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Effects of alkaline treated and untreated halloysite on the properties of poly(butylene succinate)/halloysite composite films

Alkali işlem görmüş ve görmemiş halloysitin poli(bütilen süksinat)/halloysit kompozit filmlerin özellikleri üzerindeki etkileri

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Abstract

Today, the growing use of disposable plastics, primarily obtained from synthetic polymers, requires the development of biodegradable and biobased alternatives. Here, efforts were made to improve the properties of poly (butylene succinate) (PBS), which is bio-based and biodegradable. Halloysite nanotubes (HNTs) was incorporated to improve the mechanical and thermal properties of PBS. The effects of alkaline treatment on the properties of PBS/HNT composite films were evaluated. The raw HNT powder was treated with NaOH, yielding alkaline HNT (HNT-A), which was compared with untreated HNT. Alkalization resulted in an increase in the diameters of HNTs and enhancement of thermal properties with HNT-A resulting 82% residue at 600°C. Subsequently, PBS composites reinforced with both HNT and HNT-A were fabricated through melt blending and compression molding techniques. The inclusion of HNT and HNT-A increased tensile strength of neat PBS from 13.8 MPa to around 15.9-17.7 MPa. However, alkalization had no considerable effects on the mechanical characteristic. The thermal stability changed with HNT-A reinforced films showing a residue of 5.2% at 600°C, compared to 4.2% for untreated HNT films and 1.3% for neat PBS. Also, HNT-A reinforced films exhibited higher crystallinity (up to 51.3%) compared to untreated HNT films (49.4%), indicating that HNT-A acts as a nucleating agent. This paper presents valuable insights into the development of environmentally friendly materials for food packaging and highlights the potential of alkali-treated HNTs to enhance the properties of PBS as an alternative to conventional plastics, paving the way for researchers to explore further applications such as active packaging.

Keywords: Alkalization, Halloysite, Poly (butylene succinate) film

Öz

Günümüzde sentetik polimerlerden elde edilen tek kullanımlık plastiklerin kullanımındaki artış ile birlikte biyolojik olarak parçalanabilen ve biyo-bazlı alternatiflerin geliştirilmesi gereksinimi doğmuştur. Bu çalışmada, biyo-bazlı ve biyobozunur olan poli(bütilen süksinat) (PBS)'nin özelliklerini geliştirmeye odaklanılmıştır. Boru şeklinde bir kil minerali olan Halloysit nanotüpler (HNT'ler) PBS'nin mekanik ve termal özelliklerini iyileştirmek için kullanılmışlardır. Alkalizasyonun PBS/HNT kompozit filmlerinin özellikleri üzerindeki etkileri değerlendirilmiştir. Ham HNT tozu NaOH ile muamele edilerek alkali HNT (HNT-A) elde edilmiş ve daha sonra muamele edilmemiş HNT ile karşılaştırılmıştır. Alkalizasyon HNT'lerin çaplarında bir artışa ve termal özelliklerinin gelişmesine yol açmıştır. HNT-A'nın 600 ° C'deki kül miktarı %82 olarak belirlenmiştir. Daha sonra hem HNT hem de HNT-A takviyeli PBS kompozitleri eriyik harmanlama ve basınçlı kalıplama teknikleriyle üretilmiştir. Hem HNT hem de HNT-A'nın eklenmesi PBS'nin 13.8 MPa olan çekme dayanımını 15.9 ila 17.7 aralığına artırmıştır. Ancak alkalizasyonun mekanik özellikler üzerinde belirgin bir etkisi gözlenmemiştir. TGA ile HNT-A takviyeli filmlerde 600°C'de %5,2 kalıntı görülürken, işlenmemiş HNT filmlerinde bu değer %4,2 ve saf PBS'de ise %1,3 olarak bulunmuştur. Ayrıca HNT-A takviyeli filmler, işlenmemiş HNT filmlerine (49,4%) göre daha yüksek kristalinite (51,3%'e kadar) sergilemiştir; bu da HNT-A'nın çekirdeklendirici ajan olarak davrandığını göstermiştir. Bu çalışma, ambalaj uygulamaları için çevre dostu malzemelerin geliştirilmesine ilişkin değerli bilgiler sunarak, alkali ile işlenmiş HNT'lerin, geleneksel plastiklere sürdürülebilir bir alternatif olarak PBS'nin özelliklerini geliştirme potansiyelini vurgulamakta ve akıllı ambalajlar gibi daha ileri uygulamalar için araştırmacılara zemin hazırlamaktadır.

