Article
Mechanical and Thermal Properties of Self-Assembled Kaolin-Doped Starch-Based Environment-Friendly Nanocomposite Films

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Abstract: Environment-friendly advanced materials are promising candidates for the engineering of nanoscience and nanotechnology. Here, starch–kaolin self-assembled nanocomposite films were prepared using potato starch and an indigenous layered material, kaolin. The films consist of kaolin and the matrix, which were prepared by the disruption and plasticization of starch granules with water and glycerol. Self-assembled nanocomposite films with 0%, 5%, 10%, 15%, and 20% w/w of kaolin were fabricated by casting and evaporating the mixture from homogeneous aqueous suspension at 95 °C. The thickness of the film—about 200 μm—was controlled by a predesigned glass frame. The resulting films were conditioned before testing, and the effect of accelerated aging in a moist atmosphere was investigated. The films were characterized using attenuated total reflection infrared (ATR-IR) spectroscopy for the interaction of moieties via function groups, X-ray diffraction (XRD) for crystallinity change, universal testing machine (UTM) for tensile strength Young’s modulus and elongation at break investigation. The thermal stability of the films using thermogravimetric analysis (TGA) and the effect of temperature on contraction behaviors using thermal mechanical analysis (TMA) were carried out. The distribution of kaolin into the matrix and morphology of the self-assembled nanocomposite films were observed from scanning electron microscopy (SEM) images. Developed nanocomposite materials from an indigenous source would play a vital role in the field of food packaging industries in Bangladesh.

Keywords: starch; kaolin; self-assemble; nanocomposite film; nanoscience

1. Introduction

Biodegradable and environment-friendly nanocomposite materials are highly attractive to the scientific community for sustainable development considering the fields of food packaging, separation, engineering, and structural materials [1,2]. The incorporation of indigenous nanoscale layered materials into biopolymers would meet the demand of advanced research work. It is well known that the functional properties of biodegradable films and coatings depend on the characteristics of the film-forming material [3]. There are many natural polymers that show the film-forming properties from suitable environments with specific features such as barrier properties, mechanical strength, thermal stability hydrophobicity, hydrophilicity, opacity, brittleness, etc. Lipids can produce highly dense films with hydrophobic properties due to their strong intermolecular interaction [4]. Polysaccharides and proteins have been used for the fabrication of hydrophilic films with enhanced mechanical and effective gas barriers characteristics, which depends on their monomeric chemical structure and interaction ability to solvents [5]. In general, from the technological point of view, the nanotechnology deals with the accuracy of techniques, instruments, and size of material particles below 100nm [6]. The design of the internal structures of a micro- or nano-size particle can alter the
functional properties, morphology, and stability of composites due to their surface area and structural varieties, which offer new thermodynamically stable environment during composite preparation. At present, the application of nanotechnology for the development of new nanobiocomposites from indigenous materials is crucial in terms of environmental aspects and is therefore a wide-open field for scientific community.

Recently, advanced biocomposites have been produced using different biopolymers matrices such as starch, modified cellulose, etc. Considering the easiness of extraction, solvent affinity, the necessity of chemical modification, low cost, availability, and versatility of applications, starch is the most promising renewable natural resource of biopolymer [7–10]. Starch with a plasticizing agent turns into an engineering material with improved thermoplastic characteristic [11,12]. Due to its high intractable nature, brittleness, water sensitivity, and poor mechanical strength of starch-based materials, limit its practical applications [12–14]. Cellulosic fibers into starch-based biocomposites boosted properties and play as reinforcing materials in a starch matrix [15].

