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# Ethyl vinyl acetate (EVA) composites with nanoclays and boric acid: Thermal and mechanical properties

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## ABSTRACT

The polymers are widely used materials in various applications. Their flammability is a concern when the material will be facing high temperatures and/or conditions resulting in the incidence of ignition. The flame resistance of the polymers tends to be enhanced by the utilization of inorganic materials as additives. Versatile inorganic materials can be used for this purpose, e.g., ceramics (oxides, hydroxides, clays, etc.). The addition of inorganic additives could alter the mechanical properties of the polymer-inorganic composite structure, which should be considered during composite preparation as well. In this study, two different nanoclays (up to 20/100 by weight) and boric acid (BA) were added to ethyl vinyl acetate (EVA) to investigate possible enhancement in flame retardancy of the polymer. The mechanical properties were also determined for the neat polymer and polymer-inorganic composites to determine the effect of nanoclay and BA addition. The prepared nanocomposites were evaluated in terms of their chemical structures (Fourier transform infrared spectroscopy and X-Ray diffraction analysis), thermal characteristics (thermogravimetric analysis), mechanical properties (tensile test), and flammability behaviours. The NC 1.4 sample containing the highest amount of nanoclay had the longest burning time and Young's modulus. The NC 2.3 and NC 1.3-BA samples had relatively higher stress-bearing capabilities. The addition of BA enhanced the stress-bearing capability of NC 1 containing samples and it slightly increased the burning time for NC 2 containing composites. The organic surface modifiers of nanoclays and BA addition were effective on the thermal and mechanical characteristics of the nanoclay/EVA composites.were effective on the thermal and mechanical characteristics of the nano-clay/EVA composites.

## 1. Introduction

Polymer materials are widely used in various applications due to their distinctive qualities, such as light weight, mechanical strength, viscoelasticity, and chemical durability [1]. However, because of their chemical composition and organic content, they are flammable, which limits the areas of application [2]. Research has been focused on developing environmentally friendly techniques and materials for preventing or retarding the ignition of fire in recent years. The utilization of alternative materials as flame retardant additives instead of halogenated chemicals is preferred due to the environmental and health concerns [3]. The inorganic/ceramic additives (oxides like silicates, clays), hydroxides like ($Mg(OH)_2$) are promising candidates which are environmentally friendly options, but their effect on the mechanical properties of the polymer composite should also be considered. The high loadings of inorganic fillers are adversely affect the mechanical properties of the composite.

The combustion process of the polymers should be examined to determine the flammability of them or their composites. The combustion occurs when there is heat, oxygen, and combustible material [4]. The polymers release degradation products with increasing temperature which are highly combustible. The oxidation will initiate if there is enough heat for ignition, and combustion would continue if the energy released during the process is enough to proceed with the combustion. There are several ways to prevent the initiation and progress of combustion for polymers. The diffusion of flammable disintegration components from polymer and oxygen from air can be blocked by barrier layer formation on polymer surface. The energy released during combustion are used for some side reactions (e.g., oxidation, phase transformation of fillers) which will hamper the process of combustion. The release of non-combustible gases (e.g., water vapour) from additives can dilute the oxygen and combustible gases which are stop combustion. The free radicals are be trapped by additives to decrease the rate of thermal degradation and consequently

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*Corresponding author: ilker.erdem@agu.edu.tr combustion. The most common flame retardants can be classified as halogenated additives, metal hydroxides, P, N and Si containing additives [5]. The halogen-containing additives are not healthy or environmentally friendly, and their usage was banned by Environmental Protection Agency (EPA) [6]. Current research efforts are concentrated on the other healthier and environmentally friendly alternatives [3]. Different inorganic fillers like metal hydroxides and silica-containing ceramics (e.g., clays) are promising flame-retardant additives. The mechanical properties of the composite materials prepared with inorganic fillers would be another concern. The inorganic fillers should be added at levels which wouldn't adversely affect the mechanical properties of the polymer.

Nanotechnology and nanomaterials may present promising enhancements in many applications, since the physicochemical properties of materials are superior when they are in nanosize. The decreasing size and increasing surface area make the nanomaterials more reactive. The effects of atomic/molecular interactions (e.g., interactions among charged groups like dipoles) with neighbouring materials become more abundant in the material characteristics. These new characteristics of nanocomposites result in enhanced properties. Possible enhancements can be observed for the thermal and mechanical properties of the composites with relatively lower filler content [7,8].

Nanoclays which are composed of alternating layers of tetrahedral silicate ($SiO_4^{4-}$) and octahedral aluminium oxide-hydroxide ($[AlO_3(OH)_3]_6$) are attracting the attention of researchers for the preparation of polymer nanocomposites [7]. They were reported to enhance the nanocomposite properties in terms of mechanical characteristics, ultraviolet (UV) resistance, and flame retardancy more than macro/micro forms of clays [8]. These enhancements are consequences of the larger surface area of nanoclay platelets interacting with the polymer matrix. Increased interaction of nanoclay with the polymer matrix decreases the necessary amount of clay to possess the enriched property levels (e.g., flame retardancy, mechanical properties). These clay-polymer nanocomposites can be used in different fields like packaging, electronics, automotive, aerospace, water treatment, construction, and biomedical applications [9].

Montmorillonite (MMT) is a widely used plate-like (2D) clay with a chemical formula of $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$ [7]. Its availability, high surface area (up to 750 $m^2/g$) and plate-like structure with a high aspect ratio (100-500) are some of its advantageous properties [10]. The negative charge of the alternating layers of tetrahedral $SiO_2$ and octahedral $AlO_6$ are compensated by the cations (e.g. $Al^{+3}$, $Mg^{2+}$) to have charge neutrality [9]. It can act as a thermal barrier in the polymer composite to prevent combustion and it tends to improve the mechanical properties of the polymer composite [5]. The mechanism of flame retardancy of MMT-like nanoclays are expected to take place by the formation of a barrier layer during the combustion process with the contribution of non-flammable nanoclay platelets and carbonaceous residues of polymer oxidation (i.e., formation of an improved char layer) [5]. The better dispersed the nanoclay platelets in the polymer, the better barrier formation for oxygen and combustible gases diffusion and consequently better flame retardancy. The nano form of clays can be loaded in lower ratios than micro/macro forms to provide flame retardancy (e.g. 5-15 % instead of 50%), potentially preserving or even improving the mechanical characteristics of the polymer [2]. The plate-like structure with a high surface area and aspect ratio of MMT also makes it a good candidate to increase the mechanical properties of the nanoclay polymer composites since it increases the possibility of stress transfer from the polymer matrix [10]. The Young's modulus values for MMT were reported as 51 GPa (via extrapolation using epoxy/clay data) and 14 GPa (via extrapolation using acoustic data) [8].

The nanoclay polymer composites can be prepared by different methods like the solvent solution method, melt mixing and in situ polymerization [11], and sol-gel technique [8]. In the solvent solution method, the polymer is dissolved in the proper solvent, and nanoclay is dispersed. The nanoclay platelets swell in the solvent, and polymer with solvent penetrates among the layers forming the nanoclay [8]. The penetration of polymer-solvent among the layers happens at different levels; the ultimate penetration results in total separation of the layers (Figure 1).

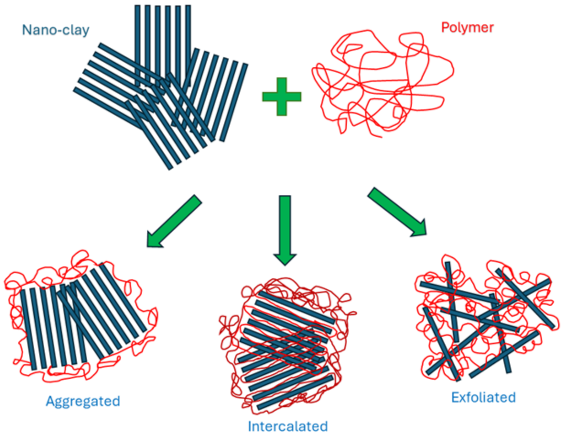


**Figure 1.** Nano-clay morphologies in polymer blends

The level of penetration can be affected by many parameters like interactions in the polymer/nanoclay/solvent system (e.g., type and ratios of clay, polymer, and solvent). The polymer/nanoclay surface characteristics (e.g,. polarity) in the presence of solvent could be determining on the separation of layers of nanoclay and penetration of polymer among them. The microstructure and properties of the composite after evaporation of the solvent are a result of these interactions among the polymer, nanoclay and the solvent. The surface of the nanoclay can be modified to enhance its compatibility with the polymer.

The organic chains added to the nanoclay surface change its surface polarity and tend to increase its affinity to the polymer chains. These surface modifications are aiming for better compatibility between the nanoclay and the polymer to suspend the nanoclay more efficiently to end up with a more homogeneous structure after solvent evaporation [9]. The aggregated clay particles become either intercalated (polymer penetrates in between the layers) or exfoliated (the layers are mostly separated from each other with the excess penetration of polymer) in the nanoclay/polymer suspension, resulting in more homogeneous suspension of nanoclay the parameters are optimized (Figure 1) [9]. The local aggregations of nanoclay result in a non-homogeneous composite structure with possibly worse mechanical properties and vice versa. Other properties of the nanocomposite can be affected by the distribution of nanoclay within the polymer matrix as well.

