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Effect of low-pressure plasma treatment on the thermal behaviour of organo-modified montmorillonite nanoclay

A. Almansoori^{a,*}, W. Alkaron^{a,b,c,}**

^a Technical Institute of Basra, Southern Technical University, Basra, Iraq

^b Doctoral School of Materials Science and Technologies, Óbuda University, 96/B Bécsi st., 1030 Budapest, Hungary

^c HUN-REN Centre for Energy Research, 29-33 KonkolyThege M. st., 1121 Budapest, Hungary

* Corresponding e-mail address: a.almansoori@stu.edu.iq

** Corresponding e-mail address: w.alkaron@stu.edu.iq; alkaron.wasan@uni-obuda.hu

ORCID identifier:  <https://orcid.org/0000-0002-9757-7724> (A.A.);

 <https://orcid.org/0000-0001-8419-6132> (W.A.)

ABSTRACT

Purpose: The thermal behaviour of nanoclay can be considered an important factor in obtaining high-performance polymer nanocomposite. Thus, the current study aims to investigate the effect of plasma treatment on the thermal stability of two organically modified nanoclays, Cloisite 30B (C30B) and Nanomer I.34TCN (I.34TCN), compared with pristine NaMMT.

Design/methodology/approach: The nanoclays were studied and characterised using Thermogravimetric Analysis (TGA). TGA was used to measure the weight loss of the plasma-treated and untreated nanoclays (C30B, I.34TCN, and NaMMT nanoclays) over a 30-630 °C temperature range.

Findings: Based on TGA results, the decomposition of all plasma-treated nano clays (C30B, I.34TCN and pristine NaMMT) was shifted to a lower temperature than in the untreated ones at all those stages. Thus, plasma treatment was successfully used as a convenient method to alter the chemical structure and surface morphology of MMT nanoclays for better thermal behaviour and filling distribution.

Research limitations/implications: This hypothesis can be corroborated by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) for a better understanding of the structural and surface changes that occurred due to the plasma action, which can provide an interpretation of the changes in the thermal behaviour of nanoclays.

Practical implications: The plasma treatment, therefore, can improve the thermal stabilisation of the nanocomposite powders for the LS fabricated parts and even for the surrounding powder for the recovery process. Plasma-treated nano clay, therefore, can be used to reinforce polymers with an expectation of increasing the thermal stability of the resultant composites. Thus, the plasma-treated composite can be fabricated for laser sintering applications in fields that require high thermal stability.

Originality/value: The surface modification of nanoclay powders via plasma treatment can be used as a convenient method to alter the chemical structure and surface morphology for better thermal behaviour and filling distribution.



Keywords: Nanoclays, Montmorillonite, Plasma treatment, Thermal behaviour, TGA

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MATERIALS

1. Introduction

Although, in recent decades, nanoclays have attracted great research interest and are widely used to reinforce polymers, some challenges need further work to address. The most crucial issue for polymer reinforcement is the poor dispersion of nanoclay due to the weak interfacial interaction and incompatibility between the nanoclay particle surface and polymer chains [1-4]. It is due to the weak interaction between the minerals nanoclays and organic polymers. The incompatibility can also occur if a hydrophobic (or relatively hydrophobic) polymer is filled by a hydrophilic nanoclay [5-7]. Thus, this behaviour may eliminate the advantages the nanoclays can offer to polymer matrices. However, several types of nanoclays can be successfully incorporated into polymer matrices with good dispersion using melt blending or extrusion methods [8]. Effective dispersion and uniform distribution enabled the produced polymer-nanoclay composites to be highly applicable in several applications.

