



New biopolymer nanocomposites-based Polycaprolactone /polybutylene succinate modified clay: preparation and characterization



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Abstract

(Polybutylin succinate)PBS / (Polycaprolactone)PCL and AZO from organic clays incorporating 2-(diethylamino)ethyl 3-((4-acetylphenyl)diazenyl)-4-aminobenzoate montmorillonite (AZO-MMT) were used to produce polymer compounds by mixing the solution. These materials have been characterized using X-ray diffraction, infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). The nanocomposites have shown increased thermal stability. Where the results obtained from the XRD indicate that the materials prepared in this research are nanocomposites. The results of TEM were confirmed by the insertion of the nanocomposite. In addition, the solution molding process was used to prepare these nanocomposites, and these results were distinguished for comparison with the above-mentioned process.

Keywords: Na- montmorillonite, Polycaprolactone, Polybutylenesuccinate, nanocomposite, procaine, 4-aminoacetophenone

2.Introduction

Currently, researchers have made great efforts in the field of materials to find, create and alter biodegradable polymers from sustainable assets [1, 2]. Polybutylene succinate (PBS) is considered to be exceptional among biodegradable engineered polymers [3].

Due to its applications in material manufacturing, PBS is an effective participant in introducing disposable packaging. At the same time, low sub-atomic weight, low rigidity, and extraordinary spending limit its implementation [4-6]. Several experiments using low-weight plasticizers have been performed to enhance the properties. [7-13]. By substituting / mixing PBS with peroxide, the physical, warm, and biologically active properties of PBS were evaluated. [14-16]. It provides many favorable conditions in construction work because it is obtained as a sustainable, biodegradable and abundant raw material [9, 17, 18].

The nanocomposite is formed by attaching the organic clay to the polymer that helps to change the properties of the material. When the weight of the organoclay was increased by 0.5-5%, an improvement in physical properties such as thermal

and mechanical stability was observed in the blank member clay polymer [19, 20].

Incorporation of organoclay into PBS and PCL could provide an attractive method for creating nanocomposites [21]. Because of the weekly concordance between PBS and PCL, efforts have been made to increase their positive properties through cross-link compatibility, or coupling factor [22-24]. Such modifications have not received much attention because they are toxic, expensive and not environmentally friendly. At present, the use of modified organoclay in polymer / AZO-MMT mixture has been mainly investigated. The clay is usually hydrophilic and modified by substituting cationic ions with alkylammonium / phosphonium to reduce its strength [25-26]. The combination of the organoclay and the polymer to produce a nanocomposite is an initial method for adjusting the properties of the polymer. Refinement may be supplemented with objective constancy. Unlike the elegant polymer, the addition of 2-5 percent organic layers changed the physical and mechanical properties. [27]. In this study, the ammonium compound used to alter montmorillonite clays to prepare PCL-plasticized PBS was AZO. For many biochemical industries, this is significant because it is extracted from raw materials that are sustainable,

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biodegradable, environmentally friendly and readily accessible.

3. EXPERIMENTAL

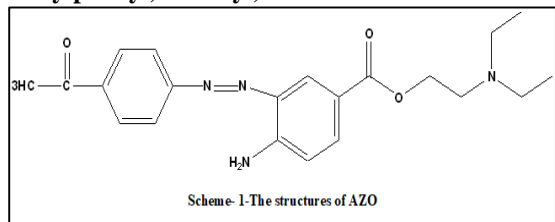
3. Materials and Methods

Fluka, Germany, supplied the procaine and 4-aminoacetophenone, while Sigma Aldrich, Germany, provided the sodium montmorillonite. Malaysia's (AOTD) was used to distribute PBS. Local suppliers, such as Nagoya, Japan, and Merck, Germany, were used to obtain chloroform (CHCl₃). J.T. Baker, USA supplied the HCl.

