



Kaolinite Review: Intercalation and Production of Polymer Nanocomposites

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Abstract

The production of polymer nanocomposites with natural clays as reinforcement has been thoroughly researched by many researchers. The authors always have been seeking better properties compared to the neat polymer without reinforcement. That is the great appeal of these types of materials. The most commonly used natural clays as reinforcement in polymer nanocomposites are montmorillonite (MMT), halloysite, and kaolinite. Thus, the organic modification of these clays has also been studied to improve the clay interlayer space (intercalation), due to the creation of an affinity with the polymer matrix and reaching better properties than neat polymer. In this context, this review article first discusses an approach regarding the intercalation techniques of kaolinite clay using different intercalate molecules. Then, it discusses polymer nanocomposite processing such as polymers in solution, melts blending, and in situ polymerization using kaolinite as reinforcement.

Keywords: Nanocomposites; Kaolinite; *in situ* polymerization; Melt blending.

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1. Introduction

Polymer nanocomposites with chemically modified layered clays have been arousing scientific and industrial interest because the final properties are better than other materials such as neat polymers, micro-composites, and traditional polymer composites.^[1] Here we can take some examples of properties that may be improved like a gas barrier,^[2] anti-flames, thermals,^[3] and strength^[4] of the polymer nanocomposites. Due to these final properties, these materials have aroused the interest of various industries including the automotive industry, aerospace, food, cosmetics, and others.^[5] The main groups of layered natural clays used as nano-reinforcement in polymers include kaolinite, illite or hydrated micas and montmorillonite, halloysite and vermiculite, and palygorskite.^[6] Kaolinite has a

formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ where it is composed of silicate sheets (Si_2O_5) bonded to the aluminum oxide/hydroxide layers ($\text{Al}_2(\text{OH})_4$), by the arrangement of tetrahedral and octahedral sheets. Then kaolinite which is a layer type 1:1 clay mineral would have one tetrahedral and one octahedral sheet per clay layer.^[6] The distance between the silicate layers is 0.72 nm, which is the basal distance. Among the layered natural clays used in nanocomposites, kaolinite gains prominence because it is one of the most abundant on Earth and it has high crystallinity.^[7] In Brazil, kaolin deposits are found in the States of Rio Grande do Norte, Paraíba, Bahia, São Paulo, and Rio Grande do Sul. However, the deposits in the Amazon River basin are larger than any others already known in the rest of the world.^[7,8] Kaolin deposits appear all over the world including in China, Italy, Japan, Australia, Mexico, the USA, the UK, Spain, Portugal, Angola, Korea, and Thailand.^[9–12]

In the production of polymer nanocomposites using clay as reinforcement, polymer-clay compatibility is essential for the success of its properties. The intercalation of organic components in layered inorganic clays claims a strategy for the compatibilization of organic material with an inorganic.^[13] Thus, in the synthesis of polymer nanocomposites using kaolinite, it is necessary to make a pre-intercalation treatment. This pre-treatment enables compatibility with kaolinite (inorganic) and organic polymer. Nanocomposites can be produced using four techniques: sol-gel,^[14] polymer in

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solution,^[15] *in situ* polymerization,^[16,17] and polymer melt mixture.^[18]

To the best of our knowledge, no published report in the past 10 years evaluates a full review like ours of polymer nanocomposite materials produced by all techniques, melt blending, *in situ* polymerization, and polymer in solution using the kaolinite as reinforcement.^[19–21] Besides, we made comparisons for the morphology of the clay in the polymeric matrix from three different techniques of nanocomposite production. Some properties of nanocomposites such as mechanical, thermal, and gas barriers obtained from these techniques were also evaluated to corroborate the importance of this work for the literature. Finally, this review also discusses the intercalation techniques of kaolinite as well as its variable influences that may help the authors who are seeking some novelties in this area.

2. Intercalation properties of kaolinite

Among the layered natural clay used in nanocomposites, kaolinite gains prominence because it is one of the most abundant on Earth and has a high crystallinity and intercalation capacity.^[22] In the production of polymer nanocomposites using clay as reinforcement, polymer-clay compatibility is indispensable for the success of its properties. The intercalation of organic components in layered inorganic clays is a strategy to ensure the compatibilization of the clay with the polymer because it turns the clay organophilic.^[13,23] Thus, the synthesis of polymer nanocomposites using kaolinite as reinforcement is a necessary treatment to intercalate the organic molecules in the kaolinite. There are nowadays two methods for the intercalation of kaolinite: displacement and mechanochemical methods.

A parameter to quantify the intercalation of the molecules in kaolinite is the rate of intercalation or reaction rate (% IR). This rate shows if the intercalation procedure succeeded, that is, how much of the sample was intercalated. The expression $\% \text{ IR} = (I_{i(001)}/I_{i(001)} + I_{k(001)})$ for the calculation of (% IR), where $I_{i(001)}$ is the peak intensity observed for intercalate and $I_{k(001)}$ is the peak intensity observed for kaolinite.^[7,24]

2.1 Mechanochemical method

Another method of intercalation of kaolinite approached in the literature is mechanochemical. In this method, a ball mill is used and kaolinite is added together with the intercalating agent under agitation. The intercalation occurs due to the mechanical contact between the clay, intercalating agent, and the spheres. This method was previously used to intercalate kaolinite with potassium acetate.^[15,25] The authors mixed 300g of kaolinite in 7.2 M potassium acetate solution in a mill of balls to the ambient temperature and agitated for 10–80 h. This method led to the total exfoliation of the kaolinite layers.^[14,25] The kaolinite was intercalated, with low and high crystalline defects, by urea in an aqueous solution. The kaolinite, blended in an aqueous solution of urea, was added to a ball mill and subjected to 1 h of milling.^[26] After this time, a% IR of almost

100% and an increase of basal spacing of 0.72 nm to 1.07 nm were obtained. The mechanochemical method used 100 g of kaolinite and 200 mL of dimethylsulfoxide (DMSO) with different milling times.^[27] It has been observed that only 2 h of milling was sufficient to obtain a% IR of 90%. The mechanic contact of the kaolinite particulates resulted in a reduction of the area of the particulates and the breaking of the hydrogen links, increasing the intercalation.^[26,27] In a recent study, an eco-friendly mechanochemical intercalation of kaolinite was reported by Albach *et al.*^[28] The authors developed a method without using solvents. For this, they use a molecule of imidazole in kaolinite to increase the intercalation because the molecules of imidazole are stabilized by H-bonds within the kaolinite interlayers. The intercalation was confirmed by FTIR and DFT using a cluster model of $\text{Al}_{10}\text{O}_{38}\text{H}_{46}$ and $\text{Si}_{10}\text{O}_{30}\text{H}_{20}$ to represent both surfaces of the mineral.

2.2 Displacement method

Kaolinite can be intercalated by molecules between its layers by the displacement method.^[17,29] This method consists of adding kaolinite in a solution containing the intercalating agent under a determined temperature, designated as the temperature of reaction (T_R), and for a certain time, designated as the time of reaction (t_R), under constant agitation. Using this method, the interlayer spacing is increased and the organic molecules can also form links with the surface of the clay turning it organophilic.^[9] Table 1 shows the previous studies up to 2020 that used this method to intercalate various molecules between the kaolinite layers. Among them are detached dimethylsulfoxide (DMSO), N-dimethylformamide (DMF), and other molecules.

2.3 Influence of the variables (t_R) and temperature (T_R) of reaction in the dislocation method

The displacement method is the most used method for the intercalation of kaolinite. Table 1 shows different studies about the intercalation of kaolinite from different countries using the displacement method. The table shows the intercalation molecules, T_R , t_R , intercalation rate (% IR), and interlayered spacing (Δd) attained by the authors. Figs. 1–3 show graphics plotted with data taken from the studies presented in Table 1, which used molecules of DMSO and potassium acetate. In Fig. 1 we can observe that the increase in the reaction temperature does not influence the interlayer spacing of potassium acetate. For DMSO we observe that the interlayer spacing is reduced when the T_R is increased. This reduction can be caused by the exit of the DMSO molecule that is found between the layers as the reaction temperature increases.^[30] At a T_R of 200 °C the DMSO in the kaolinite is already intercalated with methanol. It is also shown that there was a reaction between the DMSO and the methanol resulting in the liberation of water as a sub-product, which sent off the molecules of DMSO and increased the distance between the kaolinite layers to 0.10 nm.^[31] A similar intercalation reaction carried out in low temperatures showed that there was not a DMSO-like reaction, resulting in

Table 1. Origin, molecule, temperature, time of reaction, and spacing in the interlayer of kaolinite.