Sodium montmorillonite (NaMMT), one of the most used nanoclay for polymer reinforcing, belongs to the smectite group of layered silicate clay minerals. NaMMT has some promising advantages over other clays due to its high surface area, aspect ratio and availability [9,10]. Furthermore, it is possible to hydrate interlayer cations in an aqueous solution, increasing the interlayer space and facilitating the intercalation process. It can also be achieved by exchanging the interlayer N^+ with organic cations, a surfactant. Different types of chemical surfactants are explored to act as a cation exchanger [11]. It occurred due to the high cation exchange capacity of the MMT clays caused by the weak Van der Waals attraction forces between the MMT [11]. Organonanoclay is, therefore, obtained by exchanging the interlayer cations Na^+ by grafting organic cationic surfactants like quaternary alkyl ammonium surfactants into the interlayer space [12,13]. Therefore, the hydrophilic nanoclay is rendered organophilic due to organic surfactants in the interlayer galleries enhancing compatibility with the organic polymer matrix [5,14]. Thus, this modification can match the nanoclay surface polarity with polymer matrix polarity. However, these ammonium surfactants provide one or more functional groups, like alkyl and phenyl groups, which are classified as hydrophobic

groups and can also enhance the hydrophobicity of the interlayer space [14]. Thus, the organic surfactants change the hydrophilic nature of the MMT clays into hydrophobic with a high capacity to adsorb organic materials [5,11].

Additionally, the organic modifiers can increase the interlayer space, allowing an intercalation/exfoliation of nanoclay into the polymer matrix. An efficient intercalated/exfoliated structure requires processes like solution blending or melt compounding [8].

During the past decades, laser sintering has been considered one of the most promising manufacturing technologies. It enables the production of high-quality 3D complex geometries with high dimensional accuracy. During the LS process, the powder is warming to a temperature below its melting temperature before the laser is supplied from the top of the powder. Thus, the powder as it is received is processed in the LS chamber. In laser sintering, however, the mechanical mixing of polymers and nano clay powders only occurs before the LS process. The nanoclays are expected mainly to be aggregated into micro-sized agglomerates and tactoids [15]. The effective addition of nanoclay to LS polymer powders is hard to achieve. Therefore, it cannot significantly improve the properties of LS parts, and the LS products cannot meet the high-performance needs [16].

Thus, in our prior studies, we concentrated on exploring the potential of plasma treatment as a promising method to induce compatibility between nanoclay and LS polymer powder and de-agglomeration of highly dense nanoclay platelets [15,17,18]. Thermal behaviour is one of the most interesting behaviours of polymers, especially in applications that require high thermal stability [19-22]. Thus, the relatively low thermal behaviour of polymers limits their applications. Nanomaterials like nanoclays have potential in this area, but dispersion can be difficult [23]. Restrictions of the weak dispersion of nanoclay in LS polymer powders can be avoided by plasma treatment [15,17,18]. The effect of plasma treatment on the thermal behaviour of the montmorillonite clay powders has not been studied in detail. Hence, we aimed to provide a detailed study on the influence of plasma treatment on the thermal behaviour of three different types of MMT-based nanoclays (a pristine NaMMT and two organically modified nanoclays). The

thermal behaviour of nanoclay is an important factor in obtaining high-performance polymer nanocomposite [5]. The influence of nanoclays on the thermal stability of the polymer nanocomposites is in several ways: nature of the nanoclay, type of organo-modifier and nanoclay loadings [24-26]. The initial decomposition, dehydration or decomposition of organic surfactant can occur during polymer nanocomposite processing [27] because most organic surfactants, like alkyl ammonium, are less stable during the processing of plastics [28].

Additionally, some nanomaterials like MMT nanoclays were modified by organic surfactants with hydroxyl groups, which act as Brønsted acidic sites, which may accelerate the degradation of the polymer matrix [29]. Polyamide 12, a standard laser sintering polymer powder supplied by the EOS company, was used to investigate the effect of the plasma treatment on the behaviour of the polymer nanoclay composite. Thus, improving the decomposition rates and temperatures of the reinforcing nanomaterial that is organomodified MMT nano clays from room temperature to temperatures higher than the polymer matrix melting point is crucial.

As Thermogravimetric Analysis (TGA) has proven to be an ideal way to evaluate thermal stability [26,30], TGA was employed in this study to measure the decomposition temperatures and rates, weight loss and residues of all the nanoclay types were involved in the paper. The TGA was carried out on plasma-treated nanoclays and compared to the untreated ones to achieve the aim of the current study.