Anahtar kelimeler: Alkalizasyon, Halloysit Poli (bütilen süksinat) filmi

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1 Introduction

In recent years, the growing environmental awareness has led to a surge in demand for biodegradable materials. In particular, the detrimental consequences of single-use packaging material waste on the environment and the health of humans and animals are steadily rising due to the extensive use of plastics in industry [1]. Poly (butylene succinate) (PBS) has attracted attention as a bio-based and biodegradable polymer in recent years due to its bio-based production varying in various ratios. PBS has good melt processability, mechanical properties, thermal and chemical resistance [2],[3]. Furthermore, PBS possesses greater flexibility in comparison to commercial biopolymers like poly (hydroxy butyrate) (PHB) and poly (lactic acid) (PLA) and also PBS has a better O_2 barrier than PLA [4],[5]. PBS, a semi-crystalline polymer, can be processed as a melt without degradation as it has a melting point (T_m) of 110-115 °C and exceptional thermal stability above 300 °C. PBS has a lower T_m value than PLA, which is commonly used for food packaging, which can save energy during industrial processing [2],[3]. According to the manufacturer data of the PBS used in the research, the tensile strength is 40 MPa and the elongation value is 170%, which are between low density polyethylene (LDPE) and high density polyethylene (HDPE) [2],[6]. Thanks to its environmentally friendly and competitive properties with commercial plastics, it is used in various fields from packaging to agriculture, electronics to medical applications [7]. Also, the food contact of PBS has been approved [6]. Academic research into the use of PBS for food packaging applications has intensified in recent years. The literature contains studies in where PBS is blended with various synthetic and natural polymers such as poly (butylene adipate-co-terephthalate (PBAT) [8], PLA [9], and starch [10].

Raffaela et al. prepared compression molded films from different ratios of PBS/PBAT blends. It was reported that increasing amount of PBS decreased the flexibility of the films while improving the barrier properties [11]. In another study, Threepopnatkul et al. used sweet basil essential oil (ES) to impart antibacterial activity to a PBAT/PBS blend designed for food packaging. For controlled release of ES, ß-cyclodextrin (ßCD) was added as absorbent. As intended, the ßCD-ES containing film inhibited mould growth on tomatoes after 40 days [8]. Furthermore, various fillers have been incorporated into PBS to impart some of the properties required for use as food packaging. For example, fillers such as lignin [12] for antioxidant and antifungal effect, cinnamaldehyde [12], Ag-zeolite [13], essential oils [12],[13] for antimicrobial effect were incorporated into PBS using methods such as solution casting and extrusion, and the properties have been investigated. Furthermore, the gas barrier properties of PBS were attempted to be improved using clays such as montmorillonite [16] and graphene nanosheets[5]. Organically modified montmorillonite (OMMT) reinforced PBS nanocomposites were fabricated by melt blending and their properties were investigated by Ray et. al. It is reported that both storage modulus and tensile modulus increase with increasing OMMT amount. In addition, O_2 barrier property was also improved with the addition of clay [17].