Ethylene vinyl acetate (EVA) copolymer is widely used in many sectors, including the wire and cable sector [11]. It possesses advantageous physicochemical characteristics and ease of compounding different additives or polymers (e.g., even with hydrophilic polymers like polylactic acid (PLA) with some fillers) [12]. The relatively low tensile strength and thermal stability of EVA copolymers could potentially considered disadvantageous [11]. The varying vinyl acetate (VA) content (e.g., 10-40%) has an influence on the properties of the EVA copolymer [10]. EVA copolymers with varying VA content are reported to cover the largest market share of the ethylene copolymers [13]. The VA content in EVA was reported to be effective on its physicochemical properties (e.g., crystallinity [13], polarity, and elastic characteristics [14]). The increased VA content in the copolymer (EVA) results in higher polarity but lower crystallinity, which can affect the mechanical behaviour of the polymer (or its composites) [15]. Also, the increasing polarity with a high VA content in the polymer was reported to improve its interaction with the clay which enhance the mechanical properties (e.g., Young's modulus, yield strength) of the EVA/nanoclay composite [15]. Moreover, inorganic fillers (e.g., clays, layered double hydroxides (LDHs)) can be used to enhance the flame retardancy of EVA copolymers [11]. The EVA and nanoclay combination has numerous industrial uses, including packaging films, adhesives and cables [16].

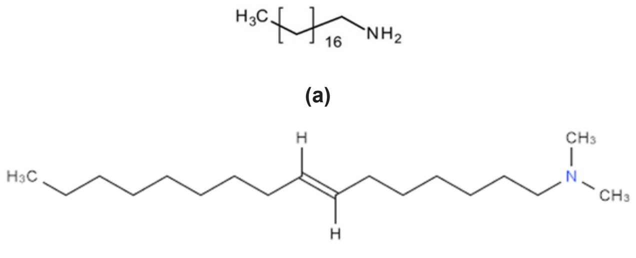
Boron compounds (e.g., boric acid (BA) ($H_3BO_3$) [17]) have significant potential as flame retardant ingredients in polymer-based products because of their low toxicity, chemical structure, and variety of flame retardant mechanisms [18]. They can act as flame retardants and smoke suppressors [19]. They are environmentally friendly and present synergistic effects with other flame retardant additives [18]. Therefore, they can be used in polymer composites either separately or with other additives [17]. Their utilization (e.g., boric acid and boron oxide) in textile materials as flame retardant additives was also reported [20]. BA was reported to degrade in 2 steps: first it was dehydrated forming meta boric acid ($HBO_2$) and then again dehydrated to form boron oxide ($B_2O_3$) resulting in 56% of mass left as char [21]. It was noted to act as a cross-linking agent hindering the oxidation of polymer during decomposition and preventing dripping (keeping the burnt material intact) [22]. Besides, the high char residue acts as a barrier and consequently hamper the combustion process [23]. BA was reported to increase the char yield and even stop afterglow when used >10% in cellulose-based films [18]. The beneficial effect of BA addition (2%) on bending strength of polymer composites prepared by using paper mill sludge (PMS) was reported [24].

Even though EVA copolymer is one of the most important copolymers which are used in various applications in different industries thanks to superior and adjustable physicochemical properties (e.g., by adjusting VA content), the studies about EVA copolymer and increasing its flame retardancy are limited in the literature. The studies about enhancing flame retardancy of polymers are not investigating the effects of flame retardant additives on the mechanical characteristics of the composite, in general. The boron-containing compounds are drawing attention as additives to be used in polymer composites for enhanced flame retardancy. In the current study, EVA/nanoclay composites were prepared by using two different organo-modified nanoclays (montmorillonite-MMT) by using the solvent solution method. The effects of clay type/content and presence/absence of boric acid (BA) on the flame retardancy and mechanical properties of the composites were investigated. The current study is expected to supply data for possible use of nanoclays and BA in the enhancement of the flame retardancy of EVA copolymer while considering the mechanical characteristics of the composite as well.

## 2. Materials and Methods

### *2.1. Materials*

EVA (containing 26 wt. % of VA) was kindly supplied by HES Cable Company (Kayseri, Türkiye). Surface-modified nanoclays were products of Sigma-Aldrich Co., Ltd. (USA). The nanoclay with the code 682632 contains 15-35 wt.% octadecylamine (Figure 2a),



(a)

(b)

**Figure 2.** Chemical structure of a) octadecylamine and b) dimethyl dialkyl (C14-C18) amine

0.5-5 wt.% aminopropyltriethoxysilane, and the nanoclay with the code 682624 contains 35-45 wt.% dimethyl dialkyl (C14-C18) amine (Figure 2b). The boric acid used in the study was a product of Amresco Co. Ltd. (USA) Other chemicals and solvents were products of Merck Co. (Germany). All materials were used in their original form.

### *2.2. Preparation of EVA/NC and the EVA/NC/BA Nanocompositess*

35 ml of chloroform were added to 3.5 g of ethyl vinyl acetate (EVA) polymer in the capped glass jar. The polymer was dissolved in chloroform using a heated magnetic stirrer ($T_{mix}$: 40-50 °C) keeping it stirred overnight. To avoid flocculation, the additives in powder form were added gradually. The amounts of additives are given in Table 1. NC 1 and NC 2 are nanoclays with codes 682632 and 682624, respectively. The samples prepared with BA addition were coded with -BA extension.

**Table 1.** Samples and their contents

| Sample | Polymer (g) | Nano-Clay (g) | Boric Acid (g) | Polymer / Nano-Clay / BA |
|---|---|---|---|---|
| **Control** | 3.5 | 0 | 0 | 100 / 0 / 0 |
| **NC 1.1** | 3.5 | 0.035 | 0 | 100 / 1 / 0 |
| **NC 1.2** | 3.5 | 0.07 | 0 | 100 / 2 / 0 |
| **NC 1.3** | 3.5 | *0.35* | 0 | 100 / 10 / 0 |
| **NC 1.4** | 3.5 | 0.7 | 0 | 100 / 20 / 0 |
| **NC 2.3** | 3.5 | 0.35 | 0 | 100 / 10 / 0 |
| **NC 1.3-BA** | 3.5 | *0.35* | 0.0175 | 100 / 10 / *0.5* |
| **NC 2.3-BA** | 3.5 | *0.35* | 0.0175 | 100 / 10 / *0.5* |

The mixtures were promptly put into glass petri dishes after being mixed and homogenized, where they were dried in the hood. The dried films were sliced into strips of 1-1.25 cm width and 10-12.5 cm length for the mechanical (tension) test and burning test, respectively. The remaining parts were used for further characterization.

### *2.3.Characterization of the EVA/NC and the EVA/NC/BA Nanocomposites*.

### *2.3.1. Fourier transform infrared (FTIR) spectroscopy*

FTIR technique was used to characterize the chemical structure of the prepared nanocomposite materials (Thermo Scientific Nicolet 6700). The ATR crystal module was used in the analysis.

### *2.3.2. Thermal analysis (TGA)*

The thermal behaviour of the samples with or without the additives (nanoclay/BA) was determined by using a multipurpose thermal analysis instrument (Perkin Elmer, STA 8000, USA). The analysis was performed under nitrogen flow (20 mL/min.) in the temperature range of 30-800 °C with an increment rate of 10°C/minute.

### *2.3.3. X-Ray diffraction (XRD) analysis*

The crystallinity of the samples was analysed by using X-ray diffraction analysis (Bruker D8 Discover, USA) (2θ: 0° to 50°, Cu Kα radiation (α = 0.15406 nm)).

### *2.3.4. Mechanical properties*

According to ASTM D882 standard for thin plastic specimens, the tensile properties were assessed on specimens cut out from dried composite sheets (100 mm × 10 mm, thin films) using SHIMADZU AG-X 50 kN universal testing equipment (Japan). The strain rate and load cell capacity were 15 mm × $s^{-1}$ and 50 kN, respectively.

### *2.3.5. Flammability tests*

Flammability tests in vertical configuration for thin material were performed via samples prepared with respect to the UL-94 VTM standard. The samples were exposed to flame for 3 seconds, and combustion times including the ignition time were recorded (Figure 3).

**Figure 3.** Flammability test

## 3. Results and Discussion

### *3.1. FTIR Spectroscopy*

FTIR spectroscopy is the measurement technique for the identification of organic and inorganic materials by scanning samples and collecting infrared spectra [25]. The purpose of using FTIR was to identify compounds/bonding by investigating the IR absorption/transmission spectrum with the presence/absence of peaks on the IR plot. The comparison of the IR spectra enables determining the resemblance/difference of the bonding and possible impurities in the material. The FTIR spectra of the samples are shown in Figure 4. The spectra of neat EVA (control) and all other samples with varying ratios of different additives are almost similar, indicating the additives are physically blended but didn't form new bonds with the EVA matrix.