Nanocomposites are usually fabricated from hybrid nanostructured materials. Newly developed hybrid materials composed of organic polymer matrices and nanoclay fillers make up a class of widely studied nanocomposites [16]. Clay is also used in some food, drug, cosmetic, and health care recipients due to its inherent characteristics. The bijoypur nanoclay kaolin consists of mainly kaolinite, which is a double-layered structure bearing around 1nm thick and 200–250 nm length of aluminosilicate layers [17]. Naturally occurring kaolin is rigid and hydrophilic in nature. Therefore, hydrophobic polymer and clay remain immiscible (phase separated) in the composites, resulting in agglomeration of the clay in the matrix and produces composites with low mechanical and thermal properties. Besides, interaction between the layered clay materials and hydrophilic polymer chains may produce intercalated or exfoliated nanocomposites, which results from the penetration of polymer into the inter layer region of the clay [18]. White clay dispersion into these glycerol plasticized starch matrices by a solvent or melt process leads to the formation of intercalated structures. Whereas, interfacially, interacted nanocomposites from polymethylmethacrylate and cholin chloride-modified kaolinite produced non-intercalated composite [17].

Crystalline structures and rigid materials and nanofillers including cellulose nanocrystals, chitin nanofibers, metal oxide nanoparticles, or clays were used for reinforcing agents to adopt versatile applications [19,20]. Chung et al. reported the starch–clay biodegradable nanocomposites, which showed an increase in modulus and strength for containing 5 wt% clay compared to the unfilled starch materials from 65% and 30%, respectively [21]. Thermoplastic starch reinforced by clay has also recently been investigated by Stepto et al. and reported that the tensile strength of composite was increased from 2.5 to 3.9 MPa with the presence of 5wt% white clay, while the elongation at break was increased from 0.01% to 0.26% [22]. When the relative water vapor diffusion coefficient of composite was decreased to 65% and the temperature was increased from 305 to 336.8 °C, then the composite lost 50% of its mass. In another article, Tomasik et al. reported that plasticized starch with glycerol shows a reinforcing effect on physical and mechanical properties when starch nanocrystal was incorporated for fillers/fillerandfiller/matrix interactions due to the establishment of hydrogen bonding [23].

In this paper, we report on the mechanical and thermal properties exploration of self-assembled kaolin doped into potato starch and glycerol-plasticized nanocomposite films. The properties have been changed with the addition of kaolin, and they gave some important indicators for further investigations of similar patterns and mechanistic views.

2. Materials and Methods

2.1. Materials

White clay was collected from Bijoypur, Netrokona, Bangladesh, which is known as kaolin, having a double-layered structure. It was used after acid (dilute HCl) treatment to remove foreign acid-soluble inorganic minerals. Potato was purchased from the local market and was processed to extract starch from it. Glycerol (99.5%) was purchased from Sigma-Aldrich, India and used as received. The
prescribed design of the glass frame was prepared from a glassware shop and used after wrapping with Teflon ribbon.

2.2. Extraction of Starch from Potato

Locally purchased potato was washed with copious water to remove adhered mud. After atmospheric drying, 100 g of potato was subjected to crushing and blended with a domestic blending machine for 10 min; afterwards, 100 mL distilled water was added. The paste-like mass produced from potato was carefully transferred into a beaker and diluted with more 100 mL of water. Then, the beaker was kept at rest for a few hours. The mass of residual potato from the beaker, leaving behind the white starch (settled at the bottom), was separated by decantation first. Then, the remaining gray mass of potato was washed several times with copious water and filtered using a cloth so that only the granular starch can pass through it. All starch was collected and after atmospheric drying, it was used for composite film preparation.

2.3. Composites Film Preparation

Starch (2 g) was first dispersed into distilled water (35 mL) in a beaker. Besides, kaolin (0%, 5%, 10%, 15%, and 20% w/w of starch) was homogeneously dispersed in 1 g of glycerol separately, and agglomeration was prevented by sonication for 10 min. Then, the starch solution and kaolin in glycerol mixtures were added together and then stirred mechanically while the solution was heated at 95 °C for 15 min. The mixture was further stirred with sonication for 10 min to remove microbubbles. Then, the mixture was poured onto the surface of a glass frame wrapped with a Teflon sheet. The nanocomposite film was dried by atmospheric evaporation at 25 °C for 24 h and then dried at 40 °C in a non-ventilated oven for another 24 h.