3.1. Preparation of azo [10]

4.15g amino acetophenone (0.04 mol) was dissolved in 3 ml concentrated hydrochloric acid, followed by 4-15 ml distilled water and cooling in an ice bath at 0-5 °C. The sodium nitrite was then dissolved (0.04 mol) (8.2 g) in 5 ml distilled water and put in an ice bath at (0-5 °C). A diazonium salt solution is gradually added to a purified water with sodium hydroxide solution of (0.04 mol) (10 g) procaine. (1.6 g) dissolved in (10 ml) distilled water at a temperature of 0-5 °C. The mixture was left for one day before the substance precipitated, during which it was purified and washed several times with distilled water before being recrystallized with ethanol to determine the percentage of the product (55%)m.p (193°C decomp.) scheme.1.

compound: 2-((diethylamino)ethyl 3-((4-acetylphenyl)diazenyl)-4-aminobenzoate



3.2. Preparation of Organic Clay

Organic clay was prepared through a positive interchange procedure, where Na⁺ was in montmorillonite and exchange with ammonium alkyl ion from AZO. 4.0 g sodium montmorillonite Na-MMT was vigorously mixed in 600 ml spicy filtered water for one hour. After that, a certain amount of AZO compound was mixed with the suspended clay containing AZO compound in 400ml of spicy water, and the necessary amount of concentrated HCL acid was added. After spinning vigorously at 80 °C for an hour, suspended organic clay was cleaned and purified with water; only one Mole AgNO₃ sol was found for some Cl. Later, dried up at 60°C for 3days. Finally, the organic layer of the particle was dried.

3.3. Preparation of PBS/ PCL / AZO-OMMT Nanocomposite

Dissolve polybutylin succinate in 50 mL chloroform, then dissolve polycaprolactone in 50 mL chloroform.

Separately, equal quantities of polybutylene succinate and Polycaprolactone were dissolved in 50 mL of chloroform, then the PCL solution was poured into PBS and the mixture was stirred for one hour. Add the mixture consisting of PCL / PBS to the required amount of modified clay(MMT - AZO) and then refluxed the mixture for one hour to ensure that the slurry is completely dissolved in PCL / PBS solution. Then the nanocomposite was placed in Petri dishes and allowed to dry. The quantities required for both PCL / PBS and the modified slurry used in this analysis were mentioned in Table 1

Table 1. PBS/PCL quantities and the altered clay

Trial	Mass of PBS in (g)	Mass of PCL in (g)	Mass of organoclay in (g)
1	0.90	0.1	0.00
2	0.86	0.09	0.05
3	0.84	0.06	0.1
4	0.80	0.05	0.15
5	0.76	0.04	0.2

4.1. Identification

4.4.1 X-ray Deviation Analysis

The Shimadzu XRD 6000 diffractometer device was used to research X-ray deviation for CuK radiation with a wavelength of (k = 0.15406 nm). The diffractogram is scanned to a degree of 2-10° at a rate of 1° min⁻¹.

4.4.2 (FTIR) Infrared Fourier Transform

The FTIR spectrophotometer was used to record the samples' FTIR spectrum using the KBr disc technique (FTIR-Spectrum BX, Perkin Elmer, USA).

4.4.3 (TGA) Analysis of Thermogravimetric Data

The Perkin Elmer TGA 7 thermogravimetric analyzer was used to determine the thermal constancy of the samples. Inside a N₂ chamber with a flow rate of N₂ 20 ml/min⁻¹, the sample temperature was raised to 35-800 °C at a rate of 10 °C/min⁻¹.

4.4.4(TEM) Transmission Electron Microscopy

Via power filtrate transport electron microscopy, the clay dispersal was performed (TEM). For a precipitation volt at 120KV, TEM was illustrated in the LEO 912 AB EFTEM. Using the Ultramicrotome Reichert-Jung Ultracut E instrument, the samples were arranged. A thinning partition of 100 nm was developed using diamond knives at a temperature of 120 °C.