The only exceptional IR absorption peak was for sample NC 1.3 at 1590.77 cm$^{-1}$ (Figure 4), which may be attributed to the increased additive (NC 1) content which has considerable organic surface modifier (15-35 wt.% (Figure 2a)). FTIR bands between 3250-3400 cm-1 and 1580-1650 cm$^{-1}$ were reported to be related with the NH stretching and bending, respectively [26]. The broadening and decreasing intensity for the NH stretching band was claimed to be an indicator of hydrogen bonding formation between the organic modifier octadecylamine and the nanoparticles [27]. The molecular formula of EVA is $(C_2H_4)_n(C_4H_6O_2)_m$. The structure of EVA appears to have ketone, alkene and alcohol functional groups. The peaks at wavenumbers of 1236 and 2916 cm$^{-1}$ was attributed to vibrations of C=O (1240 cm$^{-1}$) and aliphatic $CH_2$ group (2920 cm$^{-1}$), respectively [28]. The peak at 1733 cm$^{-1}$ (1735 cm-1 for the current study) was attributed to C=O vibration [29] while peaks at 1240 cm$^{-1}$ (1236-7 cm$^{-1}$ for the current study) and 1019 cm$^{-1}$ were related with C-O stretching due to the presence of polar VA groups in the EVA [30]. C-H asymmetric and symmetric stretching and bending were attributed to the peaks 2914 cm$^{-1}$ (2916 cm$^{-1}$ for the current study), 2816 cm$^{-1}$ (2849 cm$^{-1}$ for the current study) and 1469 cm$^{-1}$ (1464-7 cm$^{-1}$ for the current study) [30]. The peaks at 1365 cm$^{-1}$ (1371 cm$^{-1}$ for the current study) and 717 cm$^{-1}$ (719 cm$^{-1}$ for the current study) were related to $-CH_3$ symmetric vibration and C-H rocking vibration, respectively [30]. Bartolomei et al. also reported the inorganic nano-filler addition did not change the FTIR spectra which is in accordance with the results of the current study [30].

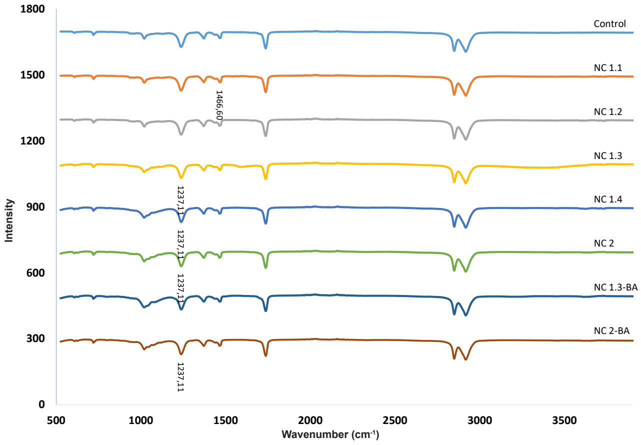


**Figure 4.** The FTIR spectra of neat EVA (control) and EVA with additives

### 3.2. X-Ray Diffraction (XRD) Analysis

The X-ray diffractograms of the neat EVA and the samples with additives are shown in Figure 5. Neat EVA has a peak at a 2θ value of 21° and there is a shouldering peak at around 23°, which were attributed to (110) and (200) planes, respectively [13, 30]. The peak intensities of these peaks were decreasing with the addition of nanoclays (especially for NC 1 addition) which can be indicating a possible decrease in the crystallinity of EVA. The crystallinity of the EVA copolymers with 24 and 28 wt. % VA was reported to be 19% and 13%, respectively [13]. The neat EVA copolymer used in this study with 26 wt. % VA content may have a crystallinity among these values, since the crystallinity of EVA was reported to decrease with increasing VA (vinyl acetate) content [13]. It was mentioned that the crystallinity of the melt-blended EVA (9, 18 or 28% VA) with surface modified MMT (Cloisite 15 A or 30 B) was decreasing with increasing nanoclay content (0, 2.5, 5 or 7.5 %) (and with the increasing VA%) [15]. There are no other characteristic peaks for NC 1 added samples, indicating the nanoclay is well-exfoliated in the polymer matrix. It was mentioned the characteristic peaks of nanoclay were absent when it is totally intercalated/exfoliated in the composite [31]. There is a peak at a 2θ value of 6.9° for the NC 2 added samples with relatively lower intensity which may be attributed to the presence of agglomerated or intercalated nanoclay/polymer morphology in the polymer matrix (i.e., the nanoclay NC 2 was not totally exfoliated) (Figure 5). The peaks for the (001) plane for montmorillonites (MMTs) were reported with 2θ values of 7.4° and 5.6° for Na- and Ca-MMT which were in accordance with the 2θ value in the current study [32].

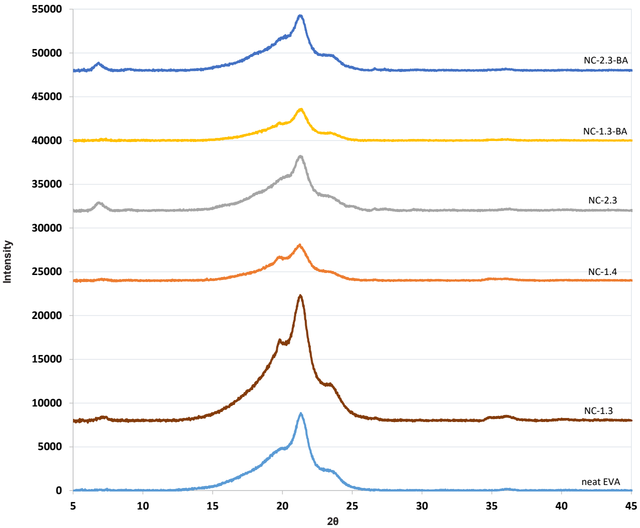


**Figure 5.** The XRD analysis diffractograms of neat EVA and nano-clay and/or BA added samples

### 3.3. Thermal Analysis (TGA/D-TGA)

Thermal behaviour of the neat EVA and the selected composites prepared by adding nanoclay 1 and 2 (NC 1 and NC 2) and/or BA were investigated via a multipurpose thermal analyser. TGA (thermogravimetric analysis) was also performed for the organically surface modified neat nanoclay (NC 1 and NC 2) samples.

The TGA (thermogravimetric analysis) results are shown in Figure 6a (for the temperature range of 30-800 °C) and in Figure 6b (for the temperature range of 200-550 °C). The onset and offset temperatures of the neat EVA (control) and EVA with additives are tabulated in Table 2 and Figure 6c.

**Table 2.** The onset, offset temperature values, % weight loss values between onset temperatures and residual weight (%) from TGA for the control (neat EVA) and the EVA composites with different additives

| Sample | onset T1 | Δ1 (mass%) | onset T1a | Δ1a (mass%) | onset T2 | Δ2 (mass%) | offset T | residue (mass%) |
|---|---|---|---|---|---|---|---|---|
| Control (neat EVA) | | | 326.07 | 25.238 | 448.69 | 73.596 | 525.53 | 1.801 |
| NC 1.3 | 280.29 | 7.465 | 334.75 | 13.159 | 454.41 | 69.538 | 533.24 | 9.669 |
| NC 1.4 | 280.83 | 13.676 | 359.96 | 7.025 | 448.00 | 64.994 | 506.86 | 15.537 |
| NC 2.3 | | | 314.40 | 20.175 | 441.38 | 72.514 | 494.68 | 8.223 |
| NC 1.3-BA | 280.43 | 8.235 | 334.02 | 13.45 | 457.92 | 71.605 | 513.95 | 9.298 |
| NC 2.3-BA | | | 319.76 | 20.104 | 443.42 | 72.299 | 495.78 | 8.135 |

**Table 3.** The 5%, 10% and 50% weight loss temperature values from TGA for the control (neat EVA) and the EVA composites with different additives

| Sample | T (-5%) | T (-10%) | T (-50%) |
|---|---|---|---|
| **Control (neat EVA)** | 333.2 | 346.9 | 459.3 |
| **NC 1.3** | 293.7 | 329.9 | 468.5 |
| **NC 1.4** | 293.1 | 305.6 | 461.3 |
| **NC 2.3** | 325.5 | *338.9* | 457 |
| **NC 1.3-BA** | 294.3 | 323.5 | 468.7 |
| **NC 2.3-BA** | 347.3 | *363.6* | 458 |

The temperature values for 5%, 10% and 50% weight loss are shown in Table 3 and illustrated in Figure 6c. The TGA graphs for the nanoclays NC 1 and NC 2 are shown in Figure 7.

The neat EVA (control) has 2 main steps of weight loss as was reported in the literature [13, 33]. The first was attributed to the deacetylation (removal of acetate groups from the backbone) and the second was related to the chain scission of the polymer backbone taking place at relatively higher temperatures [13, 21, 29]. It was the case for the TGA analysis of the neat EVA (control) (Figures 6a and 6b). The onset temperature for the first step (onset T1) was 326.07°C ended and after 25.2% weight loss. The second step initiated at (onset T2) 448.69°C and the weight loss was 73.6% (Table 2). Diez et al. performed TGA for EVA samples with varying acetic acid content (12.5-33% (w/w)) and showed the correlation of the weight loss at the first step with the acetic acid content of the EVA copolymer [13]. Luna et al. mentioned the first weight loss step was between 330-390 °C, and the second step was above 430°C for the neat EVA, which is in accordance with the current data [29].

### *3.3.1. Effect of nanoclay addition on thermal stability*

The thermal degradation profile of EVA was considerably changed, especially with the addition of NC 1 (Figures 6a and b). Interestingly, the addition of both nanoclays resulted in thermal instability for the EVA composites. The first onset temperature (onset T1) for the EVA/nanoclay composites were lower than the value for the neat EVA (326.07°C) (Table 2, Figure 6c).