Halloysite nanotubes (HNTs) in the group of nano clays are natural aluminium silicate-based nanoparticles with a hollow tubular morphology. HNTs existing in nature are low-cost, biocompatible, environmentally friendly materials [18]. The addition of HNTs can impart properties such as improved thermal and mechanical strength and high crystallinity to the matrix. In some studies, HNTs have been used to improve fibre-matrix interfacial adhesion as a cheaper alternative to carbon nanotubes [19,20], while there are also many studies in which HNT is added to the thermoplastic matrix as a filler [21–25]. Due to their tubular form, HNTs which have the potential to display antimicrobial properties can be also be used as carriers for different compounds or to absorb different gases in the packaging environment [16],[17]. A limited number of studies in which HNTs are incorporated into the PBS matrix are available in the literature [18]–[23]. In a study by Wu and co-workers, PBS/HNT samples were prepared by melt blending. To enhance the interfacial interactions, the gamma-glycidoxy-propyltrimethoxysilane was used to modify the HNT before the proces. Morphological, thermal and mechanical properties were investigated and the results were reported. It was determined that HNT behaved as a nucleating agent for PBS as a result of differential scanning calorimetry test. Moreover, mechanical tests showed that the addition of HNT increased the strength and modulus of PBS [23]. As another usage area of HNTs; Wang et al. investigated their flame-retardant effects. An intumescent flame-retardant system using HNTs as synergistic agents was prepared and samples were produced by extrusion by adding to PBS. By cone calorimetry, it was shown that the addition of HNT into IFR significantly improved the flame retardancy. Moreover, the limiting oxygen index, thermostability, was also considerably increased [25]. On the other hand, the distribution of such nanoparticles in polymer matrices is a challenge. Alkaline treatment of HNT can improve its interaction with the matrix by altering its surface properties. It is also known that alkali treatment increases the gas adsorption capacity by increasing the HNT lumen diameter [29]. Boro et al. investigated the properties of alkali-treated HNT-reinforced PLA films [30], while Boonsiriwit et al. examined the characteristics of alkali-treated HNT-reinforced LDPE films [26]. Both studies mentioned that the dispersion of ALHNT within the matrix was good, leading to enhanced properties.

In this paper, while the main purpose of alkalization is to increase the lumen diameter and thus the gas adsorption capacity of HNTs for further active food packaging studies, this study aims to investigate whether it is possible to achieve improvements in the mechanical and thermal properties of the films with alkalization. Building on this, the current paper investigated the effect of alkali treatment on the properties of PBS/HNT films. Films containing both alkali-treated and untreated HNTs were prepared, and their final properties were compared. Thus, the objective of this work was to develop a PBS film that could serve as an alternative to commonly used PE and PLA in food packaging applications. For the first time in the literature, the effect of alkali treatment on PBS films has been discussed comparatively, laying the groundwork for advanced food packaging research.

2 Experimental Method

2.1 Materials and Preparation Techniques

The matrix material PBS (FZ71) were purchased from PTT MCC Biochem Co., Ltd, with a melting temperature of 115 °C. The HNT powder was supplied by ESAN, Eczacıbaşı, Türkiye. Sodium hydroxide (NaOH) was purchased from Beyanlab Laboratuvar Ürünleri San. Tic. Ltd. Sti.

The alkalization of HNT powder was carried out using 6M NaOH solution, according to the methods of Gaikwad [29] and Wang

[31]. HNT powder was suspended in a 6 M NaOH solution under magnetic stirring at 1200 rpm for 3 h. The solution was then washed. After neutralization, the precipitated HNTs were dried in an oven at 100 °C to obtain HNT-A.

PBS/HNT and PBS/HNT-A films were produced by melt blending followed by compression molding. PBS and halloysite powders were fed into an extruder r (Xplore 15 cc) and mixed at 135 °C-100 rpm for 4 min. HNT and HNT-A were added at concentrations of 1-3-5 wt%. At the end of the mixing time, composite filaments were obtained and then granulated. The final stage involved compressing the granules at 60 bar and 140°C to produce films of approximately 200 µm thickness. (Figure 1.)

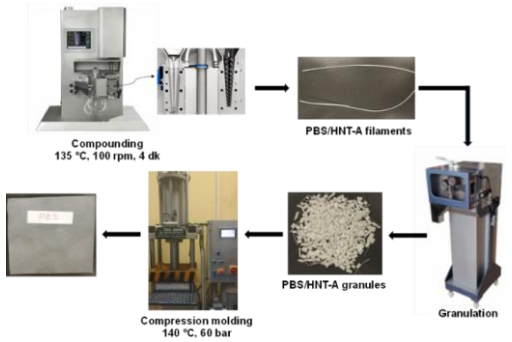

Figure 1. Schematic representation of the film production process.

