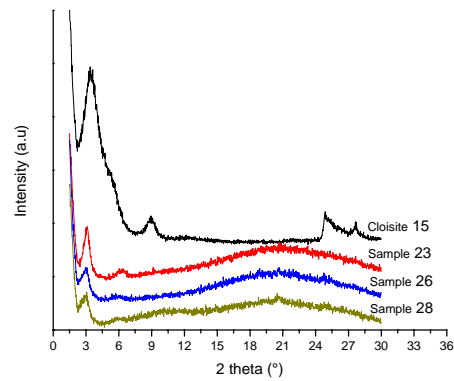Fig. 6 X-ray diffractograms of Cloisite 20 and mixtures containing Cloisite 20

Fig. 7 X-ray diffractograms of Cloisite 15 and mixtures containing Cloisite 15

Dispersion, exfoliation and intercalation are directly related with the morphology of nanocomposite. The above, are generated by shearing process during melt blending and is depends on compatibility of the polymeric matrix and organo-modified surface of the clay. In this way, the larger diffraction peak, localized at low angles is and indicative of intercalations of the layered silicates and the polymeric matrix [5].

Based on the results obtained, and taking in account the Bragg´s law equation, is possible identify the differences between interlayer distance (Δd) of organo-modified silicate in the polymeric matrix. It is possible to note in Figs. 5-7that the first pick in each of the mixtures are slightly displaced to the left with respect to the first pick of the pure nanoclay. Differences mentioned above are clearly an evidence of dispersion (greater or lesser degree depending on the mixture) of the nanoclay in the matrix (dispersion is related either intercalation or exfoliation). There is no peak observed in XRD results if clay platelets in polymeric matrix are exfoliated [6]. In this way, in Fig. 8, the samples 5, 8, 12, and 26 showed greater intercalation with respect to the other mixtures which can be verified when an estimate of the distance between the clay layers (d-spacing) is obtained.
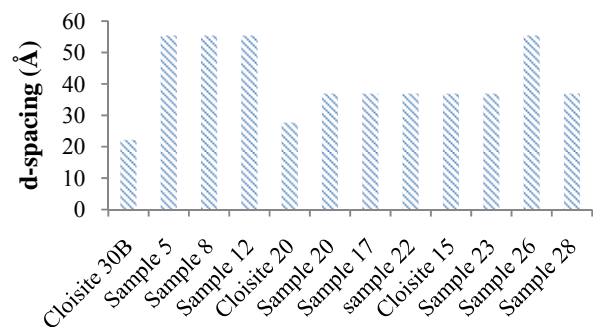

Fig. 8 d-spacing for pristine Cloisite 15, 20, 30B and different mixtures PLA/PEG/Cloisite (15, 20, 30B)

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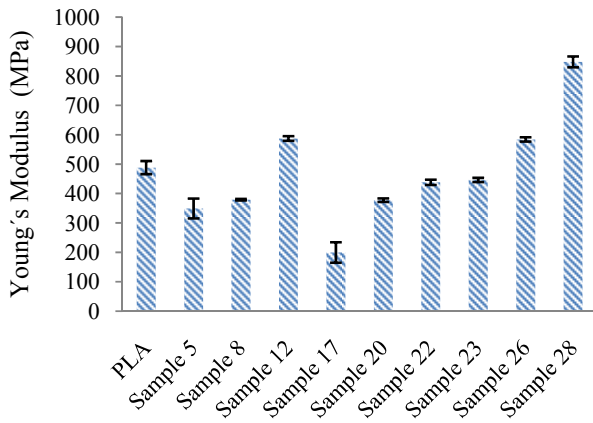
D. Mechanical Properties