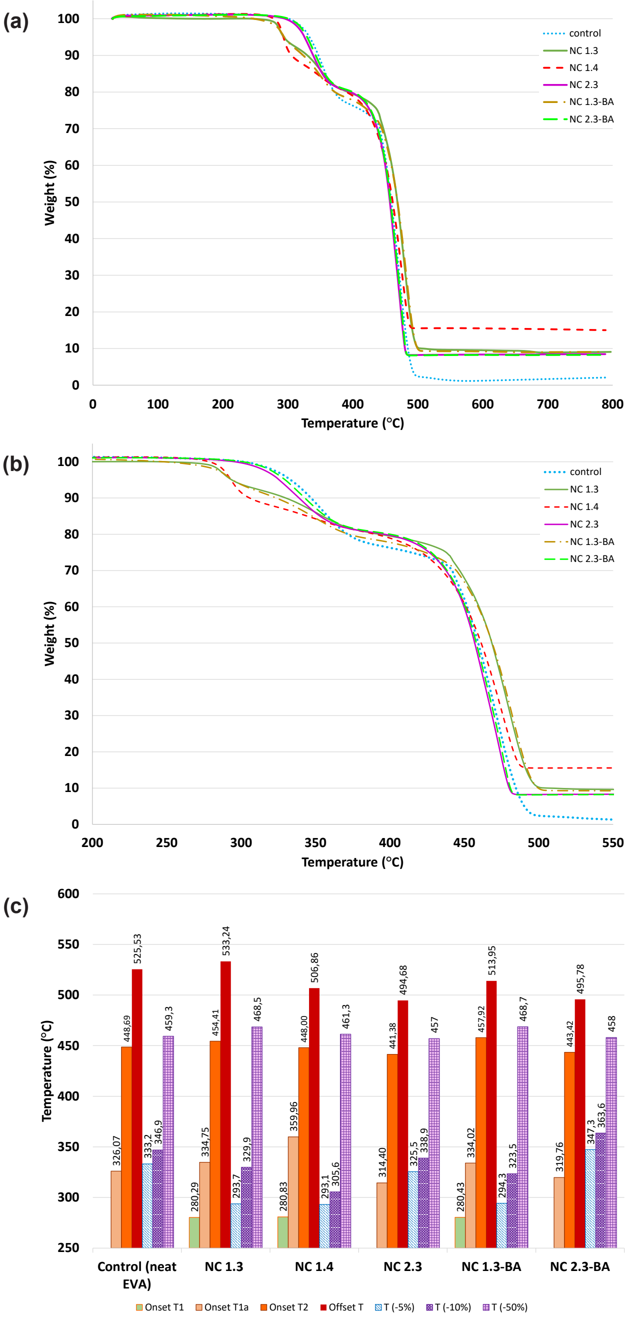


**Figure 6.** a. TGA graphs for the samples neat EVA (control), NC1.3, NC 1.4, NC 2.3, NC 1.3-BA and NC 2.3-BA (30-800°C), b. TGA graphs for the samples neat EVA (control), NC1.3, NC 1.4, NC 2.3, NC 1.3-BA and NC 2.3-BA (200-550°C), c. The onset, offset, 5, 10 and 50% weight loss temperature values from TGA for the neat EVA and the EVA composites with different additives

The organic surface modifiers of the nanoclays may be the reason for the initiation of the thermal degradation at relatively lower temperatures. The TGA results for the neat nanoclay samples (NC 1 and NC 2) also showed that the thermal degradation initiated at relatively lower temperatures (Figure 7).

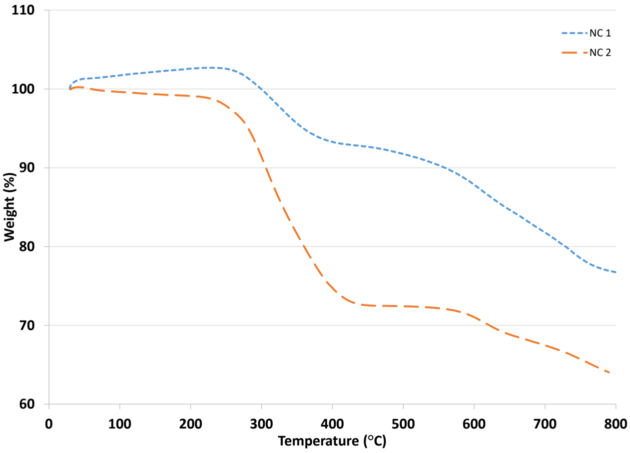


**Figure 7.** The TGA results for the neat nano-clays (NC 1 and NC 2)

TGA result for NC 1 showed that it was gaining some weight at relatively lower temperatures indicating a probable nitrogen adsorption/binding (Figure 7) followed by weight loss with increasing temperature. The onset temperatures were 264°C and 269°C for NC 1 and NC 2, respectively. The effect of thermal instability was more severe for the EVA/nanoclay samples with NC 1, which were with exfoliated morphology. The homogeneously distributed nanoclay platelets in the exfoliated morphology of the EVA/NC 1 composites let the organic surface modifier on the nanoclay surface more exposed to surface reactions which resulted in thermal degradation at relatively lower temperatures. The thermal degradation took place in 3 main steps (i.e., there was one additional step at relatively lower temperatures compared to neat EVA degradation) (Figures 6a and b). The weight loss at lower temperatures was increasing with increasing NC 1 content. NC 1.4 (nanoclay/polymer: 20/100) lost more weight (%) than NC 1.3 (and NC 1.3-BA) (nanoclay/polymer: 20/100) at these lower temperatures showing the effect of nanoclay (i.e. organic surface modifier) ratio (Figures 6a and b).

The onset temperature for the second step of degradation (onset T1a) was higher for NC 1.3 (334.75°C) than neat EVA (326.07°C) (Table 2). The weight loss at this step was relatively lower for NC 1.3 (13%) compared to the neat EVA (25%). The total weight losses at steps 1 and 2 were 7.5 and 13% (21.5 5 in total) for NC 1.3, and this was lower than the weight loss of neat EVA in that temperature range (25%)(Table 2). This may indicate the mass loss was hampered with the addition of NC 1 during TGA. The increasing amount of NC 1 resulted in an even a higher onset T1a which was 359.96°C for NC 1.4. The weight loss ratios for the first and second step were 13.7% and 7% for the sample NC 1.4 (20.7% in total), indicating the higher NC 1 content (i.e., higher organic surface modifier) resulted in higher weight loss at lower temperatures compared to NC 1.3. The total mass loss was slightly lower for NC 1.4 (20.7%) than NC 1.3 (21.5%) which may indicate an increasing resistance against mass transfer with increasing NC 1 content in the EVA/nanoclay composite.

The onset T2 for NC 1.4 was (448°C) almost similar to the value for the neat EVA (448.7°C), while it was slightly higher for NC 1.3 (454.4°C) (Table 2). The weight loss (%) values for this step of thermal degradation were decreasing with NC 1 addition. The neat EVA sample lost 73.6% of its weight, while NC 1.3 lost 69.5% and NC 1.4 (with higher NC 1 content) lost 65% of its weight at this step (Table 2). The offset T value was the highest for NC 1.3 (533.2°C) among all samples. It was 506.9°C for NC 1.4 and 525.5°C for the neat EVA (Table 2). The residual weight was 1.8% for the neat EVA, while it was 9.7% and 15.5% for NC 1.3 and NC 1.4, respectively, showing the residual mass increased with increasing nanoclay addition to EVA/NC 1 composites.

The NC 2.3 sample had 2-step thermal degradation like EVA, which may be attributed to its morphology (intercalated or partially aggregated). The onset temperatures (onset T1a and T2) were lower for NC 2.3 than the neat EVA, indicating NC 2 resulted in some thermal instability for EVA composites. The weight loss(%) ratios were lower for NC 2.3 compared to the neat EVA, indicating the resistance against mass loss was increased by NC 2 addition. The weight loss (%) was even lower for NC 1.3 (69.5%) (with a similar EVA/nanoclay ratio) than NC 2.3 72.5%) (Table 2). That lower weight loss value may be attributed to higher mass transfer resistance by NC 1.3 which was with exfoliated morphology (i.e. well-separated, more homogeneously distributed platelets in the EVA/nanoclay composite).

The temperatures for certain mass loss ratios (e.g., 5% or 10%) are also used to monitor the thermal characteristics of the composites [23, 29]. The temperatures at which there was a mass loss of 5, 10 and 50% are tabulated in Table 3 and illustrated in Figure 6c.

The samples with NC 1 were with the lowest T (-5%) and T (-10%) values which were considerably lower than the values for the control (the neat EVA: T (-5%): 333.2°C and T (-10%): 346.9°C), which may be attributed to the thermal instability due to the organic surface modifier on NC 1. Yao et al. reported a T (-5%) value for the neat EVA (14% VA) of 349.6°C, which was higher than the value determined in the current study [23]. That higher value may be attributed to the lower acetate content of the copolymer (14 vs. 26%). Luna et al. reported a T (-10%) value of 337.7°C for the neat EVA (28% VA) which was slightly lower than the current result, and it may be attributed to the different (higher) acetate content (28 vs. 26%) [29]. Nyambo et al. reported a T (-10%) value of 351°C, which was slightly higher than the value in the current study [21]. The EVA they used had a lower acetate content (18%) which may explain the higher T (-10%) value [21]. Sample with NC 2 (NC 2.3) had T (-5%) and T (-10%) values relatively closer to the values of the control (Table 3, Figure 6c).