2. Materials and methods

2.1. Materials

Figure 1 represents the structure of the natural NaMMT, and the chemical formula and structure of the organic surfactants were used to modify two types of commercial organomodified nanoclays: Cloisite C30B and Nanomer I.34TCN. The essential clay mineral in these nano clays is sodium montmorillonite (Na^+MMT), which has a chemical formula of $[\text{Al}_{1.67} \text{Mg}_{0.33} (\text{Na}_{0.33} \text{Si}_4\text{O}_{10} (\text{OH})_2]$ [31] and exchangeable sodium interlayer ions are shown in Figure 1 (left side view). On the other hand, the organonanoclays, C30B and I.34TCN are obtained by exchanging the inorganic cations- Na^+ with two different organic surfactants displayed in the right-side view in Figure 1. The nanoclays used in the study are selected due to the preferential characteristics of those organic surfactants used to exchange the interlayer cations. C30B and I.34TCN contain similar surfactant compounds- quaternary alkyl ammonium surfactant with two hydroxyl groups but different tallows. The surfactant of C30B nano clay possesses a single long tallow tail, while double hydrogenated tallows are present in the surfactant of the I.34TCN [13].

According to the literature, nanoclays with double alkyl tails (swallow tail) have higher d-spacing than those with single alkyl tails like C30B, except I.34TCN [13]. Most importantly, however, both C30B and I.34TCN surfactants have the advantage of possessing a hydroxyl group, which

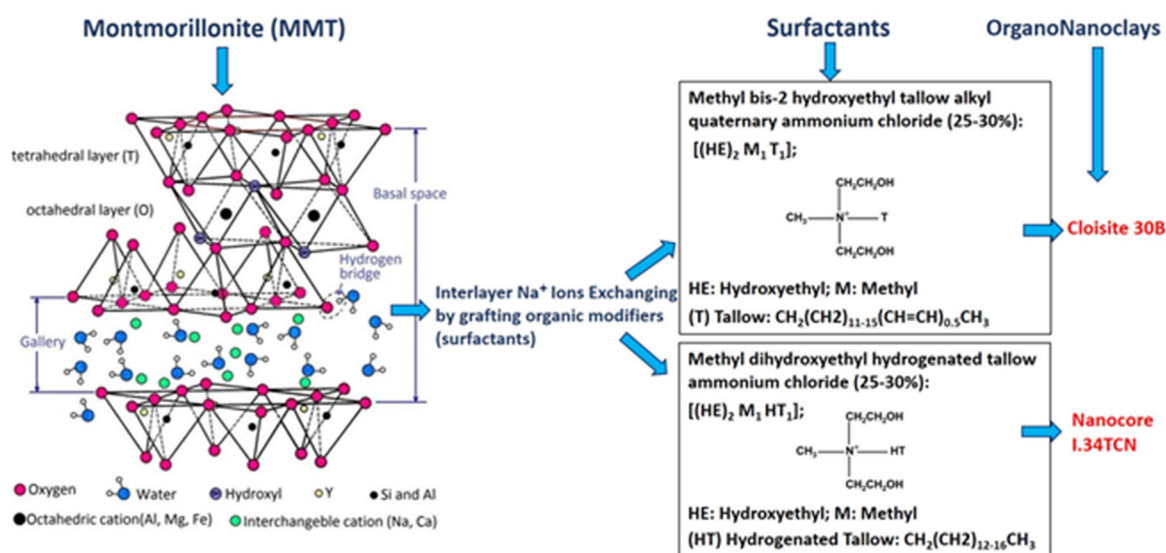


Fig. 1. Schematic illustration of the structure of natural Na^+ montmorillonite (NaMMT) (left side view) [32] and the organic surfactants used to modify the NaMMT to obtain the organomodified nanoclays: Cloisite C30B and Nanomer I.34TCN (right side view)