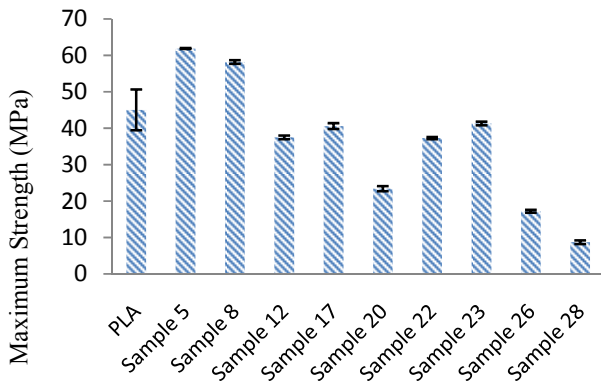

Fig. 9 Young´s Modulus of PLA nanocompositos

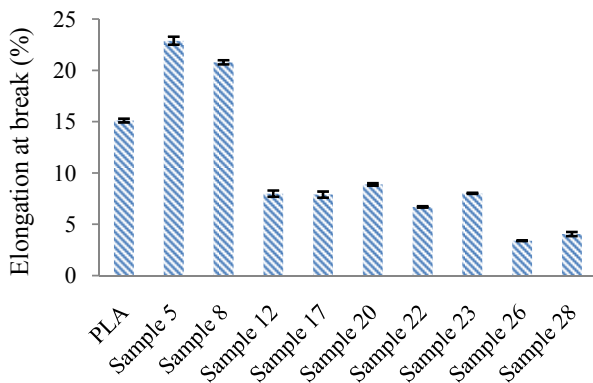Fig. 10 Maximum strength of PLA nanocomposites

Fig. 11 Elongation at break of PLA nanocomposites

The samples 12 and 28, containing 5 (wt.%) of nanoclay (see Fig. 9) have a higher Young's modulus than other mixtures and pristine PLA. This is directly related with the content of clay in the mixtures, giving they more rigidity compared with mixes containing 3(wt. %) of nanoclay [7]. Now, the addition of PEG, imparts flexibility to the material; evidence of this is the behavior showed in Fig. 9, where the

mixes with content of 3 (wt. %) of PEG show lower Young´s modulus than mixes containing 0 (wt. %) of PEG; meaning a decrease in the rigidity of the material.

Should be noted that samples 5 and 8 containing Cloisite 30B, presents values of maximum strength and elongation at break higher than any other mixes, even pristine PLA; suggesting some better performance than mixes containing Cloisite 15 and 20.
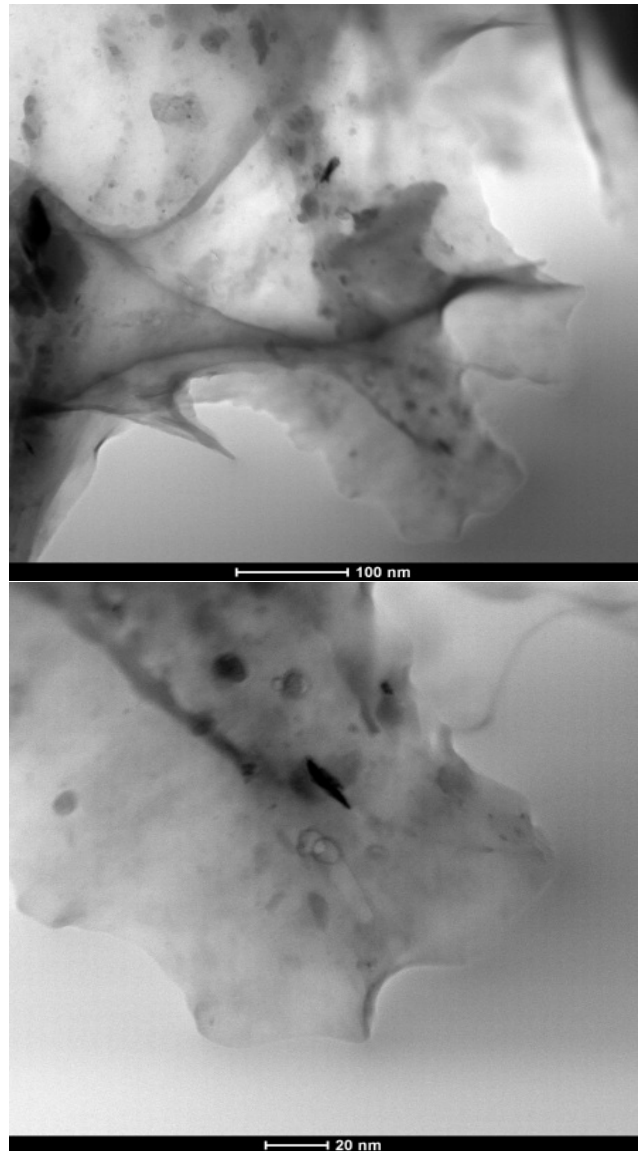
E. Transmission Electron Microscopy (TEM)