References	Origin	Molecule	IR (%)	T _R (°C)	t _R (h)	Δd (nm)
[30]	Australia	DMSO	75.00	20	220	0.44
			85.00	20	340	0.44
[32]	England	DMSO	*	25	72	0.46
[33]	USA	DMSO	81.80	60	48	0.44
[34]	USA	DMSO	*	60	5	0.36
[35]	England	DMSO	98.00	98	13	0.40
[36]	USA	DMSO	*	25	1440	0.40
[31]	USA	DMSO	89.00	200	89	0.10
			89.00	270	89	0.10
[37]	Brazil	DMSO	84.00	60	240	0.40
[38]	Brazil	DMSO	100.00	60	240	0.40
[39]	Brazil	DMSO	86.21	60	240	0.40
[40]	Spain	DMSO	98.48	60	72	0.30
[41]	Hungary	(<i>d</i> -DMSO)	98.00	85	168	0.40
[42]	Japan	DMSO and DMSO- <i>d</i> ₆	62.96	25	60	0.40
[43]	Germany	DMSO	*	65	24	0.40
[44]	Spain	DMSO	*	50	72	0.40
[45]	USA	DMSO	90.90	180	2	0.38
[46]	USA	DMSO	87.72	25	1440	0.40
[47]	Brazil	DMSO	92.10	60	240	0.40
[48]	China	DMSO	87.95	90	48	0.39
[49]	Hungary	Potassium acetate	96.00	25	80	0.68
[50]	China	Potassium acetate	82.14	25	2	0.70
			95.24	40	8	0.69
			95.24	60	24	0.69
[51]	China	Potassium acetate	91.74	20	24	0.69
			90.91	80	24	0.68
			89.29	90	24	0.69
[52]	USA	NMF	*	25	5	0.36
[53]	USA	NMF	*	25	5	0.36
[54]	China	NMF	100.00	25	72	0.36
[55]	Hungary	Formamide	99.00	25	80	0.30
[56]	USA	Hydrazine	88.90	25	2	0.31
[57]	USA	Hydrazine	84.00	65	168	0.32
[58]	Hungary	Hydrazine	98.00	85	168	0.31
[59]	Czech Republic	Urea	98.00	95	48	0.36
[60]	China	Urea	99.00	100	40	0.36
[61]	Brazil	MPDET	100.00	18	20	1.41
[62]	Hungary	Urea	*	40	24	0.35
	Hungary	DMSO	*	40	24	0.40
	Hungary	Formamide	*	40	24	0.29
	Hungary	NMF	*	40	24	0.36
[63]	Cameroon	DMSO	*	70	1	0.41
[64]	Brazil	Potassium acetate	61.28	25	2	0.68
[65]	Brazil	MeOH	*	25	168	0.36

Continued						
[66]	China	BLAC	*	60	12	0.67
[67]	China	p-aminobenzamide (PABA)	78.40	180	12	0.73

(*) There are no curves of X-ray patterns.

% IR: intercalation reaction index.

T_R: Temperature of reaction, t_R: time of reaction.

$\Delta d = d_{001} - 0.72$, where Δd : interlayer expansions (nm), 0.72 (nm): basal distance of neat kaolinite, d₀₀₁: basal distance of the substituted phase.^[37]

the basal spacing of 0.40 nm.^[37] It is possible to observe in Fig. 2 that the reaction time does not influence the interlayer spacing. This behavior can be caused by the homogeneous size of the molecules that intercalated the clay. The temperature interval indicates that the temperature does not influence the graphic analysis.

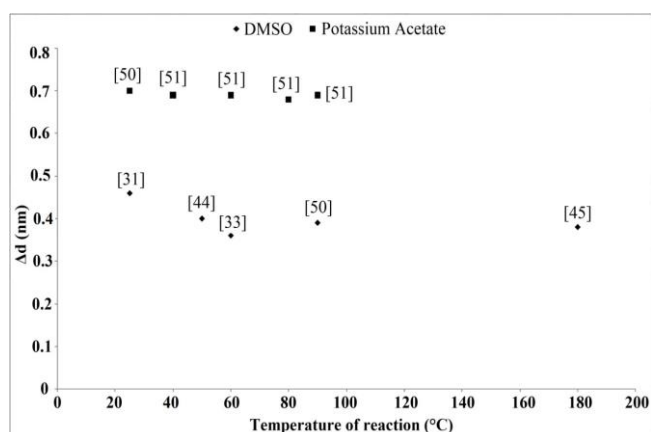


Fig. 1 Influence of the reaction temperature in the interlayer expansion.

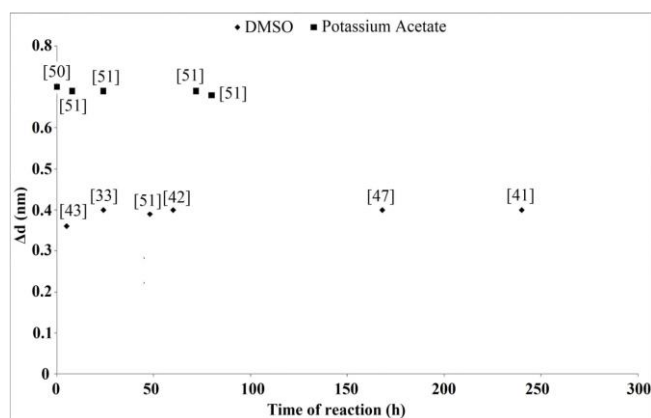


Fig. 2 Influence of the time of reaction in the interlamellar spacing. The data were taken from the work that used temperatures between 65-90 °C.

Figure 3 shows the influence of the t_R on the intercalation rate. Similar to the authors that worked with DMSO or potassium acetate, we observed that there was an increase of the RI following the increase in the t_R for temperatures between 20-25 °C. The chosen temperature interval indicates that the temperature does not influence the analysis of the graphic.

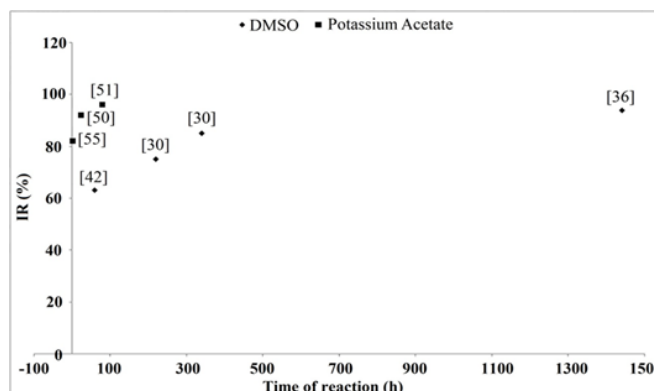


Fig. 3 Rate of intercalation (%RI) alive the time of reaction in temperatures between 20-25°C to the molecules of DMSO and potassium acetate.

Table 2 shows the previous studies pertaining to the co-intercalation of kaolinite, that is, there was a second intercalation of the organic molecules in the kaolinite already intercalated by molecules of DMSO, NMF, and others. Table 3 shows the average, maximum, and minimum temperatures (T_R) and reaction times (t_R) obtained from Tables 1 and 2. Additionally, Table 3 shows that the average reaction temperature (T_{Raverage}) for the co-intercalation of molecules was greater than the average temperature of the intercalation. The T_R increase to that of the co-intercalation facilitates the diffusion of the co-intercalant molecules to the kaolinite interlayer space.^[9] The temperature leads the co-intercalant agent to react with the intercalation agent, in general, DMSO and NMF, or react with the hydroxyl between the layers and on the surface of the kaolinite. It is also observed that the average reaction time (t_{average}) was reduced in comparison to the co-intercalation molecules.^[9] This reduction of the t_{Raverage} may have the purpose of reducing the exposition time of the molecules to high temperatures to reduce the degradation of the co-intercalant molecules.