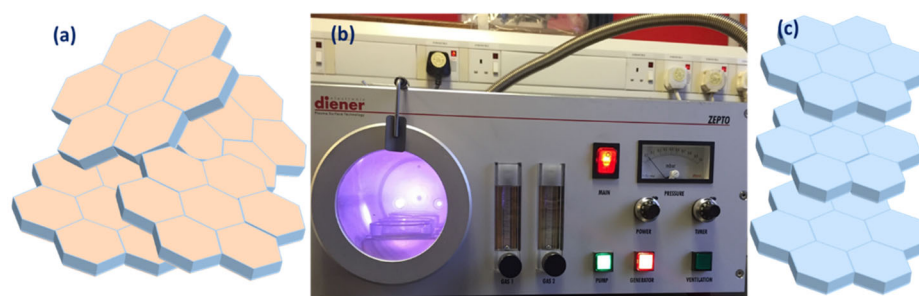


Fig. 2. A schematic diagram represents the process of plasma treatment. This shows that plasma treatment was used to eliminate the aggregation of nano clay particles: a) nanoclay particles before using plasma, b) plasma treatment machine, and c) nanoclay particles after using plasma. Inset table illustrates the decomposition temperatures at 5% and 10% weight loss of the three nanoclays

can be classified as a unique feature compared with other surfactants [13].

The hydroxyl groups enable a hydrogen bonding between layered silicate clays and organic polymers, especially those with polar nature [15,33,34].

2.2. Methods

Plasma-aided surface modification was applied on the three nanoclays, NaMMT, C30B, and I.34TCN powders, using Zepto Plasma Cleaner from Diener Electronics. Figure 2 illustrates the plasma treatment process and instrument. Plasma treatment, as shown in Figure 3, was carried out under low-pressure conditions and full power (100 W) for 30 min. The powder of those nanoclays was placed as small as 1 gram in a glass petri dish before being placed in the plasma cleaner chamber, which was then set to a pressure of 0.3 bar. The instrument chamber was evacuated using a

vacuum pump before the ambient air, the main process gas, was supplied to the vacuum chamber to generate air gas plasma using a strong electric field between electrodes.

Thus, atoms, molecules, ions, and free radicals will be generated due to the excitation of oxygen molecules resulting from the presence of plasma. The powder inside the chamber was treated twice for a maximum of 1000 sec each time. The plasma-treated powder was ready to be removed from the chamber when the vacuum chamber was ventilated after the pump was switched off. The powder must be kept from moisture by storing it in an airtight glass jar. Our previous work describes the plasma treatment process well [35].

Thermogravimetric analysis (TGA)

TGA is a powerful laboratory tool for measuring the thermal properties of various materials, including nanoclays.

TGA can measure weight loss of volatile components, e.g., loss of moisture, interlayer water, and organic surfactant, in specimens of the nanoclay powders as a function of temperature in an inert atmosphere. PerkinElmer Thermogravimetric analyser (Pyris 1) in the material characterisation laboratory at the University of Sheffield was used to determine the thermal stability of the nanoclay powders (plasma-treated and untreated nanoclays). Less than 5 mg of the tested nanoclay powders placed in an aluminium pan were heated inside the furnace of Pyris 1 TGA instrument under Nitrogen atmosphere, in the range of 30-630°C with a rate of heating of 10°C/min.

Scanning Electron Microscopy (SEM)

Nanoclay powder was studied using scanning electron microscopy (SEM). The SEM investigations were carried out using low-voltage Nova NanoSEM 450 from Oxford Instruments in the Department of Materials Science and Engineering at the University of Sheffield.

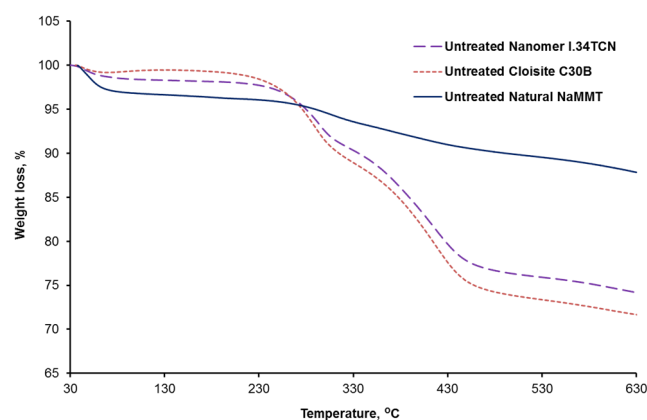


Fig. 3. TGA thermograms of the untreated nanoclays: NaMMT (dark blue line), I.34TCN (dashed purple), and cloisite 30B (dotted red)

3. Results and discussion

The TGA thermogram patterns of the untreated and plasma-treated nanoclays (C30B, I.34TCN and pristine NaMMT) and their responses to increased temperature are displayed in Figures 3 and 4. Figure 3 shows TGA curves of the three types of untreated nanoclays: an unmodified (pristine) NaMMT nanoclay (dark blue line) and two types of organomodified nanoclays, Nanomer 1.34TCN (dashed purple) and Cloisite C30B (dotted red). As demonstrated in Figure 3, all the nanoclay types showed their thermal behaviour clearly.