2.4. Tensile Properties

Tensile strength, elongation at break, and Young’s modulus of the films with dimensions of 7 × 4 × 0.25 mm (length × width × thickness), conditioned at 75% relative humidity (RH), were measured using a universal testing machine (CMT6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China). The initial gap of the jaw was fixed at 10 mm. Dry films with an average thickness of around 200 μm were obtained by measuring with a digital micrometer (Mitutoyo, Kanagawa, Japan).

3. Characterization Techniques

3.1. Attenuated Total Reflection Infrared (ATR-IR) Spectral Analysis

ATR-IR spectra were measured on an FT-IR 8400S spectrophotometer (Shimadzu Corporation, Kyoto, Japan) in the range of wavenumber 4000–400 cm⁻¹ where the resolution and number of scans were set 4 cm⁻¹ and 16 times, respectively.

3.2. X-Ray Diffraction (XRD)

The X-ray powder diffraction (XRPD) patterns of the samples were recorded by an X-ray diffractometer (Ultima IV, Rigaku Corporation, Tokyo, Japan) at room temperature. Prior to XRD analysis, the samples were finely pulverized using a mortar and pestle. Nickel (Ni)-filtered Cu Kα radiation (λ = 0.154 nm), from a broad focus Cu tube operated at 40 kV and 40 mA, was applied to the samples for measurement. The XRD patterns of the samples were recorded in the continuous scanning mode with a scan speed of 3°/min and in the scan range of 5° to 100°. The basal spacing (d_{001}) of the crystalline samples was computed using Bragg’s law.

3.3. Universal Testing Machine (UTM)

Mechanical properties (tensile strength, elongation break, Young’s modulus) were investigated using UTM.
3.4. Thermal Characterization

The samples were subjected to take thermograms using a thermogravimetric analyzer (TGA-50, Shimadzu, Kyoto, Japan) with alumina cell under nitrogen atmosphere at the rate of 5 °C/min. In order to understand the thermal behavior, the temperature was set at a range of 30–600 °C.

3.5. Thermal Mechanical Analysis (TMA) or Dilatometry

Thermomechanical analysis was conducted using dilatometry.

3.6. Scanning Electron Microscope (SEM)

The morphology of the samples were analyzed by an analytical scanning electron microscope (JEOL JSM-6490LA, Tokyo, Japan) operated at an accelerating voltage of 20 kV in the back-scattered electron mode.

4. Results and Discussion

At first, the starch was extracted from potato and the yield was obtained about 18% w/w. It is revealed that the content of starch in potato is relatively higher, which was aged for several months in cold storage. The higher yield of starch and low cost of potato indicate that it can be a potential source of raw material for pharmaceutical and starch-based industries. A white cotton fabric (cloth) was used for the separation of starch by filtration. Therefore, a portion of starch was trapped into the mass of blended potato. The yield of production of starch may be increased by using an alternative and efficient sieving technique.

In this process, a film-forming solution of starch, kaolin, water, and glycerol was cast on a non-adhesive surface of a glass frame covered with a Teflon ribbon. The casted film was exposed to atmosphere where, water i.e., solvent was evaporated from the solution in order to form the film. As a result of solvent evaporation, biopolymer content was increased in the film and the interaction within matrix increased leading to formation of the basic film structure by hydrogen bonding.

The addition of a crystalline segment into starch biopolymer would dramatically change the film properties in terms of mechanical and thermal points of views. Thus, to increase the clay/matrix affinity, different quantities (0%, 5%, 10%, 15%, and 20% w/w of starch) of white clay namely Bijoypur clay and glycerol have been incorporated. Five nanocomposite films with varying quantities of kaolin were prepared to investigate its mechanical properties. The self-assembled nanocomposite films were designated KSNC for kaolin starch nanocomposite. The different compositions of the films were represented as K0SNC, K5SNC, K10SNC, K15SNC and K20SNC for 0%, 5%, 10%, 15%, and 20% w/w of kaolin present in the self-assembled nanocomposite films, respectively. Here, we have characterized and analyzed the films using attenuated total reflection infrared (ATR-IR) spectroscopy (see Supplementary Materials, Figure S1), X-ray diffraction (XRD) (see Supplementary Materials, Figure S2), a universal testing machine (UTM), thermomechanical analysis (TMA), and thermogravimetric analysis (TGA); therefore, the results have been discussed accordingly.