Ryu et al. also observed different TGA curves for MMT-EVA composites which were prepared either with MMT without surface modification or surface-modified using different organics, which was the case observed in the current study for 2 different nanoclays (NC1 and 2) with different surface modifications [11]. Ryu et al. used the T (-50%) for comparing the thermal stability of the EVA composites prepared by different inorganic fillers which were either surface modified or not [11]. They reported a T (-50%) value of 432°C for the neat EVA (28% VA) which was lower than the value in the current study (459°C). The difference may be attributed to TGA parameters and VA %. They reported surface-modified montmorillonite (MMT) added to EVA at a ratio of 6% (among the samples 1-12%) resulted in the highest T (-50%) (ΔT=28°C, higher than T (-50%) value of the neat EVA) and claimed to be the best sample in terms of thermal durability [11]. In the current study, the T (-50%) values were slightly lower than the value of the neat EVA for NC 2.3 while it was higher for NC 1.3 (ΔT = 9°C), which may be indicating the NC 1.3 had a higher mass transfer resistance hampering the thermal degradation (i.e. weight loss).

### *3.3.2. Effect of BA addition on thermal stability*

BA addition to the samples with NC 1 did not affect the thermal degradation behaviour of the samples drastically, considering the TGA results. The TGA profiles of samples NC 1.3 and NC 1.3-BA coincide with each other considerably (Figures 6a and 6b). The onset temperatures T1 and T1a were almost similar, while onset T2 was slightly higher for NC 1.3-BA, and offset T was slightly higher for NC 1.3 (Table 2). Weight loss(%) values were also comparable for the 3 weight loss steps for NC 1.3 and NC 1.3-BA, which were slightly higher for NC 1.3-BA, and the mass residue(%) was slightly higher for NC 1.3, indicating the BA addition slightly decreased the resistance to mass transfer during thermal decomposition.

The thermal degradation behaviour of NC 2.3 and NC 2.3-BA was almost similar considering the TGA profiles for these samples (Figures 6a and 6b). The thermal degradation occurred in 2 main steps, like neat EVA (i.e., the step at relatively lower temperatures observed for the samples with NC 1 was not observed for the samples with NC 2). The onset temperatures (T1a and T2) were slightly higher for NC 2.3-BA (Table 2), which may indicate BA addition slightly increased thermal durability. The weight losses(%), offset T and residual weight (%) values were comparable for NC 2.3 and NC 2.3-BA (Table 2). Nyambo et al. reported a residue % of 6 for the EVA-BA (10%) sample and of 1% for the neat EVA after reaching 800°C, which were comparable with the current results [21].

The T (-5%) value of the sample NC 1.3 (293.7°C) was close to the value of sample NC 1.3-BA (294.3°C), while T (-10%) values were different for these samples with NC 1. It was 305.6°C for the sample NC 1.3 and was higher for the sample NC 1.3-BA (323.5°C), which may indicate the effect of BA in the suppression of thermal decomposition at relatively lower temperatures (Table 3 and Figure 6c). The T (-5%) value for the sample NC 2.3 was 325.5°C and it was 329.5°C for the sample NC 2.3-BA, showing the possible effect of BA in suppressing the thermal degradation at relatively lower temperatures. T (-10%) values for NC 2.3 and NC 2.3-BA were 338.9°C and 363.6°C, respectively. The T (-10%) value of the control sample (the neat EVA) was in between these values (346.9°C). the presence of BA in composites with NC 2 may be hindering the weight loss with increasing temperature (at relatively lower temperatures). Nyambo et al. reported T (-10%) value for the neat EVA as 351°C, which was comparable with the current result (347°C) [21]. They reported 10% BA addition resulted in thermal instability for EVA-BA composite at relatively lower temperatures (100-350°C), which was attributed to degradation of boric acid to form water and $B_2O_3$, resulting in a 4°C increase in T (-10%) value compared to neat EVA [21]. In the current study, NC 2.3-BA also had a higher T (-10%) value (343°C) than NC 2.3 (339°C) where ΔT was also 4°C, but the BA amount (used with NC 2) was relatively lower.

The BA addition (with NC 2) did not affect the thermal decomposition temperature (T (-50%)) of the EVA/nanoclay composite considerably. The T (-50%) values were comparable for the neat EVA and for both NC 2 containing samples with and without BA addition (Table 2 and Figure 6c).

### *3.3.3. Derivative TGA (D-TGA) results*

The D-TGA (derivative weight loss %, i.e., weight loss per time (%/min)) graphs are shown in Figure 8a. The peak temperatures at which the weight loss(%) with increasing temperature in time was maximized can be seen in Table 4 (and in Figure 8b). There were 2 peak temperatures (peak T1a and peak T2) for the control (neat EVA) and samples with NC 2 (with 35-45 wt.% dimethyl dialkyl (C14-C18) amine (Figure 2b) as an organic surface modifier) and 3 peak temperatures (peak T1, peak T1a and peak T2) for samples with NC 1 (with 15-35 wt.% octadecylamine, Figure 2a).

The first peak temperature (peak T1a) values were 351.19, 336.59, and 340.95°C for the control (neat EVA), NC 2.3, and NC 2.3-BA samples, respectively. The peak temperature values (Peak T1a) for the samples with NC 2 were lower than the value for the control sample. The second peak temperature (peak

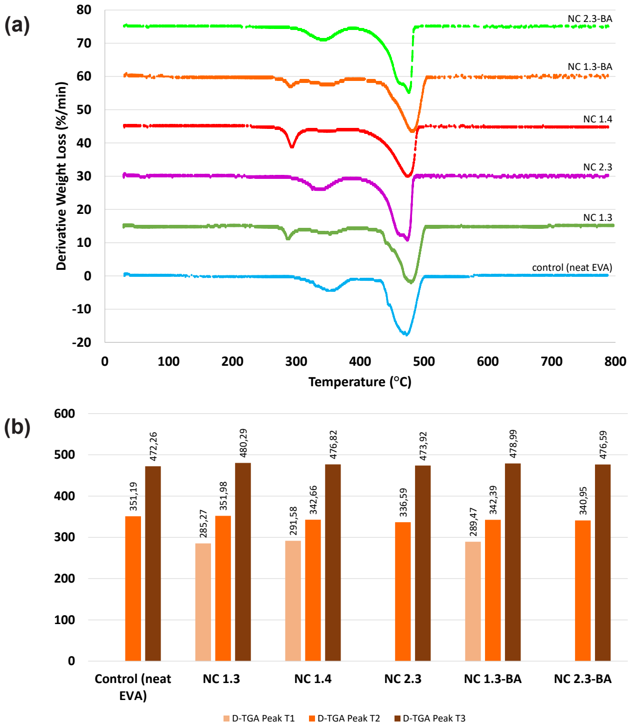


**Figure 8.** a. The TGA results for the neat nano-clays (NC 1 and NC 2), b. The peak temperature values for D-TGA graphs for the control (neat EVA) and the EVA composites with different additives

T2) values were 472.26, 473.92, and 476.59°C for the control (neat EVA), NC 2.3, and NC 2.3-BA samples, respectively. The peak T2 values for the samples with NC 2 were slightly higher than the value for the control sample. Nyambo et al. reported a peak T value for the second step of neat EVA (VA 18%) thermo-degradation as 456°C [21], which was lower than the value for the copolymer (EVA, 26%) in the current study. The peak T value for a lower acetate content was expected to be a higher value, but it was lower, probably because of TGA parameters (e.g., the heating rate was higher: 20 [21] vs. 10°C/min for the current study). Yao et al. reported the peak temperature for the second step of neat EVA degradation as 474.7°C, which was slightly higher than the value reported 472.3°C in the current study [23]. The difference may be attributed to the lower acetate content in the study by Yao et al. [23]. Osman et al. reported the peak temperature values of the first step (deacetylation) as 350, 346 and 348°C for neat EVA (18% VA), EVA with 5% MMT, and EVA with 5% pretreated MMT, respectively [33]. The peak T values for MMT-added samples (composites) were lower than the neat EVA (as was in the current study) which was attributed to the catalytic effect of degradation products (of the surface modifier) [33]. For the second step of the degradation compared to neat EVA (449°C) higher peak temperatures were reported by Osman et al. for the samples with 5% MMT addition [33]. The pretreated MMT was reported to increase the peak temperature more (495°C) than the untreated MMT (470°C) [33]. They attributed the better exfoliation of pretreated nanoclay in the composite resulted in higher thermal durability (i.e., increased the second step peak T) [33]. The peak T for the second step of degradation (peak T2) for EVA/nanoclay composites was also higher than the value for the neat EVA in the current study, but the differences were smaller (only 2°C for NC 2.3), which may be attributed to scissoring (defragmentation) of the polymer backbone being slightly hampered in the presence of nanoclay (NC 2) addition.