The TGA data corresponding to NaMMT nanoclay show that this natural nanoclay without any surfactant, decomposes in only three stages upon heating from 30°C to 630°C. The literature indicates that the first two mass loss steps occur between ambient and 200°C while the third can be observed above 400°C [36,37]. The first mass-loss step, in a transition starting from 40°C to around 100°C, is attributed to the dehydration of adsorbed water, i.e. free water accumulated

on the nanoclay particle surfaces and between particles [38–40]. The second step, which begins below 100°C and continues till 200°C, probably ended at around 135°C, is also related to the dehydration of water adsorbed by metal cations, i.e. Na^+ [12,39]. However, W. Xie [38] considered that two types of interlayer water evolved in NaMMT: directly (primary) and indirectly (secondary) linked to the cation, and both are not completely released until they reach 300°C. By understanding the structure of the NaMMT, Water molecules, which are physically adsorbed onto the external surface of the clay mineral layers, as well as weakly bonded and free water pockets inside the aggregate structure, evaporate at the lowest temperatures.

On the other hand, water molecules located in the inter-layer and hydrated water molecules around hydrogen ions and quaternary alkyl ammonium ions evolve at higher temperatures [41]. In step 3, the dehydroxylation process of MMT is completed at a temperature above 500°C, which is assigned to the dehydration of structural hydroxyl groups [38]. However, the dehydroxylation process in step loss