4.1. Mechanical Properties

Mechanical properties of the samples were studied in terms of tensile strength and percentage elongation at break.

4.1.1. Tensile Strength of the Nanocomposite Films

As the film thickness (200 μm) and maximum force (15 N) exerted onto the films were unchanged, the experiment was run to measure the ability of a film to withstand a longitudinal stress, which was expressed as the greatest stress that the film can stand without breaking. Figure 1A shows a relation between the tensile strength of the self-assembled nanocomposite film and the variable content of kaolin. The zero kaolin content film, K0SNC, gave a tensile strength of 2.5 MPa, whereas the maximum tensile strength (8.33 MPa) was found from the K20SNC film. The overall trend of the line is straight
with a positive slope, which indicates that the tensile strength increases with the increase of the amount of kaolin [24]. At 10% w/w, there was an experimental error or the film K_{0.5}SNC was not perfectly prepared (it may be that the film was not homogeneous); therefore, the value obtained (4.3 MPa) was slightly lower than that of the average values of the trend line. The explanation for this effect is ascribed to the formation of a rigid network of nanofillers, the mutual interaction and entanglement between the nanofillers (kaolin), and the starch matrix [25]. The efficient stress that arose from the starch to kaolin occurred due to the negative free energy development during the self-assembly of kaolin. This phenomenon was supported by the research group of Mathew et al. in 2002, where they proposed an increase in the overall crystallinity of the system; as a result, the nucleating effect in the composite can be beneficial for mechanical properties [26].

![Image](image_url)

**Figure 1.** Effect of kaolin content on the tensile strength (A) and percentage elongation (B) at break of the nanocomposite films produced from (a) K_{0.5}SNC, (b) K_{1}SNC, (c) K_{0.5}aSNC, (d) K_{1.5}SNC, and (e) K_{2}SNC films. KSNC: kaolin starch nanocomposite.

4.1.2. Elongation of the Nanocomposite Films at Break

Figure 1B represents the effect of kaolin content on the enlargement of the nanocomposite film before the appearance of crack formation. It is revealed that the K_{0.5}SNC film without kaolin showed very little elongation at break, this could be due to the lack of weak interaction of the starch molecules. Besides, as the kaolin content in the nanocomposite films increased from 5% to 20% w/w, the magnitude of elongation at break decreased linearly [24]. It can be explained that at K_{1}SNC film, the interaction of starch molecules and the kaolin was remarkably strong due to the ratio of matrix (starch) and kaolin crystalline segment, where the surface of the kaolin was fully covered by the starch biopolymers, and sufficient polymer between kaolin interfaces makes the film soft and less stiff. The K_{0.5}SNC film showed the lowest elongation, where the availability of soft segment (biopolymer) was decreased and the hard crystalline kaolin part was increased; as a result, the thin starch film between the kaolin particles gradually loses the expanding ability.

In Figure 2, stress (MPa) versus percentage strain was plotted and the effect of kaolin on the elastic and plastic behaviors was depicted. K_{0.5}SNC shows only the modulus of resilience, which is represented with the green zone, but when the kaolin was added with the starch, then the film showed dual characteristics, including plastic behavior. It indicates that kaolinite reinforced to incorporate the brittle nature of the film. Interestingly, with the variation of kaolin content from 5% to 20% w/w in the film, the change of rheology in terms of the elastic and plastic characteristics are explained more clearly from Figure 3. It is evident that the maximum modulus of resilience was found for K_{0.5}SNC film, which is about 5 times higher than that of K_{2}SNC film. This could be because the distribution of kaolin in the self-assembled film was homogeneous and perfectly proportionate. Besides, initially, the maximum plastic region was found for the film-produced K_{0.5}SNC materials, which decreased in the case of the K_{0.5}SNC film and further increased for the K_{2}SNC film. In the K_{2}SNC film, kaolin nanoparticles agglomerations were found, and the modulus of resilience result was lower than that of the other
composites. This can be easily explained: 20% w/w kaolin content film suffered from agglomeration and a lack of sufficient starch matrix to carry out the flow properties of the film.