2.2 Characterization

The effects of alkalization on the HNT structure were evaluated by transmission electron microscopy (TEM, JEOL JEM-1400 PLUS).

The thermal stability of HNTs before and after alkalization was determined by thermogravimetric analysis (TGA, Mettler Toledo). Measurements were performed from 25 to 600 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

TGA was also used to examine the thermal properties of PBS/HNT and PBS/HNT-A films. The temperature at 5 and 50 % weight losses (T_{d5} and T_{d50}) and the maximum weight loss peak temperature ($T_{max)}$ and residue at 600 °C were determined from the thermograms.

The chemical structure and possible interactions between the PBS and HNT powders were determined via Fourier Transform Infrared Analysis (FTIR). FTIR spectra of the films were taken by using a Spektrum 100, Perkin Elmer (USA) FTIR spectrometer. Analysis was carried out in the attenuated total reflection (ATR) mode at wavenumber between 650 and 4000 cm^{-1}.

The cold crystallization (T_{cc}), and melting (T_m) temperatures of the PBS/HNT and PBS/HNT-A were measured by using differential scanning calorimetry (DSC, Mettler Toledo). Test was conducted from − 60 °C to 150 °C with a heating rate of 10 °C/min. And then, it was cooled to − 60 °C and heated again with same heating rate. The degree of crystallinity (Xc) values of the films was calculated by following the equation;

$$x_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^* w} x100 \quad (1)$$

Where ΔH_{cc} and ΔH_m are the cold crystallization and melting enthalpies of samples, respectively. ΔH_m^* is the heat of fusion PBS (110.5 J/g) [32] and *w* is the weight fraction of PBS.

The mechanical properties of the PBS/HNT and PBS/HNT-A films were evaluated by tensile testing at a tensile rate of 10 mm/min using an Instron Universal Tester. At least 5 specimens of each film were tested, with a size of 80 × 20 × 0.2 mm^3.

3 Results and Discussions

3.1 Alkalization effect on HNT

TEM and TGA were used to determine the influence of alkalization process on the structure and thermal properties of raw HNT powder. The TEM images of HNT powders are shown in Figure 2. HNTs can be in tubular/cylindrical, sheet or spherical form due to differences in the region of mining and crystallization conditions. The cylindrical structure is the most common [29]. The cylindrical structure of the HNTs used in the study was verified by TEM. According to the images of HNTs, they include a transparent central cavity in their cylindrical structure. This cavity is more pronounced in HNT-A powder. The walls of the HNT became thinner and the inner diameter increased due to alkalization process [33]. Also the surface of HNT more rougher. The length of HNT did not alter considerably.

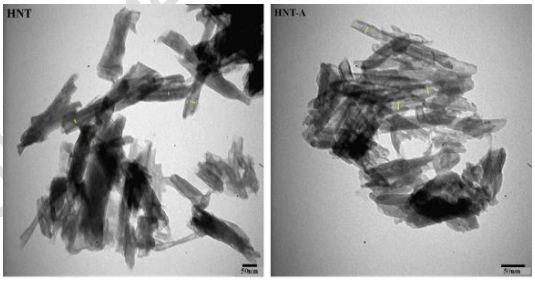

Figure 2. TEM images of HNT powders

The thermal stability of untreated and alkaline treated HNTs was determined with TGA and results are given in Table 1. Both HNTs exhibited a two-step degradation. The first can be attributed to the evaporation of water and the second to the dehydroxylation of the HNTs. Alkalization improved the thermal resistance by increasing both the degradation temperatures and the amount of residue. A similar upward trend was also reported by Wang et al [31]. They attributed this to the elimination of hydroxyl groups from the AlO_6 octahedral layer, as well as the dissolution of Al(III) during alkalization.

Table 1. TGA data of HNT powders.