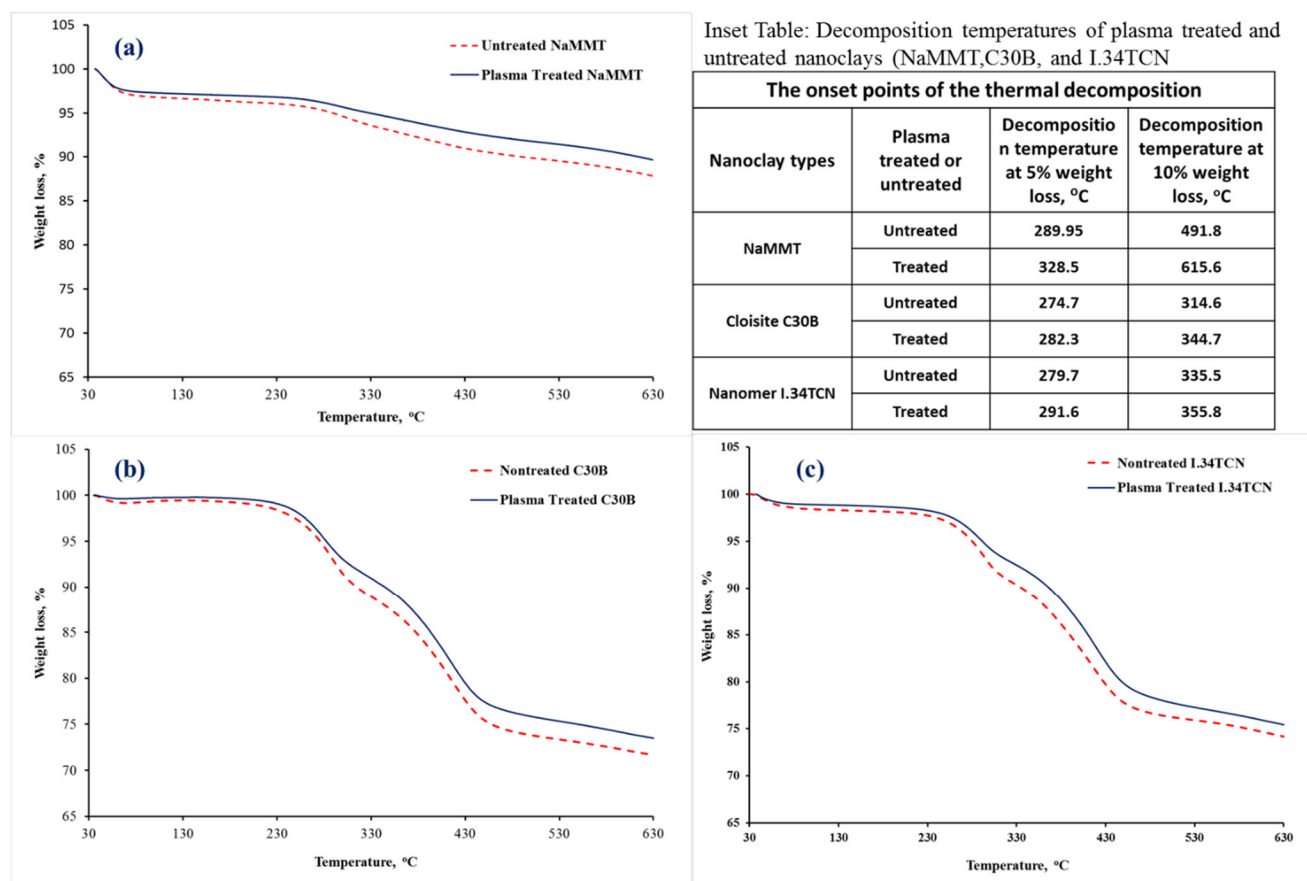


Fig. 4. TGA thermograms of the plasma treated and untreated NaMMT (a), Cloisite C30B (b), and Nanomer 1.34TCN (c) nanoclays. Inset table illustrates the decomposition temperatures at 5% and 10% weight loss of the three nanoclays

three occurs in two stages. The first stage occurs due to the release of OH groups bound to the surface of NaMMT. At the same time, the second stage completed in the temperature range (520°C to near 630°C) is related to the dehydroxylation of the structural OH units of the montmorillonite [12]. The total weight loss at a temperature of 630°C is about 10%.

Unlike pristine NaMMT, the organoclays (C30B and I.34TCN) lose their weight in four stages [38,39], as shown in Figure 3. For untreated I.34TCN and untreated C30B, the first and second mass-loss steps related to water dehydration are like NaMMT. The total weight losses of NaMMT, I.34TCN, and C30B at a temperature of 200°C are around 3.0, 2.0, and 1.0 per cent, respectively. It indicates that organoclays contain less water than NaMMT owing to the exchange of Na⁺ with a cationic surfactant. The free water in I.34TCN and C30B is released beyond 100°C, and the interlayer hydration water is removed with unexchanged Na⁺ ions at a temperature range of 200-300°C. Although organoclays are categorised with a hydrophobic nature due to the presence of the alkyl ammonium compounds, which act as a barrier to water molecules entrance between clay layers [12,39,42,43], water molecules are still absorbed on the aggregated exterior side and the hydrophilic layer edges [44]. The amount of water adsorbed depends on the relative humidity of the environment. In this weight loss stage, a partial de-surfactant occurs due to the decomposition of the quaternary ammonium salt, which was only physically adsorbed to the aluminosilicate layers without exchanging interlayer ions [12,45]. The organic surfactant, however, is mainly decomposed in the third stage between the dehydration of interlayer water and the dehydroxylation [12, 38,46] in the range between 300°C and 500°C. However, a combination of the decomposition of the organic matter and dehydroxylation can occur over 300°C and 600°C because the alkyl silts decomposed in the nitrogen environment are not completed before 600°C [37]. Thus, the next two consecutive weight losses in the I.34TCN and C30B are attributed to the decomposition of organic components from the clay structure and the structural water. For I.34TCN, the 2%, 10%, 20%, and 25% mass loss steps occurred at around 207°C, 330°C, 430°C, and 590°C, respectively. At the same time, the decomposition temperatures of C30B for the same percent mass loss mentioned above are: 240°C, 315°C, 414°C, and 458°C.