![Figure 2](image.png)

**Figure 2.** Effect of kaolin content on the modulus of resilience and modulus of toughness of the nanocomposite films produced from (a) K₀SNC, (b) K₅SNC, (c) K₁₀SNC, (d) K₁₅SNC, and (e) K₂₀SNC films.

![Figure 3](image.png)

**Figure 3.** Comparison of the effect of kaolin content on the elastic and plastic reasons of the nanocomposite films produced from starch and 0%, 5%, 10%, 15%, and 20% w/w of kaolin.

4.2. Thermogravimetric Analysis (TGA)

In Figure 4, the thermogravimetric characterization of the films designated as K₀SNC, K₅SNC, K₁₀SNC, K₁₅SNC, and K₂₀SNC produced from 0%, 5%, 10%, 15%, and 20% w/w of kaolin (by weight of starch) self-assembled nanocomposite respectively are shown. Approximately 10 mg of sample was subjected to run the experiment using an aluminum pan over 30 to 600 °C where the temperature was increased at a rate of 5 °C/min. Each graph shows three tracing curves, one for thermogravimetry, which deals with the weight loss of sample due to moisture removal and the decomposition of nanocomposite film materials, is shown at the top. The second curve (at the middle) represents differential thermal analysis (DTA), which is corresponding to the heat absorption, phase transition, and crystallization due to endothermic and exothermic oxidative reactions. The third curve shows the degradation rate of nanocomposite films as shown at the bottom.

In Figure 4A, the TG curve (top) shows that the initial weight loss (10%) occurs at about 120 °C due to the removal of free moisture and the onset decomposition occurs at 270.6 °C (about 12% weight loss) where the 2% greater weight loss that was recorded may be due to the loss of bound or trapped water (moisture). The decomposition of starch with 66% of weight that escaped at 344 °C showed a linearly decreased line, leaving 12.5% starch weight. Later, the decomposed residue was further completely burned, and the ash was found to be 0.6% approximately.
Figure 4. Thermogravimetric graphs of (A) K₀SNC, (B) K₅SNC, (C) K₁₀SNC, (D) K₁₅SNC, (E) K₂₀SNC, and (F) a comparison chart of films.

Besides, the energy profile with heat absorption and desorption was described from the middle curve, and it was found that at 80 °C and 176 °C, the initial heat gained by moisture leads to a downward tracing line, whereas during combustion, the heat produced from the system shows the exothermic reaction at approximately 300 °C. Later, the line goes downward, which indicates the
endothermic reaction for the further absorption of heat for complete combustion. The bottom graph shows that the highest rate of degradation (17.12 μg/°C) of starch films was occurred at 290.5 °C with a sharp peak. Weight loss due to the removal of free and bound water also leads a small broad peak at around 74 °C and 174 °C with rates of 5.2 and 3.5 μg/°C, respectively. Similar experiments were performed for a series of nanocomposite films prepared using 5% to 20% w/w kaolin for the comparison of the properties stated.