**Table 4.** The peak temperature values for D-TGA graphs for the control (neat EVA) and the EVA composites with different additives (na: not available)

| Sample | D-TGA Peak T1 | D-TGA Peak T1a | D-TGA Peak T2 |
|---|---|---|---|
| **Control (neat EVA)** | na | 351.19 | 472.26 |
| **NC 1.3** | 285.27 | 351.98 | 480.29 |
| **NC 1.4** | 291.58 | 342.66 | 476.82 |
| **NC 2.3** | na | *336.59* | 473.92 |
| **NC 1.3-BA** | 289.47 | 342.39 | 478.99 |
| **NC 2.3-BA** | na | *340.95* | 476.59 |

The BA addition decreased the peak temperature value at relatively lower temperature (peak T1a) and slightly increased the peak temperature at relatively higher temperature (peak T2) for the samples with NC 2 compared to the control sample. The first peak temperature (peak T1a) may be related to the removal of acetate groups from the polymer matrix which took place at relatively lower temperatures with the presence of NC 2. It was suggested that the unknown acetic acid content of a copolymer (EVA) could be determined by using D-TGA data, mentioning the correlation between the intensity of the D-TGA value for the first peak (at relatively lower temperature) and the acetic acid content in the EVA copolymers [13]. The peak temperature (peak T1a) for the sample with BA was slightly higher than the value for the sample only with NC 2. The peak temperature value at relatively higher temperature (peak T2) was also slightly higher for NC 2.3-BA compared to NC 2.3. Yao et al. also reported a slight increase in the peak temperature (Tmax2, peak T2 in the current study) with the addition of BA in the presence of some other additives [23].

There were 3 peak temperatures for the samples prepared via NC 1 (with 15-35 wt.% octadecylamine (Figure 2a), 0.5-5 wt.% aminopropyltriethoxysilane as an organic surface modifier). The additional peak temperature (peak T1) values were 285.27, 291.58, and 289.47°C for the samples NC 1.3, NC 1.4, and NC 1.3-BA, respectively (Table 4). This additional peak may be related to the relatively less thermostable character of the surface modifier used for NC 1 and the exfoliated morphology of the EVA/NC 1 composite. The peak T1 value was slightly higher for the sample with higher nanoclay addition (NC 1.4), which may be attributed to the possible additional mass transfer resistance with increased nano clay content. The peak T1a for NC 1.3 was slightly higher than neat EVA (Table 4). Increasing the NC 1 content decreased the peak T1a from 351.19°C to 342.66°C for NC 1.3 and NC 1.4, respectively, which may be attributed to the increasing organic modifier content with the increase in the NC 1 content. The peak T1a values were 351.98 and 342.39°C for NC 1.3 and NC 1.3-BA (Table 4). BA addition to EVA/NC 2 composite decreased the peak T1a, indicating a possible catalytic effect of BA in VA group removal from the EVA copolymer. The nanoclay addition at higher content (NC 1.4 with EVA/nanoclay: 100/20) and BA addition resulted in decreasing thermal stability at the relatively lower temperatures (i.e., the removal of acetate groups was happening at relatively lower temperatures). The peak T2 values for NC1 and BA-added samples were all higher than the peak T2 of the neat EVA (Table 4). The value increased from 472.26°C to 480.29°C for NC 1.3 (the highest among NC 1 containing samples). The increasing nanoclay content resulted in a relatively lower peak T2 (476.82°C for NC 1.4) which was still higher than the value for the neat EVA. BA addition to EVA/NC 1 composite resulted in peak T2 value of 478.99°C (NC 1.3-BA), which was lower than peak T2 for NC 1.3 (480.29°C), but was still higher than the value for the neat EVA (472.26°C). The NC 1.3 having the highest peak T2 indicates that certain EVA/NC 1 ratio may supply better thermal stability for the defragmentation (scissoring) of main backbone of EVA copolymer and BA addition (NC 1.3-BA) may have some adverse effect on the copolymer's thermostability at this step of thermal degradation.

### 3.4. Mechanical Properties

#### 3.4.1. Effect of nano-clay content

The effect of nanoclay content in the EVA/nanoclay composites on the mechanical properties of the composites was determined by performing tensile tests using EVA/NC 1 samples. The stress-strain graphs for the neat EVA and EVA with varying NC 1 ratios are shown in Figure 9. The addition of NC 1 at a lower ratio (NC 1.1, nanoclay/polymer: 1/100) worsens the mechanical durability of the composite under stress when compared to the control sample (neat EVA), while a higher amount of NC 1 addition (NC 1.2, nanoclay/polymer: 2/100) resulted in a composite with comparable stress-bearing capability with the control. Further increase in NC 1 content enhanced the mechanical durability. NC 1.3 (nanoclay/polymer: 10/100) and NC 1.4 (nanoclay/polymer: 20/100) had higher stress-bearing capacity compared to neat EVA and EVA with relatively lower nano-filler content (Figure 9). It was reported that the increasing inorganic filler content (1-12%) enhanced the stress-bearing characteristics of the EVA composites prepared with different inorganic fillers including montmorillonite (MMT) [11]. It was. also mentioned the decreasing mechanical strength when a small quantity of nanoclay (e.g., 1%) was used, and they attributed this to the dominance of the debonding phenomenon at lower nanoclay concentrations [12]. The results were in accordance with the former studies. The maximum sample elongation was higher for the neat EVA (control), indicating the nanoclay addition resulted in relatively more brittle characteristics.

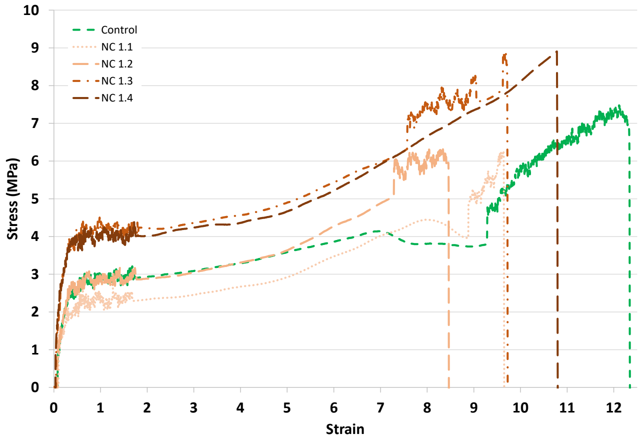


**Figure 9.** The stress-strain curves for neat EVA (control) and EVA with varying nano-clay (NC 1) content

#### 3.4.2. Effect of nanoclay type and boric acid (BA) addition

The effect of nanoclay type (i.e., the type of organic surface modifier on the nanoclay surface) on the mechanical characteristics of EVA/nanoclay composites was determined by applying tensile tests using EVA/NC 1 and EVA/NC 2 composites. The stress-strain curves for this analysis are shown in Figure 10. Both sample NC 1.3 (nanoclay/polymer: 10/100) and NC 2.3 (nanoclay/polymer: 10/100) could bear higher stress values than the control (neat EVA). Sample NC 2.3 was superior to sample NC 1.3. This difference may be attributed to the morphology of the composites. Sample NC 1.3 was totally exfoliated, as was determined via XRD analysis, that there were no peaks of nanoclay on the XRD diffractogram (Figure 5). But sample NC 2.3 had either agglomerated or intercalated nanoclay/polymer morphology. The morphology of the polymer/filler nanocomposites (e.g., exfoliated, intercalated, agglomerated) were reported to affect mechanical properties [34]. The more homogeneous distribution of nanoclay platelets in the EVA matrix for the sample NC 1.3 might result in higher stress-bearing characteristics, but it was not the case. Sample NC 2.3 with intercalated (or partially agglomerated) morphology could bear higher stress values (Figure 10). The mechanical characteristics of EVA/nanoclay composites may be affected not only by the morphology of the composite but also by the interaction of EVA and the organic surface modifier on the nanoclay. The higher stress-bearing capacity of the sample NC 2.3 may be attributed to a better surface interaction of the polymer and the organic surface modifier on NC 2 (Figure 2b) which has a double bond in the middle and two methyl groups at the end of the polymer chain that may form secondary bonding more efficiently with the EVA copolymer (e.g., hydrogen bonding with the oxygen at the VA groups of the EVA copolymer).