3. Clay morphology in the polymeric matrix

The literature commonly refers to three types of morphology: immiscible or conventional micro composite, intercalated, and miscible or exfoliated.^[3,68] Fig. 4 shows the three morphologies found in polymer-kaolinite layer nanocomposites. In the first (immiscible kaolinite), the polymer is not found between its layered silicate. In this case, two distinct phases are observed, kaolinite and polymer, which characterize a traditional

Table 2. Molecule, temperature, and reaction time of kaolinite co-intercalation.

Reference	Origin	Molecule	T _R (°C)	t _R (h)	Δd (nm)
[34]	USA	DMSO-EG	191	12	0.25
				48	
	USA	DMSO-EGMM	124	12	0.34
				48	
	USA	DMSO-DEGMB	131	12	0.40
	USA	DMSO-1,2-PD	181	12	0.37
USA	DMSO-1,3-PD	214	12	0.26	
USA	NMF-EG	191	12	0.23	
[36]	USA	DMSO-EG	25	16	0.22
	USA	DMSO-EG-10% W	25	16	0.36
[31]	USA	DMSO-OH	200	89	0.10
			270		
	USA	DMSO-OH	190	35	0.14
USA	DMSO-OH	230	20	0.13	
		190			
[38]	Brazil	DMSO-BZ	140	4	0.71
[54]	China	NMP	25	72	1.22
[69]	Georgia	MOH-NMF-pNA	25	72	0.77
		NBZ			0.73
[70]	Georgia	NMF-1,2 PD	25	24	0.36
		NMF-1,3-PD			0.39
[71]	Georgia	DMSO-D-sorbitol	125	216	0.47
			110	144	0.35
			DMSO-adonitol	104	156
[72]	Poland	DMSO-1,3BD	110	144	0.31
			24	24	0.30
[73]	Brazil	PP-hyd	95±5	480	0.79
[74]	EUA	APTES	195	48	0.92
[75]	China	MeOH-sodium stearate	80	72	0.38

Table 3. Average, maximum, and minimum temperatures, reaction times, and spacing in the interlayer for intercalation and co-intercalation were obtained from Tables 1 and 2.

Average, maximum, and minimum temperatures	Intercalation (Table 1)	Co-Intercalation (Table 2)
T _R average (°C)	62.29 ± 51	133.16 ± 77.05
Maximum	270	270
Minimum	18	24
t _R average (h)	163.74 ± 317.59	63.56 ± 90.98
Maximum	1440	480
Minimum	1	2
Δd _{average} (nm)	0.45 ± 0.20	0.43 ± 0.25
Maximum	1.41	1.22
Minimum	0.10	0.10

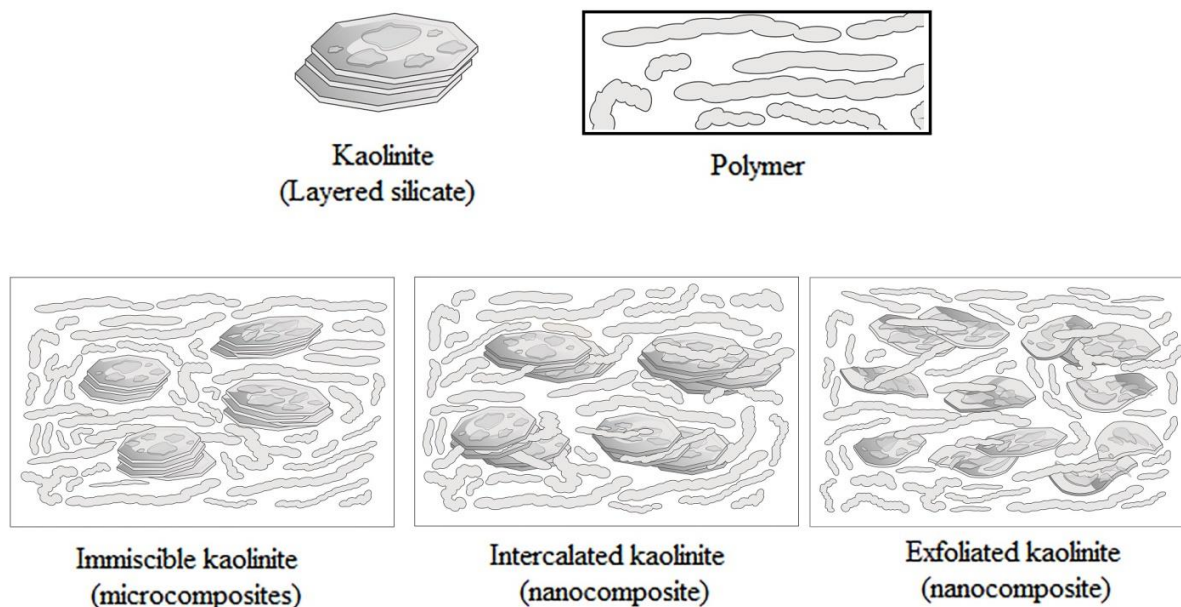


Fig. 4 The three principal types of interaction morphology lamellar polymer-clay. Based on the literature [76,77].

micro composite.^[78,79] The second (intercalated kaolinite) only happens when one polymeric chain spreads out the distance between the layers. A well-ordered structure can be observed in the region of a low angle by X-ray diffraction.^[76] This is what indicates the existence of a spacing d between the layers.^[77]

And in the third morphology (exfoliated kaolinite) the silicate molecules are uniformly dispersed into the polymeric matrix in average distances between the layers.^[78] In this case, peaks in the X-Ray diffractometer (XRD) that indicate interlayered spacing are not observed.^[77] The dispersion of the clays, together with the polymer-clay adherence has a fundamental influence on its properties, for example, improving its mechanical properties, thermals, rheological,^[80] morphology control,^[81] barrier by gases, and flammability which does not happen when there is little clay in the polymeric matrix (thermoplastic and/or thermoset).^[3,68,82] In this case, the behavior of these materials is compared to the traditional composites with inferior properties compared to the nanocomposites.^[78,79]

4. Synthesis of nanocomposites by means of *in situ* polymerization

Although various works have already had success in the production of polymer-clay nanocomposites, a great difficulty that remains is the intercalation of polymeric molecules between the layers of the layered clays.^[83] The *in situ* polymerization consists of the intercalation of the liquid monomer between the silicate layers leading to the polymerization of the monomer and the growing of the polymeric chains between the layered clay, resulting in a polymer nanocomposite. An advantage of this method is found on the surfaces of the layers, which stay well-disposed between the polymeric molecules as an effect of "binding" the

layers. Research about the production of nanocomposites *in situ*, using the kaolinite as reinforcement, will be summarized in this work.

The *in situ* polymerization in solution has been used for the production of poly(acrylamide)-kaolinite(PAAm) nanocomposite.^[84] Initially, the kaolinite was pre-intercalated by molecules of N-methylformamide (NMF), and subsequently, it was intercalated with the monomer for one hour at 300 °C. After the polymerization, X-ray analysis showed that the interlayered distance increased from 0.72 nm (neat kaolinite) to 1.13 nm after the polymerization. Meanwhile, it was observed that there was no exfoliation of the kaolinite in the polymeric matrix. After the polymerization, thermal treatment of the polyacrylonitrile-kaolinite nanocomposite was also conducted at two temperatures (460 and 620 °C) using a heating tax of 4 °C/min. At 460 °C, an interlayered spacing of 1.27 nm was obtained, and at 620 °C a spacing of 1.5 nm. This increase in the interlayered spacing of 0.55nm and 0.78 nm for the temperatures of 460 °C and 620 °C, respectively, was due to the desidroxilation between the kaolinite layers. The authors did not achieve the exfoliation of the kaolinite layers in the polymeric matrix, despite the thermal treatment. The intercalation of the degraded polymer between the layers of another phase of the kaolinite called metakaolinite was obtained at 620 °C. This result, despite the hard work, does not have a technologic importance as a polymer nanocomposite with the polymer was in the degraded form. The author could have predicted the result, as the transformation of kaolinite into metakaolinite happens between 700-900 °C.