5. Discussion and Results

5.1. XRD analysis

(n = d sin) denotes the distance between two consecutive layers of clay and the length of the X-ray wave traveled at the angle of incidence, according to

Bragg's law. Since the galleries contain AZO chains, the hydrophilic silicate is converted to an organophilic silicate, allowing the distance between Na-MMT layers to be increased [28]. Normal montmorillonite interlayer gap. The d001 diffraction peak corresponds to a basal spacing of 1.27 nm of Na-MMT at $2\theta = 9.610$, as calculated by X-ray diffraction. Na-MMT was treated on the surface with azo via a cation exchange technique as an intercalation agent. The intercalation agent molecule's aromatic tail would radiate outward, while the cationic head groups would preferentially reside at the surface layer. The optimal amount of Azo to achieve full dspacing was investigated, as shown in **Table 2**. The findings were as follows when the Azo and HCl concentrations were 4.0g and 16 ml, respectively, there was no substantial rise in d-spacing.

AZO-MMT has raised its overall basal spacing from 1.27 to 1.94 (**Table 2**), suggesting that Azo has been effectively intercalated into the Na-MMT galleries.

The Azo MMT has a lower basal spacing than the Na-MMT, meaning that Azo molecules form a monolayer although Na-MMT molecules are arranged in the silicate layer form a monolayer arrangement in the interlayer spacing.

Table 2 displays the XRD patterns of nanocomposites made with AZO (alkyl ammonium groups) modified montmorillonite nanocomposites. For 70 PBS 30 PCL/ AZO-MMT, The clay's basal spacing has increased by 2.45 nm in nanocomposites where the montmorillonite surface has been pretreated.

As previously mentioned, as the size of the surfactant increases, the basal spacing of the organoclay in the polymer matrix increases. All nanocomposites generated are intercalated compounds, according to these XRD patterns.

Table .2. Diffraction angle and basal spacing of natural clay (Na-MMT), modified clays with the AZO -MMT and PBS/PCL-OMMT nanocomposite

Sample	Exchanged cation	2Theta degree θ	d-spacing, nm
Na-MMT	Na ⁺	6.91	1.27
AZO -MMT	C ₂₁ H ₂₃ N ₃ O ₃ NH ₃ ⁺ AZO	4.56	1.94
70PBS30PCL/ AZO-MMT	-	3.45	2.45

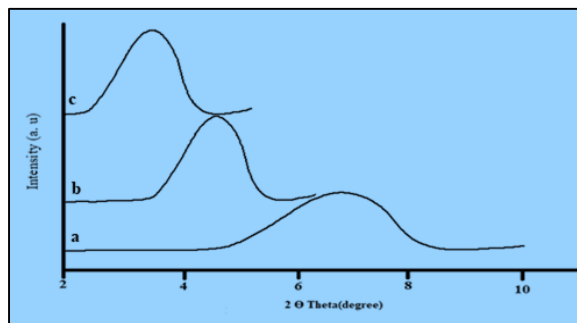


Fig.1: Layer silicate: (a) Modified Na-MMT, (b) Na-MMT by AZO and (c) PBS/PCL-AZO-MMT nanocomposite

5.2. Fourier transform infrared (FTIR): O-H stretching, interlayer water deformation, and Si-O stretching vibrations trigger peaks in the FTIR spectra of Na-MMT at 3625, 1632, and 1033 cm⁻¹, respectively. In addition to the bands of the original Na-MMT, the FTIR spectra of the AZO-MMT display the main bands of the AZO spectra [16]. The presence of the ammonium ion is indicated by the band at 1438 cm⁻¹. As a result, the AZO was intercalated in the silicate layers, according to these findings. The FTIR spectra of Na-MMT, procaine and AZO-MMT are shown in Table 2. (See Figure 2).