According to the results, for the I.34TCN, the dehydration of adsorbed water occurred beyond 330°C, whilst for C30B, it was released before 315°C, which reveals that the I.34TCN adsorb more water than C30B. In the next stage, around 20-25% in the range of (430-590°C) for the I.34TCN and (414-458°C) for C30 B. weight loss occurred

at this step, which is by the amount of surfactant in these two types of nanoclay.

The decomposition of organic surfactant (i.e. quaternary alkyl ammonium salt) probably happens via the Hoffmann elimination reaction due to the proximity of the Lewis base sites (i.e. hydroxyl groups) and the basic aluminosilicate surface to the intercalated alkyl ammonium salt [44]. The hydroxyl group in this reaction abstracts the H-atom to the octadecyl groups (alkyl groups) and yields octadeca-1-ene, which is classified as alpha-olefin, water and 2-diethylaminoethanol (free amines) [47,48]. The products of the procedure are alkanes, alkenes, and gases like NH₃, CO₂, CHO, COOH, and amines, according to a previous study [40]. Upon degradation, the entire structure of the surfactant is destroyed, while the layered morphology of the aluminosilicate remains stable. For the organoclay, C30B and I.34TCN, the tallow/hydrogenated tallow residue is the main component of the degradation products due to its high molecular weight compared to the methyl groups and nitrogen-containing groups [40]. However, I.34TCN showed slightly better thermal stability, probably due to the hydrogenated Tallow group, which is more stable than Tallow. The last mass-loss stage (over 520-630°C), similar to NaMMT, is attributed to the dihydroxylation of the crystal lattice [38,39]. To understand the effect of plasma species on thermal behaviour Figure 4 demonstrates TGA patterns of plasma treated and untreated NaMMT, I.34TCN, and C30B nanoclays, respectively. Inset Table in Figure 4 also highlights the decomposition temperatures of all nanoclay types at 5% and 10% weight loss. The overall patterns of treated and untreated nanoclays are similar; however, all three plasma-treated nanoclays showed higher thermal stability. For example, for untreated C30B, according to the inset table in Figure 3, the 5% and 10% decomposition stages occurred at 274.7°C and 314.6°C, respectively. At the same time, this happened at 282.3°C and 344.7°C for the treated one. Plasma treatment causes the breaking down of the Si-O-Si bond and substituted OH groups in the nanostructure. It resulted in intramolecular hydrogen bonding formation inside the nanoclays structure. It may lead to the formation of a network of hydrogen bonding. The energetically favourable finite or infinite hydrogen bond chains result in a stabilised structure.

Additionally, we attributed the improvement in thermal behaviour to plasma treatment action, which we suspect releases some of the free water, relatively delaying the decomposition of the clay [15]. Moreover, the oxidative layer on the nanoclay, which we assume results from the plasma treatment, might lead to less moisture absorption [15]. The feature suggests a significant change in the clay lamellar organisation that influences the resonance vibration energy and, consequently, the spectrum.