Polycondensation was used to produce poly(β -aniline)-kaolinite nanocomposite through polymerization.^[85] Initially, kaolinite was pre-treated with N-methylformamide (NMF) in an aqueous solution. Afterwards it was changed to a solution

of ammonia acetate. The solution was centrifuged, and the kaolinite was intercalated with the ammonia acetate. Afterwards, β -anil one was intercalated in the kaolinite through an aqueous solution. This product was heated to 205 °C in a nitrogen atmosphere so that polymerization could take place. X-ray diffraction showed an increase in the interlayer spacing from 0.72 nm, referring to the pure kaolinite, to 1.11 nm, after the polymerization. The curves of thermal differential analysis (TDA) showed that the nanocomposite exhibited better thermal stability than the neat polymer. Despite the intercalation pre-treatments with molecules of NMF and ammonia acetate, the nanocomposite was not exfoliated.

The oxidative properties of kaolinite were utilized to polymerize the aniline monomer instead of using ammonium persulfate and other oxidant agents.^[86] The intercalation and the polymerization of the aniline in the clay were conducted in ambient acid, where the mineral clay was treated with a 0.50 M solution of aniline and 1M sulfuric acids for 5 days under agitation. The catalytic capacity of the mineral clay was due to the level of iron, together with other catalytic properties. X-ray diffraction (XRD) was used to observe the spacing that the authors reported between 8.95 Å and 13.6 Å. Despite the increase in the interlayer, exfoliation of the clay in the polymeric matrix was not established. The authors also did not run mechanical tests or the barrier by gases to evaluate the performance of the material.

A polymer nanocomposite of poly(styrene-alt-maleic anhydride) /kaolinite (PSMA/kaol) was prepared through radical polymerization.^[87] A dimethylsulfoxide (DMSO) pre-treatment was also utilized, and then the polymerization was carried out in a solution of dimethylformamide DMF, which was used as a solvent. The initiator benzoyl peroxide (BPO) was dissolved in a solution of anidride-maleic/Kao-DMSO/DMF under agitation. Via DRX analysis, no peak was observed in the diffractogram which corresponded to PSMA/Kao (3 wt. %), suggesting that complete exfoliation had occurred. This result was confirmed by transmission electron microscopy. With respect to the PSM/kaol (7 wt. %) nanocomposite, TGA analysis showed greater thermal stability in relationship to the 1 %, 3 %, and 5 wt. %-Kao.

The polystyrene/kaolinite(PS/kaol) nanocomposite was produced by free radical polymerization.^[88] For this, it was first necessary to pre-intercalate the kaolinite with dimethyl sulfoxide (DMSO), generating the DMSO/Kao composite. The polymerization was produced through free radicals using benzoyl peroxide (BPO) as an initiator. X-ray analysis showed a peak of 7.1 Å for the neat kaolinite, and 11.2 Å for the kaolinite intercalated with the polystyrene (PS/Kao). The thermogravimetry analysis (TGA) for the PS/Kao nanocomposite showed a mass loss of almost 12 % between 505.8 °C and 370 °C, which corresponds to the interlayered organic fraction and the desidroxilation of kaolinite. The remainder of the mass formed the metakaolinite. DTA analysis of the kaolinite-polystyrene nanocomposite does not show

endothermic peaks, indicating the absence of crystalline substances in the nanocomposite. Despite being intercalated, kaolinite did not exfoliate in the polymeric matrix.

The polymer nanocomposite was produced through the technique of copolymerization by inverse suspension using kaolinite (kao) and the initiator potassium persulfate (KPS). The authors used the monomers acrylic acid (AA) and sodium acrylate (AA_{Na}), together with the kaolinite in quantities of wt% (0 g), 5 wt. % (0.321 g), 10 wt. % (0.642 g), 15 wt. % (0.963 g), and 20 wt. % (1.248g). Dimethylsulfoxide (DMSO) was used for the intercalation of kaolinite to obtain the DMSO/Kao product. Afterwards, the intercalation of the DMSO/Kao was conducted with the potassium acetate (AcK), to obtain the product DMSO-AcK-kaol. X-ray analysis showed an increase in the interlayered distance from 0.72 nm (neat kaolinite) to 1.43 nm (intercalated kaolinite). An exfoliation to nanocomposite was observed which was formed by copolymer poly (AA-AA_{Na}) intercalated to the DMSO-KAc-kaol product. In this case, kaolinite (20 wt. %, 1.248 g) was utilized. The other nanocomposite using the copolymer plus kaolinite in quantities of wt% (0 g), 5 wt.% (0.321 g), 10 wt.% (0.642 g), and 15 wt.% (0.963 g), did not exhibit exfoliation. The authors presented only the characterizations by XRD, TEM, and FTIR. No additional tests for characterization of the product, such as mechanical tests for traction and impact, and also anti-flames and gases barrier were shown.^[24]

A poly(metacrilamide)-kaolinite nanocomposite was produced by polymerization solution.^[89] For this, dimethyl sulfoxide (DMSO) and N-methylformamide (NMF) were used as pre-intercalators. The kaolinite and NMF (NMF/Kao) solution was kept for 1 month so that the maximum intercalation (10.5 Å) could take place. Then, the intercalation with the monomer metacrilamide (MAC) was conducted to produce NMF-Kao-MAC. In this work, thermal treatment was utilized to polymerize the metacrilamide between the kaolinite layers without the presence of a catalyst. For the thermal treatment, the sample was heated at 4 °C.min⁻¹ in a programmable oven and kept for 2 h at 150 °C and 3 h at 100 °C. The results showed a rapid expansion of the basal spacing to 12.5 Å (150 °C) and 12.9 Å (100 °C) due to the polymetacrilamide/kaolinite (Kao-PMAC) product. However, no exfoliation was observed. TGA analysis for the Kao-MAC (1 wt. %) sample showed a loss of mass corresponding to the organic molecules between the layer sat 491.7 °C. Yet, the Kao-PMAC nanocomposite had a 2.5 % loss in weight concerning the degradation of the polymeric chains at 503.1 °C. This demonstrates the greater thermal stability of the Kao-PMAC nanocomposite, in comparison to the Kao-MAC sample, which is an indication that the polymerization of metacrilamide was achieved in the interlayer spacing by thermal treatment.

Nanocomposites composed of poly(methyl methacrylate)/kaolinite (PMMA)/kao by polymerization in emulsion using the redox initiator potassium persulfate (K₂S₂O₈) have been produced. The kaolinite was pre-

intercalated with dimethylsulfoxide (DMSO) and methanol resulting in the kaolinite/DMSO/methanol product.^[90] After the polymerization with MMA, the exfoliation of the kaolinite in the polymeric matrix was observed. The exfoliation was confirmed by transmission electronic microscopy (TEM). The layers of the kaolinite were found uniformly dispersed in the PMMA matrix. The thermal stability was analyzed by thermogravimetry. For the PMMA/kaolinite nanocomposite, the degradation temperature was kept around 200-210 °C. The degradation temperature of the pure PMMA was 11-28 °C more than the PMMA/kaolinite nanocomposite. This increase is due to the kaolinite layers, which were exfoliated in the polymeric matrix, together with the adhesion between the polymer and the layers, which have a great superficial area. The DSC analysis showed that the glass transition temperature (T_g) of the nanocomposite reduced by around 16-23 °C compared to the neat PMMA polymer, which has a T_g value near 100 °C. This decrease was attributed to the distribution of the silicate layers in the polymeric matrix. The presence of the layers in the matrix hinders the movement of the PMMA macromolecules.