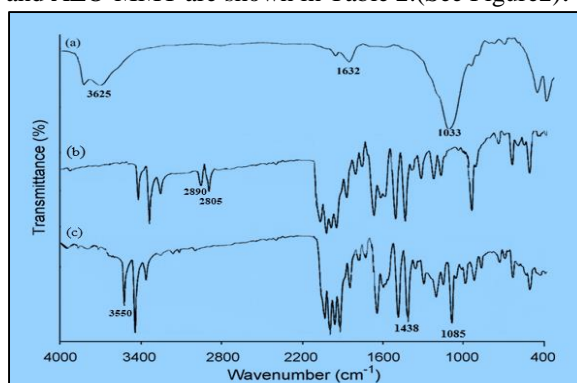


Fig. 2: FTIR spectra of (a) Na-MMT, (b) procaine and (c) AZO-MMT

5.3. TGA Analysis

The majority of thermoanalytical studies reveal new information about intercalated clay structure. The weight reduction measures in TGA provide details on the intercalating molecules' composition. When MMT is exposed to fire, it degrades in two phases. The first occurs before 200 °C when water trapped within the interlayer space and water adsorbed on the MMT's external surfaces volatilizes. Due to the loss of hydroxyl groups in the MMT structure, the second step is in the range of 200 to 500 °C. The updated MMT's thermal degradation can be broken down into four stages. The vaporization of water causes the first phase to occur at temperatures below 200 degrees

Celsius. In the second stage, the surfactant decomposes between 200 and 500 degrees Celsius. The third step involves dehydroxylation of the aluminosilicates at temperatures between 500 and 800 degrees Celsius. At about 800 degrees Celsius, Inorganic oxygen reacts with organic carbon (combustion reaction). In the final step, organic carbon reacts with inorganic oxygen at about 800 degrees Celsius (combustion reaction) **Figure.3.** portrays the MMT and AZO- MMT's weight loss curves (TGA). The hydrated sodium (Na⁺) cations intercalated within the clay layers provide MMT with its water content. The presence of alkylammonium within the MMT interlayer spacing reduces the inorganic structure's surface energy, converting organophobic materials to organophilic. The organic constituents in organoclay decompose in the range of 200 to 500 °C, while the organic constituent in unmodified clay decomposes in this range, As the temperature increased from 180° C to 305°C, the AZO decomposed, as shown in **Figure.3.** The fact that these AZO decompose at higher temperatures in organoclays means that the alkyl ammonium cations and the clay have a near intermolecular relationship.

5.4. TEM

The TEM technique was used to examine PBS-based materials in more detail. Tiny stacks of swollen clay layers and single scattered layers can be seen in the TEM micrograph of PBS/PCL nanocomposites made with AZO-OMMT, indicating a high degree of intercalation and exfoliation of the silicate layers (Fig. 4a).The presence of micro-aggregates (Fig. 4b) of the silicate layer in the presence of AZO in the PBS/PCL matrix indicates a certain degree of intercalation.

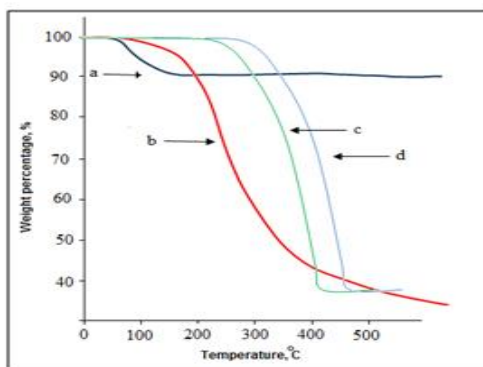


Fig. 3: TGA of (A)Na-MMT (B) AZO- MMT, PBS/PCL blend and nanocomposite PBS/PCL-OMMT

6. Conclusion

PBS and clay modified by AZO was used to create new polymer nanocomposites. The cation exchange method was used to successfully prepare organophilic