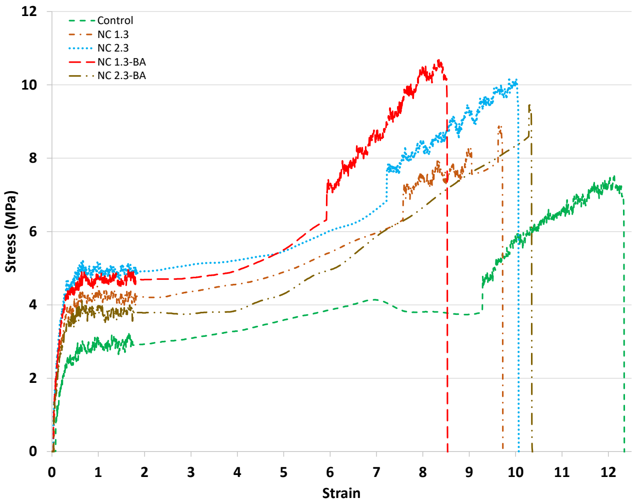


**Figure 10.** The stress-strain curves for neat EVA (control) and EVA with additives (lower stress-strain region)

The possible effect of BA addition on the mechanical properties of EVA/nanoclay composites was investigated by using samples with both NC 1 (NC 1.3, nanoclay/polymer: 10/100) and NC 2 (NC 2.3, nanoclay/polymer: 10/100) either with or without BA addition. The stress-strain curves for these samples are shown in Figure 10. Both samples NC 1.3-BA and NC 2.3-BA could bear higher stress than the neat EVA (like the samples NC 1.3 and NC 2.3 without BA addition). The stress-bearing capacity of the sample NC 1.3-BA was superior to NC 1.3. The NC 1 nanoclay was determined to have a totally exfoliated structure in the EVA matrix with respect to XRD analysis where peaks for the nanoclay were missing in the diffractogram (Figure 5). BA addition did not change the morphology. But the hydroxyl groups of boric acid may serve as extra sites to form hydrogen bonds with the organic surface modifier on the nanoclay with the amine group (N element) (Figure 2a) and EVA copolymer (vinyl acetate group, O and H elements). There was no considerable new primary bonding formation observed with the nanoclay and/or boric acid addition to the EVA copolymer (determined via FTIR analysis, Figure 4), but the strong hydrogen (secondary) bonding formation with the presence of BA might be increasing the stress-bearing capacity of the composite (NC 1.3-BA) (Figure 10). The homogeneous (exfoliated) morphology might be supporting the surface interaction of the nanoclay (i.e., organic surface modifier) with the BA and EVA (i.e., increasing the surface area for interaction). BA addition did not enhance the stress-bearing capacity of the sample with NC 2 (NC 2.3-BA) as it did for NC 1.3-BA. The stress-bearing capacity was still better than the control (neat EVA) but not as satisfactory as the sample without BA (NC 2.3). The reason may be related to the morphology of the sample. Samples with NC 2 (with or without BA addition) had intercalated (or partially agglomerated) morphology (considering the XRD analysis, Figure 5). The nanoclay was not exfoliated in the EVA copolymer, and the surface interaction between filler and polymer is limited compared to the exfoliated morphology. It may be expected that BA will not be as effective as in an exfoliated morphology to enhance bonding, but the negative effect (decreasing the stress-bearing capability) of BA addition was not expected. The organic modifier of NC 2 and EVA had a better bonding capability in the absence of BA, which adversely affected the secondary bonding in the EVA/NC 2/BA matrix.

### *3.4.3. Mechanical characteristics at elastic region*

The Young's modulus (elastic modulus) values for the neat EVA and the composites with a different additives are shown in Figure 11.

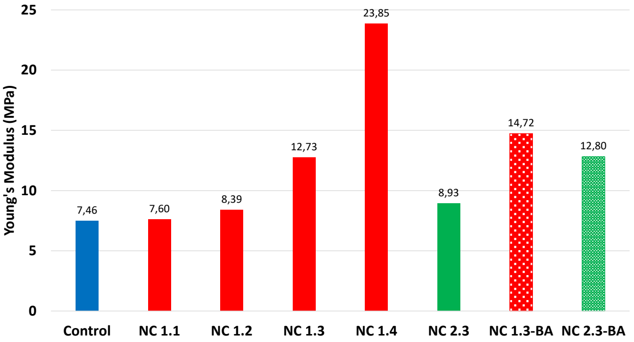


**Figure 11.** The elastic moduli of the neat EVA (control) and EVA with additives

The elastic modulus of the control sample (neat EVA) was 7.46 MPa, which was the lowest among all samples. It was slightly higher for the sample NC 1.1 (nanoclay/polymer: 1/100) with relatively low nanoclay addition (7.46 MPa). The Young's modulus value was increasing with increasing nanoclay (NC 1) content in the composite (almost linearly, Figure 11). Osman et al. reported a slight decrease in the Young's modulus value compared to neat EVA (18% VA) with the addition of 5% surface-modified MMT pretreated either with water or toluene and dried before melt mixing (at 160°C) with EVA [33]. They commented the pretreated surface-modified nanofiller resulted in some plasticizing effect which was attributed to possible interaction of the EVA copolymer and surface modifier of the nanoclay [33]. The numerical values of Young's modulus for neat and 5% MMT-added composites were relatively lower (less than 2.5 MPa) which may be related to the difference in material preparation (melt mixing vs. solvent solution method) [33]. The Young's modulus values for higher NC 1 content were 8.39, 12.73, and 23.85 MPa for the samples NC 1.2, NC 1.3, and NC 1.4, respectively (which had 2/100, 10/100, and 20/100 nanocaly/EVA ratios, respectively). The increase of Young's modulus with increasing NC 1 addition in comparison to the control's value was considerable (e.g., 71% for NC 1.3 and 220% for NC 1.4). Ryu et al. determined the mechanical characteristics of the EVA composites prepared by using different inorganic fillers (including MMT) [11]. It was mentioned that the Young's modulus of the neat EVA (12 MPa) increased with increasing amounts of MMT addition (26 MPa (117% higher) for

12% MMT) [11]. It was also reported the inorganic filler (MMT) addition to EVA increased the Young's modulus value compared to the neat EVA (13 MPa) [2]. The values were 17.1 MPa and 19.3 MPa for the MMT without and with surface modification (via low MW DNA strands) [2]. Aforementioned studies were comparable with the Young's modulus values determined in the current study (Figure 11) [2, 11]. The Young's modulus values for neat EVA were reported as 44 MPa (18% VA) [12] and less than 2.5 MPa (18% VA) [33], which were not that comparable with the values determined in the current study, which may be related to the used EVA copolymer and sample preparation/testing parameters.

The nanoclay type (i.e., the organic modifier on the nanoclay surface) was effective on the Young's modulus values of the nanoclay/EVA composites. The Young's modulus values for NC 1.3 and NC 2.3 (which were both with a nanoclay/EVA ratio of 10/100) were 12.73 and 8.93 MPa, respectively. The possible reason might be the morphological and chemical differences of the composites. NC 1 samples were exfoliated while NC 2 samples were intercalated (or partially agglomerated) with respect to XRD analysis. The exfoliated NC 1-containing sample was lacking the peaks for the nanoclay in the XRD diffractogram while the peak was observed for the NC 2-containing samples (Figure 5). The separated platelets of NC 1 were forming a more homogeneous distribution in the EVA matrix with an enhanced surface interaction between the nanoclay (i.e., organic surface modifier) and the EVA copolymer. That strong interaction between the nanofiller and the polymer might result in a higher Young's modulus value for NC 1.3 compared to NC 2.3 (Figure 11). The difference in the chemical structure of the different organic surface modifiers for NC 1 and NC 2 may also be partially effective on the Young's modulus values. BA addition to EVA/nanoclay composites was increasing the Young's modulus values for both NC1 and NC 2 containing samples (Figure 11). The moduli were 14.72 MPa for NC 1.3-BA (16% higher than NC 1.3) and 12.8 MPa for NC 2.3-BA (44% higher than NC 2.3). The increasing Young's modulus for the EVA/nanoclay composites may be attributed to extra secondary bonding formation between organic surface modifiers on the nanoclay surface and the EVA copolymer due to BA presence in the matrix. Tambe et al. reported even the addition sequence of components in the composite preparation was influential on mechanical characteristics of EVA (28% VA)/LDPE (low density polyethylene)/NC (nanoclay: MMT) composites, indicating the composites composed of EVA/nanoclay/other additives should be prepared and characterized diligently [31].

## 3.5. Flammability Tests

The fire durability of the neat EVA and its composites prepared via nanoclays (NC 1 and NC 2) and BA was determined by using samples prepared with respect to the UL94 VTM standard test. The time for complete burnout (including the 3 seconds for ignition) was determined for each sample. The samples were not self-extinguishing in the time limits of the UL94 VTM test, and drippings were observed (i.e., the samples failed in the UL94 VTM test). The burning time of samples was recorded for comparing the relative contribution of different additives on flame retardancy (Figure 12). It was 29 seconds for the neat EVA.

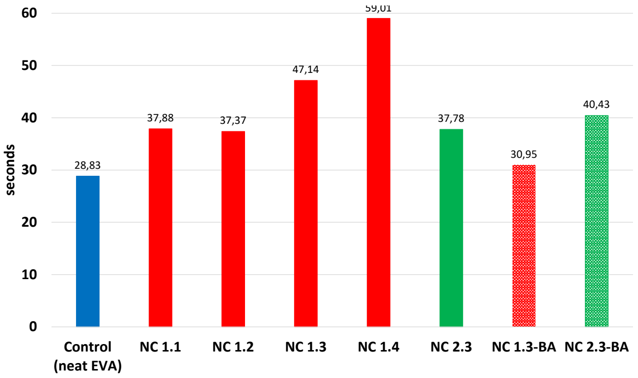


**Figure 12.** Burning durations for the control (neat EVA) and samples with NC and/or BA

### *3.5.1. Effect of nanoclay addition*

The nanoclay addition was observed to increase the burning time. The increasing amount of NC 1 addition (from NC 1.1 (nanoclay/polymer: 1/100) to NC 1.4 (nanoclay/polymer: 20/100)) resulted in an increase in burning time from 38 seconds to 59 seconds (which were 31% and 105% higher than the time for the neat EVA). The addition of 20 parts of NC 1 in the EVA matrix increased the burning time for the composite by 105% (i.e., more than double). NC 2 addition was also beneficial in the elongation of the burnout time. The sample NC 2.3 (nanoclay/polymer: 10/100) had a burning time of 38 seconds which was 31% higher than the time for the neat EVA. The enhancement was not as high as NC 1 addition at a similar ratio. The sample NC 1.3 (nanoclay/polymer: 10/100) had a burning time of 47 seconds, which was 64% higher than the time for the neat EVA. Therefore, the NC 1 is more effective at elongating the burnout time (i.e., suppressing the burning process) than NC 2.