Fig. 12 TEM images on thin section of sample number 8

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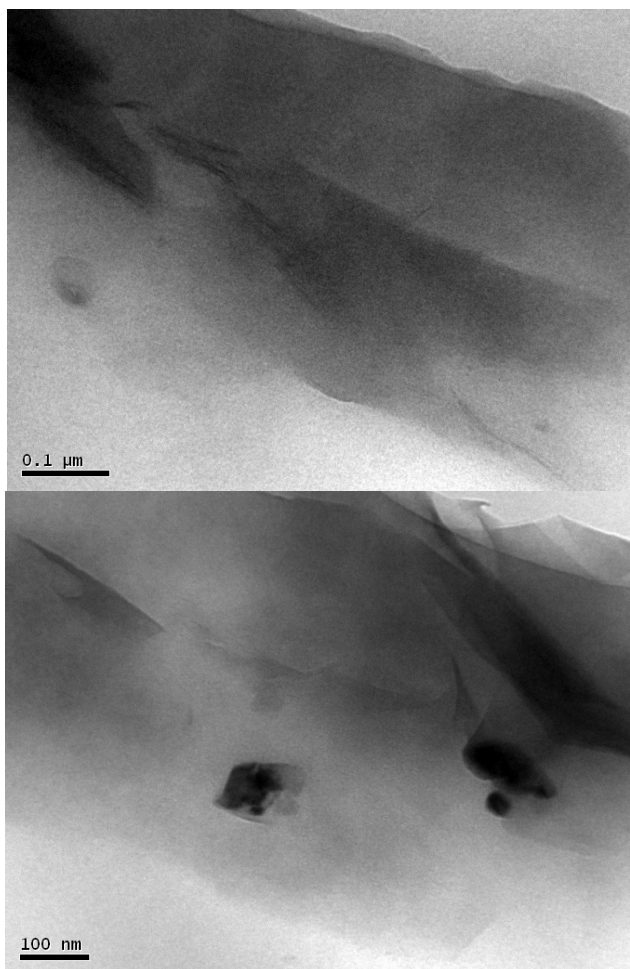International Journal of Materials and Metallurgical Engineering
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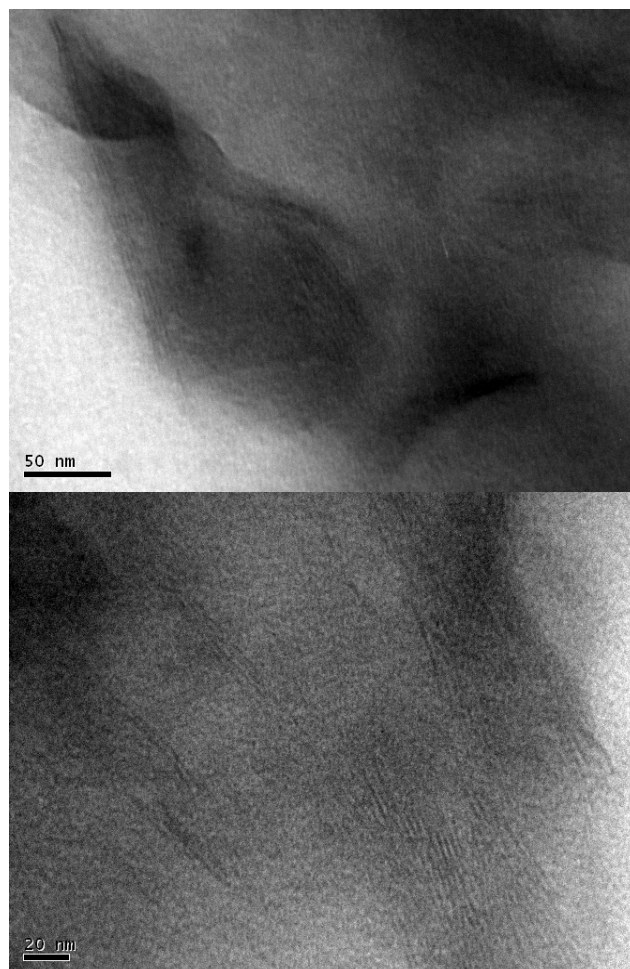Fig. 13TEM images on thin section of sample number 20

Fig. 14 TEM images on thin section of sample number 20

On Figs. 12-14, the bright regions correspond to the PLA polymer matrix and the dark regions of the nanoclay. The clay layers distributed in the polymer matrix can be observed. In some areas, is possible to note agglomerations of clay in polymeric matrix and it is an indicative that exfoliation expected is not present in any case. It is expected it could be achieved and exfoliation by melt mixing via extrusion process.

V. CONCLUSION

The results have allowed determining the behavior of the mixtures according to the incorporation of nanoclays and additives. Thus, the influence of PEG content, Cloisite 30B 20 and 15, has been identified in the PLA polymer matrix on thermal and mechanical properties, as well as the level of dispersion and exfoliation of nanoclays in the PLA matrix. Due to the above and based on the results obtained, it is possible to move forward in achieving the objectives stated and reaching optimal values for future different mixtures of nanocomposites that can be developed.

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