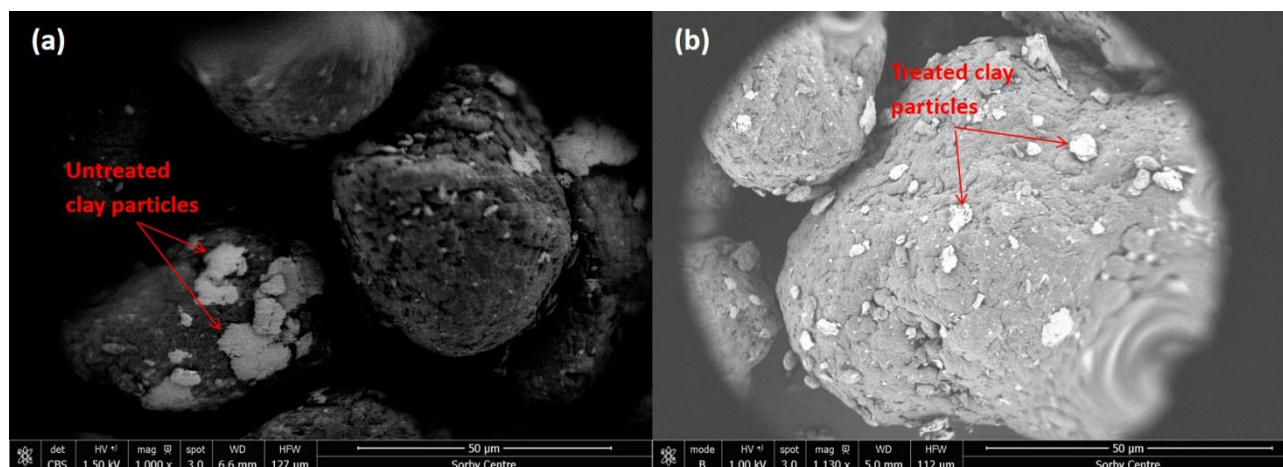


Fig. 5. SEM images of polyamide12 mixed with: a) untreated nanoclay and b) treated nanoclay

The hypotheses find confirmation in the morphological analysis; Figure 5 (a and b) shows SEM images for untreated and treated PA12/nanoclay composites, respectively. In these images, the white particles are clay, and the darker background is the PA12 materials. Figure 5b clearly shows that the distribution of treated clay within polymer particles is more uniform than untreated clay. As a result, the use of air plasma etching for clay succeeded as the large clay accumulations, as in the picture, were avoided. This hypothesis was also explained in the schematic diagram in Figure 1.

In our previous study, X-ray diffraction (XRD) verified the structural changes of the montmorillonite cloisite 30B clay [17]. As demonstrated in our previous work, both organoclays showed peaks at positions (2θ of 19.7° and 2θ of 19°) at higher angles [17]. On the other hand, at low angles, the XRD patterns of untreated and treated clays are slightly different. Untreated C30B showed a characteristic intense peak at $2\theta = 4.8^\circ$ with a $d_{001} = 1.8$ nm (001 crystal lattice) by Bragg's law while the amount of basal space for NaMMT is 1.14 nm [43] and for I.34TCN is 1.96 nm [13]. It comes from the expansion of basal plane in organoclay due to the exchange of alkyl quaternary ammonium with Na^+ cations [44]. Most notably, C30B with surfactant from the single tallow tail group and I.34TCN from the group with two tallow tails have the lowest d-spacing compared to their family groups because both possess hydroxyl groups [13]. The plasma pattern of treated nanoclay showed decreased intensity and a small shoulder on the right side. The decreased intensity of the basal reflection indicates the separation of the clay mineral layers [49,50].

The shoulder may arise from disorder and defects in a lattice structure. During plasma treatment, massive dehydration or thermal degradation can take place, and

water molecules or gases move out of the inter-layer space, leading to disorder in the interlayer structure and resulting in the inhomogeneity of basal spacing. Production of volatile gas leads to an increase in internal pressure. It causes the expansion of the structure, layer disorder, and defect generation [33,51]. Moreover, as explained in the TGA section, plasma treatment, due to the breakdown of the Si-O-Si bond, intramolecular hydrogen bonding formed inside the nanoclays structure, which resulted in a network of hydrogen bonds. This can also increase defects in the organoclay structure [52]. Thus, we conclude that the treated sample displays a weaker and broader band that can be attributed to increased disorder of the lamellae (disruption after plasma treatment) [53].

4. Conclusions

The study studied the effect of plasma treatment on the thermal stability of three commercial montmorillonite nanoclays, one pristine MMT, and two organo-modified MMTs (C30B and I.34TCN). The TGA results obtained for these nanoclays show that the decomposition is due to free water desorption and dehydration, followed by decomposition of the organic modifier for only C30B and I.34TCN, and finally, dehydroxylation. It was evident that the organic surfactant of C30B and I.34TCN will likely decompose via Hoffmann elimination reaction. It was also stated that the decomposition temperatures and rates showed slightly higher thermal stability for I.34TCN, probably due to the double tallow tail in its organic surfactant. Plasma treatment, most importantly, was found to improve the thermal stability of the organoclays in all the temperature ranges studied. The plasma treatment had similar effects on all types of nanoclays.

We concluded that the plasma treatment causes the breaking down of the Si-O-Si bond and substituted OH groups in the nanostructure. This resulted in intramolecular hydrogen bonding formation inside the nanoclay structure and led to the formation of a network of hydrogen bonding. These energetically favourable finite or infinite hydrogen bond chains result in a stabilised structure.

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