A polymer nanocomposite of poly(vinyl alcohol)/kaolinite (PVA-Kao) was produced through free radical polymerization using benzoyl peroxide (BPO) as an initiator.^[91] The kaolinite was pre-treated with dimethyl sulfoxide (DMSO-Kao) and hydrolyzed with NaOH resulting in the PVA/Kao nanocomposite. The PVA-Kao nanocomposite (5 wt. %) was characterized by XRD, and no peaks were found corresponding to the intercalated kaolinite in the matrix, suggesting that there was exfoliation, which was confirmed by transmission electronic microscopy (TEM) images. Analysis of the nanocomposite by TGA showed that the greater quantity of kaolinite improved thermal stability. Thus, the thermal stability of the kaolinite must be related to the PVA. The glass transition temperature (T_g) and the melting temperature (T_m) were analyzed by DSC. The results showed that by increasing the quantity of kaolinite, the T_g values may also increase. This indicates that as the kaolinite content increases, the polymer molecules lose a little bit of their movement. The exfoliation of the kaolinite in the polymeric matrix caused a greater interaction with the silicate layers and the PVA polymer. An influence of the kaolinite was observed at the melting temperature (T_m), which indicates that the crystals were prevented from being formed due to the silicate layers. This result demonstrates that there was an influence of the nano-reinforcement in the properties of the nanocomposite.

A polymethacrylate nanocomposite composed of methyl/kaolinite (PMMA/kao) was produced by a technique known as solution polymerization.^[92] Benzoyl peroxide was utilized as an initiator. A pre-intercalation treatment was conducted with DMSO/Kao and the reaction was performed at room temperature under agitation. For the production of the nanocomposite quantities of 5 wt. % kaolinite was used in relation to the monomer. X-ray analysis showed that for the PMMA/Kao nanocomposite there was no peak in relation to

the pure kaolinite peak (0.72 nm), and electron microscopy confirmed the exfoliation of the kaolinite in the polymeric matrix. Thermogravimetry analysis also confirmed that the PMMA/Kao nanocomposite was more stable than the PMMA. This indicates that the nanocomposite has thermal stability due to the intercalation of the PMMA in the kaolinite layers. DSC analysis showed that the T_g of the PMMA/Kao nanocomposite is greater compared to that of neat PMMA, which was also attributed to the intercalation of the molecules between the kaolinite layers, which have greater thermal stability. Mechanical tests were also carried out in this study. The mechanical properties such as the Young modulus and the yield strength of the PMMA/Kao were greater than pure PMMA, due to the interaction between the layers of the kaolinite and the PMMA.

The nanocomposite was synthesized through polymerization in an emulsion.^[93] The kaolinite was used as pre-intercalated with urea (Kao-U). In this work, the authors used potassium persulfate as a redox initiator. The cost of polymerization was measured with this initiator and compared with the cost of polymerization of the non-modified (K) kaolinite nanocomposite as well as that modified with urea (K-U). The kaolinite modified with urea exhibited a small increase in the polymerization tax in comparison to the redox initiator. This increase was due to the intercalated urea between the kaolinite layers.

A polyacrylonitrile/kaolinite (PAN/kao) nanocomposite was produced from polymerization in the emulsion.^[94] The kaolinite was pre-intercalated with DMSO, methanol (MeOH), and potassium acetate (Ack) in an ambient aqueous solution. For this polymerization, potassium persulfate (KPS) was used as an initiator, and sodium laurel benzene sulfate (DBS) was used as a surfactant. DMSO-MeOH-AcK-Kao (5, 10, 15wt. %)/PAN was intercalated for 24, 48, and 72 h. The nanocomposite containing the kaolinite which had been intercalated for 72 h exfoliated the polymeric matrix, while no exfoliation was found when the intercalation occurred for 24 and 48 h. This was confirmed with transmission electronic microscopy (TEM) using kaolinite (20 wt. %) which had been intercalated for 72 h. With respect to the thermal properties, the 10 wt. % nanocomposite exhibited greater thermal stability in relation to the 5 and 10 wt. % of kaolinite. This occurred due to the layered nanoparticles which prevent the movement of the polymer molecules. Thus, the nanocomposite was obtained with efficiency. Other tests like anti-flame and traction were not carried out by the authors. [Table 4](#) summarizes the references up to 2020 presented in this work for obtaining *in situ* polymer-clay nanocomposites.

Among the various techniques shown in [Table 4](#), all of them show an increase in the kaolinite interlayers after the polymerization. It may also be noted that in the majority of the works, there was exfoliation of the clay layer in the polymeric matrix. The intercalation molecules are also shown and they contributed to the increase of the interlayer spacing.

Table 4. Production techniques of the in situ of the nanocomposite, polymeric matrix, intercalant molecules, and the achieved spacing and realized characterizations.

References	<i>In situ</i> Polymerization	Polymer	Intercalation Molecule	Δd (nm)	Characterizations
[84]	Suspension	PAAm	NMF	0.41	NMR, XDR, (C, H, N), IR
[85]	Polycondensation	P β A	NMF	0.39	XDR, IR, NMR, TG-TDA
[86]	Solution	PANI	Did not used	0.65 e 0.19	XDR, FTIR
[87]	Solution	PSMA	DMSO	exfoliated	XDR, TEM, FTIR, TGA
[88]	Solution	PS	DMSO	0.40	XDR, NMR, FTIR, TGA
[89]	Solution	PMMA	DMSO	0.54 e 0.76	XDR, FTIR, NMR
[90]	Emulsion	PMMA	DMSO	exfoliated	XDR, FTIR, DSC, TGA, TEM
[91]	Solution	PVA	DMSO	exfoliated	XDR, FTIR, DSC, TGA, TEM
[92]	Solution	PMMA	DMSO	exfoliated	XDR, FTIR, SEM, TGA- DTA, UV
[93]	Emulsion	PMMA	Urea	exfoliated	XDR, TGA, DSC,
[94]	Emulsion	PAN	DMSO	exfoliated	XDR, FTIR, TGA, DSC, TEM
[95]	Suspension	P(2,3 DMA)	DMSO	0.41	XRD, FTIR, SEM, TGA, DTA
	Suspension	P(2,3 DMA)	CH ₃ OH	0.56	XRD, FTIR, SEM, TGA, DTA
[96]	Polycondensation	Resorcinol/ formaldehyde	Did not used	Did not exfoliate	XRD, FTIR, SEM, SAXS, TGA

Despite the variety of works in this area, some exfoliation is not observed. Table 4 shows that the majority of the polymeric matrixes are PS or PMMA. It is noted that the great majority of the studies present only thermal analysis, leaving the mechanical and optical analysis to the background. This shows that there is still plenty to be explored in this area.

5. Production of polymer nanocomposites by melt blending technique

This technique does not require that the clay is immersed in the solvent. The layered clay is intercalated by a polymer in a molten state. The thermoplastic polymer can be mechanically blended by conventional methods such as extrusion and injection, and also by non-conventional methods such as polymer fusion in powder, polymer fusion in solution, and other methods that are not reported in this review.^[83] The technique of melt blending is an industrially viable method and already has industrial applications. It is widely used in polyolefins, which are the majority of the polymers used in engineering.^[97]

In this section, several techniques were discussed for the production of polymer nanocomposites by melt blending using kaolinite as reinforcement. Nanocomposite using polyethyleneglycol (PEG-1000 and PEG-3400) and modified

kaolinite (PEG-1000-Kao) and (PEG-3400-Kao) was produced.^[98] Kaolinite was intercalated with dimethylsulfoxide (DMSO) resulting in kao-DMSO, and intercalated with N-methylformamide (NMF), resulting in kao-NMF. For this, PEG-1000 and PEG-3400 around 50 mL were heated in a bath. Initially, two steps were carried out: one with PEG-1000 + Kao-DMSO and another with PEG-1000 + Kao-NMF. The first (PEG-1000 + Kao-DMSO) was carried out in a bath with a temperature of 155 °C for 216 h (9 days). The product was centrifuged with methanol and the product was dried at 100 °C for 3 days. The product was analyzed by X-ray and the authors observed a spacing of 11.12 Å against 7.8 Å of neat kaolinite. For the second (PEG-1000 + Kao-NMF), using the same conditions as the first fusion, the NMF was not stable at a temperature of 155 °C. Then another procedure was made, slowly heating the PEG-1000 together with Kao-NMF from room temperature to 70 °C. This mixture remained at this temperature for 3 days, where upon it was increased to 160 °C, becoming stable at this temperature for 4 days. X-ray analysis showed a basal spacing of 11.01 Å compared to 7.8 Å for neat kaolinite. Three fusions were also prepared with the Kao-PEG-1000 at temperatures of 200 and 100 °C and solutions in a water base and 1,4 dioxane. X-ray showed that the distance was 7.16 Å for all three samples. For

the fusion of the 3 samples of PEG-3400, the same conditions as those for PEG-1000 were used, however at temperatures of 155, 190, and 200 °C, using only DMSO as an intercalation agent. X-ray analysis showed a basal spacing of 11.16, 11.19, and 7.2 Å at fusion temperatures of 155, 190, and 200 °C respectively. The spacing increase between the layers happened due to the intercalation of the PEG molecules. In this work, there was no exfoliation of the kaolinite in the polymer.