### *3.5.2. Effect of BA addition*

The effect of BA addition was also investigated. Co-utilization of BA with NC 1 did not elongate the burning time. The sample NC 1.3-BA (nanoclay/polymer: 10/100) had a burning time of 31 seconds, which was slightly higher (7%) than the time of the neat EVA (29 seconds) and lower than the NC 1.3. sample (47 seconds) without BA. The contribution of BA addition in the composite prepared by using NC 2 elongated the burning time relatively. The burning time for the sample NC 2.3-BA (nanoclay/polymer: 10/100) was 40 seconds (40% higher than the time for the neat EVA). It was slightly higher than the NC 2.3 sample

(38 seconds) without BA. BA was reported to enhance flame retardancy [23]. It was claimed that BA may result in crosslinking during combustion which may hinder dripping [22]. It was also mentioned boron containing additives may form a glassy layer and create an extra resistance against heat transfer and mass transfer of flammable components [23]. The enhancing effect of BA as a boron-containing additive was observed for the composites prepared via NC 2 slightly, but it was not enhancing the flame durability of composites prepared by using NC 1. The difference in organic surface modifiers for NC 1 and NC 2 may be adversely affecting the possible crosslinking contribution of BA in NC 1 composites, while it was possible for NC 2, which has a different surface modifier.

### *3.5.3. Effect of additives (nano-clays with and without BA)*

The additives (nanoclays with and without BA) increased the burn-out time for the EVA composites. But they were not able to prevent the burning out of the composites. There were drippings during the burning test. The burning tests showed that the current amounts/ratios of additives are not supplying total flame retardancy for the prepared composites, but they were resulting in some considerable enhancements in burning time. The amounts of the additives may be altered to investigate a better flame retardancy. NC 1 was more effective in terms of flame retardancy for EVA composites than NC 2. Increasing NC 1 content in the EVA composite was increasing the burning time. BA addition was slightly beneficial for NC 2-containing composites, but not for NC 1-containing samples (Figure 12). Different BA amounts/ratios may be investigated for better flame retardancy performance. 30% and 40% of BA addition were reported to result in epoxy composites with V1 and V0 score for the UL-94 V test, respectively, indicating the higher BA content may be used for better flame retardancy [35]. The burning times were not totally in accordance with the TGA data. The sample NC 1.3-BA had the highest temperature values during thermal degradation analysis (e.g., D-TGA peak T3, T (-50%)), which were higher/slightly higher than the values for the sample NC 2.3 which had the longest burning time. This may be due to the difference in testing/analysis conditions and may be indicating the importance of using different characterization methods for evaluating the performance of composite materials.

## 4. Conclusion

In the current study, the effects of the addition of two different nanoclays (NC 1 and NC 2) with different organic surface modifiers and boric acid (BA) on both the thermal characteristics/flame retardancy and mechanical characteristics were investigated. The morphology of the polymer/nanoclay composite was very effective on the characteristics of the composites. The nanoclay in the EVA/NC 1 composites was more exfoliated, while the EVA/NC 2 samples were either intercalated (or aggregated). The more homogeneous mixing of nano platelets for the exfoliated morphology resulted in higher surface area and surficial interaction between the organically modified nanoclay surface and EVA matrix. Consequently, the mechanical and thermal characteristics were varying with the nanoclay type (and polymer/nanoclay ratio). The nanoclay type (i.e., with different surface modifiers) was effective on the thermal degradation characteristics of the nanoclay/EVA composites (Figure 6c). Samples with NC 1 had 3 thermal degradation steps in TGA, while neat EVA and samples with NC 2 had 2-step thermal degradation. Both nanoclays decreased the peak temperature for deacetylation of EVA (at 341-352°C) but increased the second peak temperature related to the defragmentation of the polymer backbone (at 474-480 °C) (Table 4). The higher temperatures for the second step degradation may be considered as an enhancement in the thermal durability of the composite [33]. BA addition increased both peak temperatures (for deacetylation and defragmentation of the EVA copolymer) for NC 2 added samples, which may be indicating a beneficial effect on flame retardancy. The nanoclay addition at a lower ratio (NC 1.1, EVA/nanoclay: 100/1) decreased the stress-bearing capability of the EVA/nanoclay composite, but increasing the nanoclay ratio to higher values increased the stress-bearing capability of the composite (Figure 9). The Young's (elastic) moduli increased with increasing nanoclay content. The increase was only 1.9% for NC 1.1 (EVA/NC 1: 100/1) while it was 220% for NC 1.4 (EVA/NC 1: 100/20) (Figure 10). The lower Young's modulus value of NC 1.1 may be interpreted as a higher ductility, which may be beneficial for certain applications (e.g., biomaterials), while a higher value of Young's modulus may be preferential for different applications. The nanoclay type (i.e., organic surface modifier) affected the mechanical characteristics of the EVA/nanoclay composite. The NC 1.3 and NC 2.3, both with a similar EVA/nanoclay ratio of 100/10, had elastic modulus values of 12.7 MPa and 8.9 MPa (which were 71% and 20% higher than the modulus of the neat EVA) (Figure 11). The considerable difference between the moduli of NC 1 and NC 2 containing EVA composites may be attributed to the difference in their morphology. BA addition to the EVA/nanoclay composites was effective on the mechanical characteristics of the composite. The stress-bearing of composites, either with or without BA addition, was better than the neat EVA (Figure 10). The stress-bearing capability was increased for the EVA/NC 1 composite, while it decreased for the EVA/NC 2 composites with BA addition (Figure 10). This may also be a consequence of having different morphologies in NC 1 and NC 2 containing composites. Increasing stress bearing capability of EVA/nanoclay composite with NC 1 (NC 1.3-BA) indicates the BA should be contributing to the interaction between the organic modifier on the nanoclay surface and the EVA matrix in an enhancing way. The enhancing effect of BA on stress bearing was not observed for NC 2.3-BA, which was with intercalated/partially agglomerated morphology, which relatively decreased the surface area between the nanoclay (i.e., organic surface modifier) and the EVA matrix (Figure 10). The elastic moduli increased with BA addition for both composites with different nanoclays. The moduli for NC 2.3 and NC 2.3-BA were 8.9 and 12.8 MPa, respectively, showing the enhancing effect of BA addition on elastic modulus (44%) (Figure 11). The used additives (nanoclays: NC 1 and NC 2 and BA) at the ratios investigated were not sufficient to prepare self-extinguishing composites (i.e., the samples examined were all burnt out, dripped, and failed the UL94 VTM test). The additives and their ratio may/should be altered for higher flame resistance. The most effective nanoclay in terms of flame retardancy was NC 1. The burn-out time for NC 1.4 was 105% longer than the neat EVA (Figure 12). The burning time was increasing with the increasing nanoclay content (105% for NC 1.4) (Figure 12). Nanoclay type was effective on burning time, too. NC 1.3 with exfoliated morphology burnt out in 47.1 seconds, while it was 37.8 seconds for NC 2.3, indicating the exfoliated morphology of the EVA/NC 1 composite resulted in more hampering effect on burning process (Figure 12). BA addition was also effective on the burning characteristics of the EVA/nanoclay composites. The effect was adverse for NC 1.3-BA. The burning time of NC1.3-BA was 34% shorter than the time for NC 1.3 (and 7% longer than the time for the neat EVA) (Figure 12). The burning time for NC 2.3-BA was 7% longer than NC 2.3 (Figure 12). The burning times were not totally in accordance with the TGA data. The samples NC 1.3 and NC 1.3-BA had the highest temperature values during thermal degradation analysis (e.g., D-TGA peak T2, T (-50%)), which were higher/slightly higher than the values for the sample NC 1.4, but NC 1.4 had the longest burning time. This difference may be attributed to the steps of thermal degradation and differences in their progress under different conditions of TGA and burning tests. It was also showing that the composites should be characterized diligently to estimate their performance. The stress-bearing behaviour of the EVA composites was altered considerably with the additives, but the types and ratios of the additives should be revised to prepare composites with a better flame retardancy. The co-utilization of NC 1 (enhancing burning time) and NC 2 (enhancing stress-bearing) in the EVA composites may reveal a possible synergistic effect of two different nanoclays. The effect of a higher amount/ratio of the inorganic fillers (nanoclays) may be investigated. BA can be used at different (higher) ratios to investigate possible enhancement in flame retardancy of the composites. Different inorganic fillers, like metal hydroxides (e.g., magnesium hydroxide (MH), aluminium trihydroxide (ATH)), which are also environmentally friendly additives, may be used simultaneously with nanoclays and BA for possible enhancement in the flame retardancy. One of the important findings of the study may be the fact that additives may affect different properties of the composites in different ways, e.g., they may enhance the flame retardancy while not enhancing (or worsening) the mechanical properties. The EVA composites should be prepared and characterized diligently for the specific application, considering all important characteristics of the composites.

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## 6. Author Contribution Statement

*İlke Erdem*: Conceptualization, methodology, laboratory work, research, sources, data curation, manuscript-review and editing, supervision, project management.

*Şeyma Avcı*: laboratory work, manuscript-original draft research.

*Mehmet Fazıl Kapçı*: laboratory work, manuscript-original draft.

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