Sample	T_{d5} (°C)	T_{d10} (°C)	T_{max-1} (°C)	T_{max-2} (°C)	Residue (%, 600 °C)
HNT	132.4	404.1	78.7	486.3	80.0
HNT-A	339.5	450.8	69.6	488.9	82.3

3.2 Fourier Transform Infrared Analysis

The effect of alkalization on the HNT structure was determined via FTIR and the results were reported in our other study [34]. The results showed that peak heights decreased and some peaks disappeared with alkalization. Peaks indicating the presence of hydroxyl groups on the HNT surface were eliminated by alkalization.

The FTIR spectra of untreated and treated HNT reinforced PBS films are presented in Figure 3 (a-b). PBS, a condensation biopolymer, exhibits -OH and -COOH end groups depending on the polymerization conditions. In the pure PBS film, peaks observed at 3430 and 3433 cm^{-1} correspond to the stretching vibrations of the hydroxyl end groups. Peaks associated with C-H and -CH_2- stretching are detected in the 2800–2900 cm^{-1} region [35]. The sharp peak at 1714 cm^{-1} is attributed to the C=O stretching vibration in the crystalline phase [36]. Additionally, the prominent peak at 1150 cm^{-1} corresponds to the stretching vibrations of -C-O-C- bonds, while the -C-OH bending of carboxyl end groups is observed at 954 cm^{-1} across all films [11]. Notably, no significant changes were observed in the spectra upon the addition of HNT and HNT-A to PBS. The absence of changes in peak wavelengths and intensities indicates that no chemical interaction occurred between PBS and HNT powders, and alkalization did not influence this outcome.

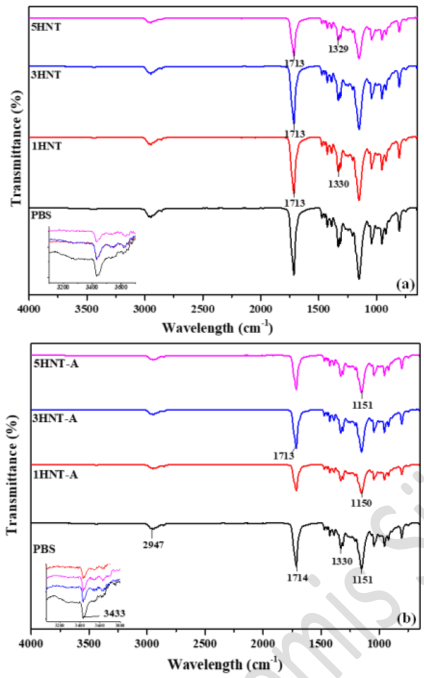

Figure 3. FTIR spectra of (a) PBS/HNT and (b) PBS/HNT-A films

3.3 Tensile Properties

The mechanical properties of untreated and treated HNT reinforced PBS films were examined by using tensile test. The tensile strength (TS, modulus and elongation values of the films can be seen in Table 2.

Neat PBS has a TS of 13.8 MPa and 10% elongation. The tensile strength is close to the results published by Zhang et al. [37], whereas the elongation is close to the finding of Basbasan et al [38]. The addition of untreated HNT and HNT-A increased the TS of PBS matrix which can be assigned to reinforcement effect of HNTs. Films containing HNT-A exhibited slightly higher TS. The increase in both HNT types and all ratios compared to pure PBS can be attributed to the interfacial adhesion of PBS and HNT. The good interaction between the filler and the matrix contributes to the mechanical strength of the film by successfully transferring the applied tensile stress from the matrix to the filler. A similar development was observed for polyvinyl chloride (PVC)/HNT films. The addition of 4 wt% HNT increased tensile strength by over 35%. This increase was attributed to a better distribution of the filler in the matrix [21]. For example, in the study by Wattanawong and Aht-Ong, zeolite, an alumina-silicate structure similar to HNT, was added to PBS. As the amount of zeolite increased, the strength of PBS, which was approximately 47 MPa, decreased to 40 MPa. This was attributed to the weak interaction between zeolite and PBS [13]. In this study, the increase in tensile strength, regardless of the amount of HNT added, suggests that HNT is properly incorporated into the polymer chains due to its tubular structure. Boonsiriwit and co-workers fabricated HNT-A/LDPE films and determined their tensile strengths. The strength of pure LDPE, which was 17.4 MPa, reduced to 13 MPa with the incorporation of 5 wt% HNT-A [26]. As can be seen, the strengths of PBS/HNT and PBS/HNT-A films are higher than those of LDPE. The claim of PBS to be an environmentally friendly alternative to LDPE is supported in terms of strength.