Polyethylene oxide (PEO) and polyhydroxybutyrate (PHB) were used together to pre-intercalate kaolinite with dimethyl sulfoxide, resulting in the powder form of the Kao-DMSO product. Then, kaolinite was blended with the PEO polymer, also in powder form. The mixture was homogenized in a vibrator chamber for 30 min. Afterward, the mixture was transferred to a beaker that was heated until its fusion (130 °C for 4 days in an open atmosphere). For the PHB and Kao-DMSO, the same procedure was conducted as the one used for the POE and Kao-DMSO. In this case, a fusion temperature of 140 °C was used for 5 days in an open atmosphere. X-ray analysis showed that the interlayer distance obtained for the nanocomposite (PEO-Kao-DMSO) was 1.116 nm, and for the PHB-Kao-DMSO was 1.170 nm, compared to pure kaolinite (1.170 nm), which was confirmed by the morphology of the kaolinite after the intercalation of the polymers. Thus, no exfoliation was found.

A polymer nanocomposite was obtained using the fusion technique, resulting in Nylon 6 and kaolinite.^[99] The kaolinite was pre-intercalated with 6-aminohexanoic (AHA) acid. Initially, they blended the modified kaolinite with the Nylon 6, using a heated double screw extruder, obtaining the Nylon 6-kaolinite product. Afterwards, it was also blended by extrusion to pure Nylon 6 and the Nylon6-kaolinite mixture. An izod impact test was carried out and the results were similar for the nylon with and without reinforcement. So, it has been concluded that the reinforcement of Nylon 6 with the modified kaolinite did not have significant improvements. Through the fusion, technique nanocomposite was obtained using an extruder for 10 min at 210 °C with a thread rotation of 100 rpm.^[100] The polyethylene vinyl alcohol (EVOH) polymer was used with pre-intercalated kaolinite with DMSO and methanol. X-ray analysis showed that there was exfoliation of the kaolinite in the polymeric matrix.

Polymer nanocomposite was produced using poly(m-xylene adipamide)-kaolinite and poly(m-xylene adipamide)-montmorillonite.^[101] A double screw extruder was used at 262 °C at 134 rpm. Transmission electron microscopy (TEM) showed that there was exfoliation of the kaolinite in the polymeric matrix, however, the montmorillonite exfoliated much more easily. DSC analysis showed that the poly(m-xylene adipamide)/kaolinite nanocomposite showed a slight increase at the T_g compared to the pure polymer. The crystallinity of the poly(m-xylene adipamide)/kaolinite nanocomposite was greater than the poly(m-xylene adipamide)-montmorillonite nanocomposite.

A polymer nanocomposite formed by nano-sized hydroxyl

aluminum oxalate (nano-HAO), nano-kaolin, and a polymeric blend composed of low-density polyethylene (LDPE) and a rubber composed of ethylene-propylene-diene (EPDM) was produced.^[102] The nano-HAO was produced by the thermal decomposition of the kaolinite at 320 °C, resulting in a solid aluminum hydroxide of 200-300 nm in diameter and 80-90 nm in thickness. Yet, the nano-kaolin was also produced by the thermal decomposition of the kaolinite at 209 °C, resulting in a particle thickness of 20-50 nm and diameter of 80-90. The nanocomposites were obtained from a double-screw extruder, and afterward, test bodies were manufactured using a mono-screw extruder. Anti-flame tests were carried out with flames with a limited oxygen index (LOI) and flame retardant UL94, and the heat release rate (HRR), total heat release (THR), and effective heat release combustion (EHC) were determined as a function of time. The LOI test showed that the nanocomposite which utilized a combination (1:5) of the nano-kaolin and nano-HAO gave a superior result compared to the nanocomposite which utilized two reinforcements in isolation. This result is due to the synergistic effect between the nano-kaolin and nano-HAO, which contributed to preventing the development of gases involved in combustion.

The polyhydroxybutyrate polymer (PHB) is thermally unstable becoming difficult to process. Nanocomposite using polyhydroxybutyrate (PHB) and chemically modified kaolinite was produced to improve its thermal stability.^[103] An internal blender was utilized at 182 °C for 60 min at a rotation of 60 rpm. Afterward, the PHB-1% kaolinite/neat PHB and PHB-4% kaolinite/neat PHB were blended. The same quantity of PHB/kaolinite was processed in the presence of a compatibilizer agent poly (ϵ -caprolactones) PCL. Electron microscopy analysis showed the PHB-kaolinite/pure PHB/PCL polymers. It was noted that the kaolinite particulates were much more dispersed in the blend when using the compatibilized than without the compatibilized. X-ray analysis showed that in the PHB-1% kaolinite/PHB/PCL nanocomposite there was an increase in the intercalation from 0.70 nm to 1.13 nm. Yet, for the PHB-4% kaolinite/PHB/PCL nanocomposite there was exfoliation of the clay in the polymeric matrix. The PHB-4 % kaolinite nanocomposite showed a 10 % increase in crystallinity in comparison to neat PHB. Probably, the kaolinite reacted with the nuclear agent during the crystallization.

The influence of different types of processing by fusion has been studied in the degradation of the poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with 5% of kaolinite nanocomposite (PHBV-5%-Kao) and PHBV with 5% of montmorillonite (PHBV-5%-MMT) were studied.^[104] The processing types used cast solvent, mini extruder, and molten mixture. Subsequently, X-ray analysis was conducted for the nanocomposites produced by mini-extrusion. The PHBV-5%-Kao and PHBV-5%-MMT sampled showed a good dispersion in the polymeric matrix. Extrusion processing showed that the PHBV-5%-Kao nanocomposite did not change the basal spacing compared to neat kaolinite (0.72 nm), however, the

size of the kaolinite particulates decreased during the processing. The degradation during the processing by mini-extruder showed that the PHBV-5%-Kao nanocomposite was more stable than the other nanocomposites. It was observed that the water released by the clay during the processing contributed to the degradation of the PHBV. They verified that as kaolinite releases less water than montmorillonite (MMT), the PHBV-5%-Kao nanocomposite exhibited less degradation than the others.

A polymer nanocomposite of low-density polyethylene and kaolinite (LDPE-Kao), and low-density polyethylene and montmorillonite (LDPE-MMT) was produced by the fusion technique.^[105] A double screw extruder was utilized with different configurations. The temperature during the extrusion varied between 170-190 °C. The microstructure was analyzed by small angle X-ray scattering (SAXS), optic microscopy (MO), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and geometry of small amplitude. This work also presented a new microscopy technique that used low-energy ultra-sound and allowed observation of the nanocomposite during the extrusion process. The analysis detected that the LDPE-MMT samples showed intercalation of the polymer between the layers of the organo-modified MMT. Yet the kaolinite did not present the intercalation, which may also indicate that have some clusters of aggregates. These results were confirmed by MO, MET, and MEV. The small amplitude geometry test, used in this work, detected that the LDPE-Kao presented a greater increase in the resistance than the LDPE-MMT. LDPE-Kao did not present in the aggregate form during the fusion and running, while LDPE-MMT was present in the aggregate form. This result probably indicates that the LDPE-Kao nanocomposite using kaolinite as reinforcement will be able to be used in the processing using extrusion and blow molding.