Table 1 shows a summary of thermogravimetric analysis for five samples—KoSNC, KsSNC, KaSNC, KsSNC, and KaSNC—in terms of onset temperature, temperature at which decomposition was completed, the amount of composite decomposed in percentage, the type of reaction occurred, and the temperature at which the maximum decomposition rate recorded. It is clear from the onset temperatures envisaged in Table 1 that after the addition of 5% kaolin, the change of temperature was significant, i.e., 9 °C was increased, whereas from 5% to 20%, the increase of kaolin lead to 5 °C more tolerance at 284 °C for onset decomposition. This phenomenon indicates that kaolin plays a crucial role in stabilizing the composites against temperature. The films without kaolin decomposed completely at 334°C, but except for KsSNC and KoSNC, all the other films showed only slightly higher temperatures. However, it was not remarkably high compared to KsSNC film. The decomposition amount from KoSNC to KaSNC films within the temperature range from onset to complete decomposition gradually decreased from 76% to 54%. It is noticed from the data that there is an inverse relationship between decomposition quantity and kaolin content. As the content of kaolin increased in the composite films, the amount of decomposition was decreased, since the residue was gradually increased. The reactions involved with the whole temperature profile from 30 to 600 °C are endothermic and exothermic due to heat absorption by moisture and the starch biopolymer and the later desorption of heat that occurs by the burning of starch for char formation. Interestingly, it is found that the rate of decomposition was increased with the increase of kaolin content in the films. At 290 °C, the rate of maximum decomposition (Rmax) was 17 μg/°C for KsSNC film. A slightly higher decomposition rate, 22 μg/°C, was found for the KsSNC and KoSNC films at 300 °C and 312 °C. Besides, the KsSNC film showed a drastically increased decomposition rate of 30 μg/°C at 314°C, which is lower than that obtained from KaSNC, Rmax = 36 μg/°C, at Tpeak = 316 °C, indicating that the KoSNC film is more thermally unstable that the KsSNC film [27–36].

| Sample ID | Top | Middle | Bottom Curve |
|-----------|-----|--------|--------------|
|           | T_onset, °C | T Decomp, °C | Decomposition % | Reaction Pattern * | Tpeak (°C) and R max decomposition (μg/°C) |
| KsSNC     | 270 | 334    | 76           | Endo, Exo         | 290 and 17 |
| KoSNC     | 279 | 320    | 65           | Endo, Exo         | 300 and 22 |
| KsSNC     | 280 | 336    | 61           | Endo, Exo         | 312 and 22 |
| KsSNC     | 280 | 333    | 56           | Endo, Exo         | 314 and 30 |
| KaSNC     | 284 | 338    | 54           | Endo, Exo         | 316 and 36 |

*Endo-Endothermic and Exo-Exothermic

4.3. Thermal Mechanical Analysis (TMA)

Figure 5 shows TMA and differential thermal mechanical analysis (DTMA) graphs obtained from 0% to 20% kaolin containing starch films. Here, the top curve is for the DMA and the bottom curve for the DTMA obtained for the KoSNC film. The TMA curve shows that the first onset of contraction occurs at 37 °C, the value of which is 0.38 μm, and the second onset of contraction occurs at 93.5 °C, the value of which is 9.64 μm. The DTMA curve also shows two stages of contraction that occur at a rate of 0.068 μm/°C at 31.7 °C, and at a rate of 0.196 μm/°C at 98.5 °C. There is also an expansion that occurs at 47.3 °C with 0.21 μm contraction. Similar data were acquired from the kaolin self-assembled starch nanocomposite films. Table 2 represents the two-phase contractions within the range of 30 to 100 °C. The first onset contraction of nanocomposite occurs within the temperature range 37–38 °C, but the deformation significantly varies from 0.38 to 1.86 μm for KoSNC and KaSNC films, respectively. It
indicates that the kaolin assisted in contracting the film more strongly within the temperature range of 37–38 °C. Interestingly, at higher temperature (93.5 °C), contraction was increased dramatically from 0.38 to 9.64 μm for KsSNC.