Table 2. Mechanical properties of films.

Sample	Tensile Strength *(MPa)*	Elongation *(%)*	Modulus (MPa)
PBS	13.8 ± 0.5	10.1 ± 0.5	217 ± 13
1HNT	16.8 ± 0.7	8.4 ± 0.8	225 ± 9.0
3HNT	16.5 ± 0.8	7.6 ± 0.5	219 ± 11
5HNT	15.9 ± 0.5	7.2 ± 0.3	220 ± 20
1HNT-A	17.1 ± 0.2	8.6 ± 0.2	229 ± 17
3HNT-A	16.9 ± 0.2	7.5 ± 0.7	223 ± 7.0
5HNT-A	17.7 ± 0.6	7.8 ± 0.6	227 ± 15

The modulus value of pure PBS film was 217 MPa which is close to the result of Cosquer et. al [5]. The modulus of PBS films increased with addition of untreated and treated HNTs. This can be attributed to the increase in stiffness, which is associated with the addition of nanofillers to the structure, restricting the mobility of polymer chains. Both types of HNT contributed to an increase in properties regardless of their amount, with films containing treated HNT exhibiting relatively higher moduli. According to FTIR results, the nanotubes and PBS were physically mixed. This suggests that the enhanced mechanical properties observed with alkalized HNT may be attributed to the increased surface roughness of the HNT, which strengthens mechanical interlocking.

The addition of untreated and treated HNTs resulted in a decrease in elongation value of neat PBS. Alkalization had no appreciable effect, and all films showed almost similar elongation. The decrease in elongation value is due to the restriction of polymer chain movement with the addition of nanofiller.

3.4 Thermogravimetric Analysis

The thermal resistance and stability of the untreated and treated HNT reinforced PBS films were determined by using TGA. The TGA and derivative weight curves (DTG) thermograms of the films are presented in Figure 4 and 5 and the corresponding data are tabulated in Table 3.

All films exhibited single step degradation thermograms indicating the main polymer chain degradation of PBS. The neat PBS film, which loses 5% of its weight at 346.3 °C, has a residue of 1.3% at 600 °C.

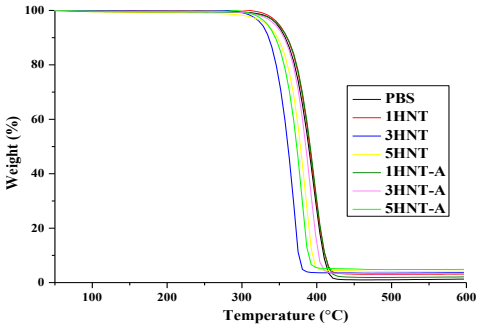

Figure 4. TGA curves of films

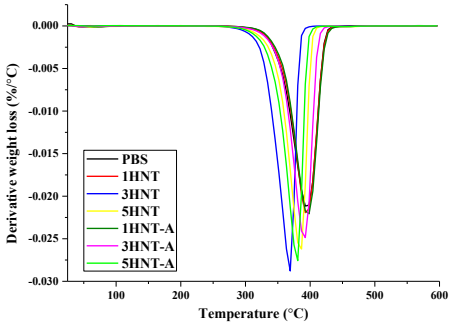

Figure 5. DTG curves of films

3.5 Differential Scanning Calorimetry

The T_{cc}, T_m and percentage crystallinities of the PBS/HNT and PBS/HNT-A films were tabulated in Table 4.

Table 4. Thermal properties of films

Sample	T_{cc} (°C)	T_m (°C)	Crystallinity (%)
PBS	102.2	116.1	47.4
1HNT	103.4	117.2	48.5
3HNT	102.9	116.6	49.4
5HNT	101.9	116.7	47.7
1HNT-A	101.9	115.5	51.3
3HNT-A	102.4	115.6	50.9
5HNT-A	102.7	117.1	50.7

Table 3. Thermogravimetrical properties of the films.