The morphology and the physical properties of nanocomposites using copolymers functionalized of ethylene as polyethylene-grafted maleic anhydride (PE-g-MA), poly(ethylene-co-acrylic acid), poly(ethylene-co-vinyl acetate), and an ionomer of poly(ethylene-co-methacrylic acid) prepared with a small fraction of polyamide-6 and two types of kaolinite clays and organic modified MMT were studied.^[106] The production of nanocomposite by fusion was conducted by a double screw extruder at 140 °C and at a rotation of 100 rpm, where the nanocomposite pellets were blended. Afterward, molded boards were manufactured by compression at 150 °C in order to remove bodies of proof. X-ray analysis showed that the organically modified kaolinite has an interlamellar spacing of 1.11 nm (neat kaolinite has 0.72 nm) for all mentioned matrices. The thermal degradation and the mechanical reinforcement better fit the polymer nanocomposite with the kaolinite than the montmorillonite. Yet for the properties of thermo-oxidative degradation with respect to the oxygen barrier, the montmorillonite nanocomposite was better when compared with the kaolinite. TEM showed that the kaolinite

was partially exfoliated in the studied polymers.

Polymer nanocomposites using a matrix of poly(methyl methacrylate) (PMMA)^[107] were produced. The clays used as nano-reinforcement were kaolinite (Kao), montmorillonite (MMT), and Layered Double Hydroxides (LDH). The kaolinite was pre-intercalated with N-methylformamide (NMF) and intercalated with dodecylamine. A blend was used in the preparation of the nanocomposites at 60 °C and 180 rpm for 10 min. PMMA was used as a matrix for each clay concentration 3, 5, and 10 wt. %. The mixture produced in the blend was taken and milled for analysis. The nanocomposites were analyzed by XRD, thermogravimetric analysis, and TEM to characterize the morphology, thermal stability, and anti-flame properties. XRD analysis showed that the spacing between the kaolinite layers was reduced from 0.71 nm to 0.70 nm when the PMMA-Kao nanocomposite was produced, in other words, no exfoliation occurred. The processing conditions could have degraded the dodecyl amine, which reduced the basal spacing of the kaolinite.

With respect to the other two nanocomposites, there was an increase between the clay layers when the PMMA-MMT and PMMA-LDH nanocomposites were prepared. TEM analysis confirmed that there was a greater intercalation in the PMMA for the LDH and MMT than for the kaolinite. The results showed that the LDH and the MMT became more dispersed in the PMMA than in the kaolinite. The PMMA-MMT and PMMA-LDH nanocomposites showed greater thermal stability than the PMMA-kaolinite. MET analysis confirmed that the intercalation was greater in the PMMA for the LDH and MMT clays than for the kaolinite. So, the lack of exfoliation of the kaolinite in the PMMA could be the cause of the inferior properties compared to the other nanocomposites. The exfoliation causes the layers to be more dispersed in the matrix, improving the properties of these materials. [Table 5](#) summarizes the results of the works presented in this review and shows the interlayered spacing of the kaolinite when it is used with various polymer matrices. The table also shows the main techniques for obtaining the nanocomposite by melting. So, in the majority of the studies carried out for the production of nanocomposites using kaolinite as reinforcement, by the fusion technique the kaolinite was treated with DMSO or NMF. This treatment had the objective of turning the clay into organophilic and increasing the interlayered spacing. It has been noted that the polymer-clay nanocomposites produced by fusion exfoliation of the clay did not occur in all the polymeric matrices. An increase in the interlayered spacing was observed for the kaolinite intercalated by DMSO and NMF. These achieved increases confirm greater thermal stability during the processing of DMSO and NMF. The high viscosity of the blended polymers during the processing could have contributed to the few clay exfoliations observed in the polymeric matrix. The characterization techniques were alike for all studies since XRD and TEM are essential techniques for the characterization of polymer nanocomposites.

Table 5. Production technique by fusion of nanocomposite, polymeric matrix, and intercalant molecule, achieved spacing and the realized characterizations.

References	Melt Blending	Polymer	Molecule of Intercalation	Δd (nm)	Characterizations
[98]	Heated bath	PEG 1000	DMSO	0.33	XDR, TGA, FT-IR, DSC, NMR
	Heated bath	PEG 1000	NMF	0.32	XDR, TGA, FT-IR, DSC, NMR
[99]	Heated powder	PEO	DMSO	0.44	XDR, TG/DSC, FT-IR
	Heated powder	PHB	DMSO	0.45	XDR, TG/DSC, FT-IR
[100]	Extrusion	Nylon 6	AHA	Not cited	(C, N, H), Impact test
	Extrusion	EVOH	DMSO	Partially Exfoliated	XDR, DSC, TGA, TEM
[101]	Extrusion	MDX6	Carboxylic acid with ammonium functionality	Exfoliated	TEM, rheology, DSC, gas barrier
[102]	Extrusion	LDPE	Not used	Did not intercalate	XDR, TEM FTIR
	Extrusion	EPDM	Not cited	Did not intercalate	XDR, TEM FTIR
[103]	Internal mixer	PHB 1% Kao/ PHB/PCL	Not cited	0.43	XDR, SEM, gas barrier
	Internal mixer	PHB 4% Kao/ PHB/PCL	Not cited	Exfoliated	XDR, SEM, gas barrier
[104]	Extrusion	PHBV	Not cited	Did not intercalate	XDR, SEM, GPC
[105]	Extrusion	LDPE	Not cited	Did not intercalate	XDR, TEM, TGA, DSC
[106]	Extrusion	PMMA	NMF-dodecylamine	Did not intercalate	XDR, TEM, TGA, DSC

6. Production of polymer nanocomposites by intercalation of polymer from solution

This technique is used for layered reinforcement of the kaolinite material in which the polymer may intercalate. This technique applies to layered silicates, with intercalation of the polymer or pre-polymer from the solution. This technique utilizes a solvent in which the polymer or pre-polymer is soluble and the silicate layers are swellable.^[90]

Polymer nanocomposites with polyvinylpyrrolidone (PVP, MW 10,000 g/mol) and kaolinite were produced.^[108] Previously a kaolinite-NMF intercalation compound was prepared, and then the NMF was displaced by methanol. PVP was dissolved in methanol and then it was added to kaolinite-methanol. The mixture was stirred for 1 day, at room temperature, and the product was centrifuged. XRD results indicated the intercalation of PVP, arranged in a monolayer, in the kaolinite interlayer spacing, indicating that the basal spacing was increased by 1.24 nm.

Nanocomposites containing PVA reinforced by kaolinite or functionalized kaolinite were produced.^[109] Initially, they

intercalated kaolinite with dimethylsulfoxide. After that, the kaolinite was reacted with different polyols (ethylene glycol (EG), glycerol (GLY), 1,2 propanediol (PRO)). Finally, polymer nanocomposites were prepared through a polymerization solution. PVA was dissolved in distilled water and was subjected to heating at 60 °C for one hour. The product obtained was dried in an oven for one hour. To disperse the reinforcement agent, potent ultrasound was utilized. An XRD evaluation of the composites was not conducted, so it is not possible to know if a nanocomposite was produced, or the morphology of the clay in the polymeric matrix. The hardness and elastic modulus of the composites were evaluated, and all the composites presented greater hardness. The Young's Modulus of the nanocomposites containing 0.5 and 8 wt. % reinforcement agent was evaluated through DMA. Only the nanocomposites with Kaolinite-glycerol at 0.5 wt. % of the clay and kaolinite-ethylene glycol at 8 wt. % of the clay exhibited an elastic modulus value greater than neat PVA polymer.