Figure 5. TMA and DTMA curves for contraction analysis from the thermal analysis of (A) KsSNC, (B) KsSNC, (C) KsSNC, (D) KsSNC, (E) KsSNC, and (F) a comparison chart.
Table 2. Summary of thermal mechanical analysis (TMA) and differential TMA. DMTA: differential thermal mechanical analysis.

| Sample ID | Onset (Top Curve) TMA | DTMA (Bottom Curve) |
|-----------|------------------------|---------------------|
|           | °C | μm | °C | μm | °C | μm/°C | °C | μm/°C |
| KOsSNC    | 37.0 | 0.38 | 93.5 | 9.64 | 31.7 | 0.068 | 98.5 | 0.196 |
| KoSNC     | 38.0 | 0.56 | 94.1 | 6.34 | 31.7 | 0.037 | 98.5 | 0.190 |
| K10SNC    | 36.2 | 1.08 | 97.0 | 7.03 | 31.3 | 0.088 | 94.3 | 0.086 |
| K15SNC    | 37.2 | 1.26 | 96.0 | 7.8 | 31.2 | 0.083 | 95.2 | 0.130 |
| K20SNC    | 38.2 | 1.86 | 95.6 | 8.19 | 31.4 | 0.080 | 95.7 | 0.154 |

The temperature increased plastic flow of the starch matrix originated from loosening the entanglement of the polymer chain, which is the reason why the contraction increases. Whereas, in the case of the K5SNC film, contraction was changed from 0.56 to 6.34 μm, which indicates that kaolin plays a crucial role as a crystalline phase to prevent expansion by increasing the interfacial interaction with the soft polymer matrix. It is evident that the contraction of K5SNC film was the lowest in magnitude compared to other nanocomposites produced using kaolin. Interestingly, the contraction was increased gradually up to 8.19 μm for K20SNC film from 6.34 μm for K5SNC film. DTMA shows the contraction rate at two different temperatures. Initially, at around 31 °C, the contraction rate decreased to 0.037 μm/°C when 5% kaolin was added, after further addition of the kaolin contraction rate maintains almost steady (approximately 0.08 μm/°C) up to 20% kaolin content. Likewise, the films within the range of 94–98 °C show a similar pattern: the rate initially decreased from 0.196 to 0.086 μm/°C; then, it increased to a contraction rate of 0.154 μm/°C, which indicates that the K20SNC film was more unstable than the other K10SNC and K15SNC films [37–43].

4.4. Studies of Surface Morphology of Films

The morphological structures of the composite films were investigated using SEM. In Figure 6, SEM images are inserted, and Figure 6A represents the image of film produced without kaolin. The arrow indicates the dark spot of the film where a porous structure was found. The pore was distributed almost homogeneously in the film. The porosity was decreased after the addition of kaolin, as shown in Figure 6B–D. The least number of pores were observed from the K15SNC film, indicating the homogeneous distribution of kaolin in the film. Besides, the surface of the K20SNC film looks rough due to the agglomeration of excess kaolin, which is depicted in Figure 6E.
5. Conclusions

In this report, we have successfully prepared nanocomposite films of kaolin dispersed and self-assembled in starch biopolymer. The ATR-IR spectrum shows the presence of the functional groups of starch and kaolin in the nanocomposite films and their interaction. The self-assembled nanocomposite film produced from 15% w/w kaolin and starch exhibited moderate mechanical strength (stress 6.3 MPa) at break but showed the highest workable mechanical strength (stress 4.3 MPa) within the area of modulus of resilience. The thermal stability of composites was increased with the addition of kaolin, but the optimum stability was found for K15SNC film with T\text{onset} = 280 °C, a maximum rate of decomposition R\text{max} = 30 (μg/°C) and T\text{peak} = 314 °C. The contraction of all K5-20SNC nanocomposite films at around 95 °C were found to be lower in magnitude compared to the K0SNC film. SEM images proved that the nanofiller kaolin reduces the porosity of the film, and the minimum number of pores was envisaged in the K15SNC film. Such structural nanocomposite advanced materials produced from starch biopolymer and indigenous layered materials would play a crucial role in the field of nanoscience and nanotechnology.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2504-477X/3/3/83/s1. Figure S1: ATR-IR spectra of (A) K0SNC, (B) K5SNC, (C) K10SNC, (D) K15SNC, (E) K20SNC, and (F) kaolin recorded within the range of 500–4000 cm⁻¹. Figure S2: XRD patterns of XRD pattern of the films K0SNC, K5SNC, K10SNC, K15SNC, K20SNC, KaSNC, and kaolin.

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