Sample	T_{d5} (°C)	T_{d50} (°C)	T_{max-1} (°C)	Residue (%, 600 °C)
PBS	346.3	389.5	394.1	1.30
1HNT	346.0	390.2	393.2	1.90
3HNT	338.3	386.1	392.0	3.31
5HNT	332.4	378.1	384.8	4.21
1HNT-A	347.9	391.1	396.2	2.20
3HNT-A	344.2	385.3	391.6	3.50
5HNT-A	334.1	376.0	381.5	5.18

Considering the effect of HNT addition, several studies in the literature have reported that HNTs generally improve thermal stability [29]–[31]. This improvement has been attributed to the fact that HNTs act as a barrier in the matrix and prevent the diffusion of volatile components by creating a tortuous path effect. However, in this study, TGA results showed that the addition of HNTs decreased the degradation temperatures independently of alkalization. The addition of both treated and untreated HNT reduced T_{d5}, T_{d50}, and T_{max} temperatures. Increasing the amount of HNT resulted in a further drop. The outcomes demonstrated that HNTs did not provide a useful thermal barrier. In particular, the significant decreases observed at high HNT amounts are attributed to the heterogeneous distribution and agglomeration of HNT and HNT-A. Another factor may be the catalytic effect of clays on thermal degradation [20],[32]. Wu et al [23]. studied the thermal characteristics of HNT-reinforced PBS composites and found that HNT reduced thermal resistance. They then computed the thermal degradation activities for a more thorough examination. The results showed that adding HNT reduced the thermal decomposition activation energy of PBS. This has been attributed to the catalytic effect of HNTs caused by the abundance of Al Lewis acid sites in the HNT structure. Looking at the DTG curves shown in Figure 4, it can be seen that the peak height of PBS increases with the addition of HNT. This indicates that HNT accelerates degradation. On the other hand, the amount of residue increased with increasing HNT amount and alkalization process. Since HNT-A gives about 82.3 % residue at this temperature (see Table 1) the HNT-A added to the structure increased the residue.

Neat PBS and all HNT reinforced films exhibited an exothermic peak during the heating scan, indicating the cold crystallization. The polymer chains that remained uncrystallized during cooling after molding exhibited cold crystallization. The addition of untreated HNT and HNT-A did not significantly change the T_{cc} value of PBS. All T_{cc} values vary between 101-103.4 °C. Concerning the T_m values, it was observed that all films melted at close temperatures, while the T_m changed by around 1-2 °C with the addition of HNT powders. On the other hand, untreated HNT and HNT-A increased the percentage crystallinity of neat PBS. The crystallinity of the HNT-A films was higher than that of the untreated HNT films. This shows that HNT-A acts as a nucleating agent [39].

4 Conclusions

The present study aimed to improve the properties of PBS with HNT as an environmentally friendly food packaging option. HNT was alkali treated, thus increasing its thermal resistance and enlarging its lumen diameter. In terms of PBS films, HNT-A increased the amount of residue and thus thermal stability. The addition of HNT and HNT-A had no significant effect on thermal transition temperatures, but increased crystallinity. 1HNT-A film exhibited highest crystalllinty as 51.3%. The addition of HNT and HNT-A to PBS composites increased the tensile strength from 13.8 MPa to 15.9–17.7 MPa. As a result of increasing crystallinity with alkalization, PBS/HNT-A films exhibited higher strength. In summary, although the alkalization process improved certain thermal and crystalline properties, its overall effect on the mechanical and physical performance of the films was limited. However, the films were obtained without significant loss of thermal and mechanical properties. Considering that the gas adsorption capacity of HNTs will increase due to their enlarged lumen diameter, the use of the produced films as active food packaging can be investigated in detail.

5 Declaration of ethics committee approval and conflict of interest

"The article does not necessitate a research ethics committee approval."

"There is no conflict of interest with any person/institution in the prepared article."

6 Declaration of authors' contribution

In this paper author 1 contributed to the realization of experimental studies, conducting tests, evaluation and writing of the results.

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