7. Outlook of the future

In this section, an outlook of future studies with polymers and kaolinite will be reported, as well as their challenges. Due to its characteristic properties, kaolinite should be used as nanofillers in the production of new functional hybrid materials to reach new properties. In this context, the emergence of new diseases causes researchers to develop materials that are resistant to various microorganisms that are pathogenic. Neji *et al.*^[110] developed a bionanocomposite with chitosan and kaolinite. They produced films by the casting method and the kaolinite was exfoliated by the mechanochemical method. The antimicrobial activity tests showed that the films showed good inhibitory activity against all tested bacteria. Zhang *et al.*^[96] produced a hybrid nanocomposite through prolonged contact of the monomer with kaolinite aiming to be used as an adsorbent. They observed an increase in the adsorption affinity of the produced nanocomposites and this shows a promising application of these materials as high-performance adsorbent materials. Another future scenario is the difficulty of accessing drinking water free from pathogenic microorganisms. All over the world, drinking water is becoming increasingly scarce and contamination of water by bacteria is a health risk. Isah *et al.* developed a method using kaolinite modified with chlorhexidine and zinc to inhibit the growth of bacteria.^[111] Kaolinite intercalation methods aimed at the exfoliated morphology that are used in nanocomposites often used toxic molecules or solvents.^[112] Additionally, long intercalation times make industrial use a challenge.^[113] Therefore, intercalation methods of kaolinite that are non-toxic and present fast intercalation or exfoliation should be developed.^[28,114]

8. Conclusions

Kaolinite can be intercalated by various molecules and the most commonly used are dimethylsulfoxide (DMSO) and N-methylformamide (NMF). The majority of the intercalation studies using these two molecules increased the basal spacing of the kaolinite as well as turned the clay organophilic, making it compatible with the formation of nanocomposite polymers. There are two methods of kaolinite intercalation which are dislocation and mechano chemistry methods, with the first category being primarily used and easier to carry out experimentally. Many authors used the dislocation method and observed the influence of T_R , t_R , and Δd , as well as the influence of the t_R on the %RI for the DMSO and Potassium Acetate molecules. Referring to the influence of the T_R , a greater temperature is observed as the Δd of kaolinite is reduced. No influence of the t_R in the Δd was observed. With respect to the %IR, the greater the t_R the greater the % IR. The achieved interlayered spacing was greater in the nanocomposites produced *in situ* than by fusion. The high viscosity is associated with high temperatures (100-300 °C) because the production of nanocomposites by fusion could have contributed to the low index of exfoliation. DRX and

TEM are the techniques most commonly used for the characterization of nanocomposites because these two techniques are capable of obtaining information about the clay morphology in the polymeric matrix. The matrices used in the *in-situ* production of nanocomposites were polystyrene and poly methylmethacrylate, which are amorphous polymers. For the production of nanocomposites by fusion, matrices of polyethylene, which is a semi-crystalline polymer, were used in most cases. TGA and DSC were used for thermal characterizations, to verify the influence of the clay in the polymeric matrix.

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Supporting information

Not applicable.

Conflict of interest

There are no conflicts to declare.

Abbreviature	Nomenclature
AA	Acrylic acid
AA _{N a}	Sodium acrylate
AHA	6-Aminohexanoic acid
AcK	Potassium acetate
APTES	(3-Aminopropyl)triethoxysilane
BPO	Benzoyl peroxide
CHN	Carbon, hydrogen, and nitrogen, analysis
DBS	Sodium dodecyl benzene sulfonate
DCA	Dodecylamine
DEGME	Diethylene glycol methyl ether
DEG2EHE	Diethylene glycol-2-ethyl hexyl ether
DMF	Dimethylformamide
DMSO- <i>d</i> ₆	Deuterated dimethyl sulfoxide
DMSO-BZ	Dimethyl sulfoxide-Benzamide
DMSO-13BD	Dimethyl sulfoxide-1,3 butanediol
DMSO-DEGMB	Dimethyl sulfoxide-diethylene glycol monobutyl ether
DMSO-EG	Dimethyl sulfoxide ethylene glycol
DMSO-EG-10%W	Dimethyl sulfoxide ethylene glycol 10% Water v/v
DMSO-EGMM	Dimethyl sulfoxide ethylene glycol monomethyl ether
DMSO-MOH	Dimethyl sulfoxide Methanol
DMSO-1,2-PD	Dimethyl sulfoxide-1,2-propanediol
DMSO-1,3-PD	Dimethyl sulfoxide-1,3-propanediol
DSC	Differential Scanning Calorimetry
DTA-TG	Differential Thermal Analysis and Thermogravimetric analysis
EHC	Effective heat combustion
EPDM	Ethylene propylene diene rubber

EVOH	Ethylene-vinyl alcohol	PMMA	Poly(methyl methacrylate)
EVA	Poly(ethylene-co-vinyl acetate)	PMMA/kao	Poly(methyl methacrylate) with kaolinite
FTIR	Fourier Transform Infrared	PMMA-MMT	Poly(methyl methacrylate) with Montmorillonite
GLY	Glycerol	PMMA-LDH	Poly(methyl methacrylate) with Layered double hydroxide
HRR	Heat release rate	POE-kao-	Polyethylene oxide-kaolinite-
Kao-PMAC	Kaolinite-poly(methacrylamide)	DMSO	dimethylsulfoxide
KPS	Potassium persulfate	PP-hyd	Phenylphosphonate
Kao-U	Kaolinite-urea	PRO	Propanediol
LOI	Limiting oxygen index	PS	Polystyrene
LDPE	Low density polyethylene	PS/kao	Polystyrene with kaolinite
LDH	Layered double hydroxide	PSMA	Poly(styrene-alt-maleic anhydride)
MAC	Metacrylamide	PSMA/kao	Poly(styrene-alt-maleic anhydride) with kaolinite
MeOH	Methanol	PVA	Poly(vinyl alcohol)
MOH-NMF-	MOH-N-methylformamide-p-	PVA-kao	Poly(vinyl alcohol) with kaolinite
pNA	N-[3-	PVP	Polyvinylpyrrolidone
MPDET	(trimethoxysilyl)propyl]diethylenetriamine	PVC	Poly(vinyl chloride)
MMT	Montmorillonite	% IR	Rate of intercalation or reaction rate
MXD6	Poly(m-xyleneadipamide)	SEM	Scanning Electron Microscope
nano-HAO	Nano-sized hydroxyl aluminum oxalate	T _R	Temperature of reaction
NBZ	Nitrobenzene	t _R	Time of reaction
NMF-EG	N-methylformamide-ethyleneglicol	T _{RAverage}	Average temperature of the reaction
NMF-1,2-PD	N-methylformamide -1,2 propanediol	t _{Average}	Average time of reaction
NMF-1,3-PD	N-methylformamide-1,3 propanediol	TDA	Thermal Differential Analysis
NMF-Kao-	N-methylformamide- kaolinite-	THR	Total heat release
MAC	Metacrylamide	TPGBE	Tri(propylene glycol) butyl ether
NMP	1-methyl-2-pyrrolidone	UV	Ultraviolet absorbance
NMR	Nuclear Magnetic Resonance	D	Basal distance
P2CA	Pyridine-2-carboxylic acid (2-Picolinic acid)	Δd	Interlayer expansions
PAA	Poly(acrylic acid)	Δd _{Average}	Interlayer expansions average
PAAm	Poly(acrylamide)	I _{i(001)}	Peak intensity observed for intercalate
PAAm-kao	Poly(acrylamide) with kaolinite	I _{k(001)}	Peak intensity observed for kaolinite
PAMAM	Poly(amidoamine)		
PANI	Polyaniline		
PAN	Polyacrylonitrile		
PβA	Poly-β-aniline		
PAN/kao	Polyacrylonitrile /kaolinite		
PEO	Polyethylene oxide		
LDPE-kao	Low density polyethylene with kaolinite		
LDPE-MMT	Low density polyethylene with kaolinite with montmorillonite		
PEG 3400	Poly(ethylene glycol) with 3,400 g/mol		
PEG 1000	Poly(ethylene glycol) with 1,000 g/mol		
PE-g-MA	Polyethylene-grafted maleic anhydride		
PEAA	Poly(ethylene-co-acrylic acid)		
PHB	Polyhydroxybutyrate		
PHB1%kao/PHB/PCL	Polyhydroxybutyrate-1%-Kaolinite/Polyhydroxybutyrate/poly(ε-caprolactones)		
PHBV	Polyhydroxybutyrate-co-valerate		
PHB-kao-	Polyhydroxybutyrate-kaolinite-		
DMSO	dimethylsulfoxide		

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