To put it another way, after the ion exchange, the AZO is intercalated and bound to the clay's silicate layers, raising the decomposition temperatures[28]. The alkyl ammonium cations and the clay have a strong intermolecular relationship, as shown by the increased temperatures at which the AZO decomposes in organoclays In other words, after the ion exchange, the AZO is intercalated and bound to the clay's silicate layers, increasing the temperature of decomposition. To evaluate the effect of modified clay content in the polymer matrix on thermal properties, On PBS/PCI/AZO-MMT nanocomposites, thermogravimetric analyses were performed. The TGA results are depicted in Figure.3. The temperature at which the nanocomposites begin to degrade (Figure.3) is higher for PBS/PCI containing AZO-MMT (318° C) than for the PBS/PCI blend (286° C).The results show that when AZO is applied, the thermal stability improves. The presence of uniformly spaced silicate layers in the polymer sheet helps to delay the degradation of nanocomposites by lowering the permeability of volatile degradation products out of the material.

individual clay layers or agglomerates is represented by the dark lines[10].Figure 4(b)The organoclay has lost its layering and is distributed in the PBS matrix, particularly when PBS/PCI/AZO-MMT is present. Tactoids aggregates, intercalated lamellae, and Similar structures are referred to as tactoids, which are made up of a variable number of lamellae. The TEM micrograph of (Figure 4(b)) revealed a higher degree of intercalation as well as some exfoliated areas. This is most likely the product of two AZO chains interacting.

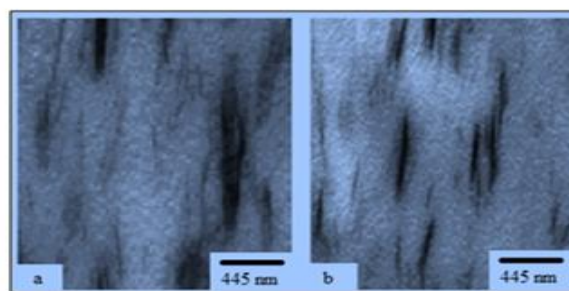


Fig. 4: TEM of a) PBS/PCL blend and b) PBS/PCL-OMMT nanocomposite

montmorillonites (AZO-MMT). The existence of an alkylamidonium group as a result of the modification is indicated by FTIR spectra.The decomposition temperature of AZO in the organoclay is higher than

in pure AZO, according to thermogravimetric analysis, implying that the alkyl ammonium and the montmorillonite have a heavy intermolecular interaction. By integrating 3% of AZO-MMT into PBS clay nanocomposites, they were made. The prepared nanocomposites were intercalated (PBS/PCI) and partially exfoliated, according to TEM review (AZO-MMT). As compared to PBS composites, The decomposition temperatures of PBS/clay nanocomposites are higher in TGA thermograms. The interlayer gap of organoclays in the PBS blend was substantially increased, as shown by the XRD patterns. It would be unnecessary to use petroleum-based surfactants if AZO was used to modify clay. These nanocomposites are valuable renewable resources and environmentally sustainable materials, in addition to being biodegradable.

7. Conflict of interest:

The authors confirm that this original article content has no conflicts of interest, financial or otherwise.

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9. References

- [1] Oishi A., Zhang M. , Nakayama K. , Masuda T. , Taguchi Y., Synthesis of poly(butylene succinate) and poly(ethylene succinate) including diglycollate moiety. *Polym.J.*, **38**(7): 710-715(2006).<http://dx.doi.org/10.1295/polymj.PJ2005206>.
- [2] Chieng B. W. , Ibrahim N. A., Then Y. Y. and Ying Loo Y., Epoxidized Vegetable Oils Plasticized Poly(lactic acid) Biocomposites: Mechanical, Thermal and Morphology Properties. *Molecules*, **19**(10), 16024-16038(2014). <https://doi.org/10.3390/molecules191016024>
- [3] Reddy M. M., Mohanty A. K. , Misra M. . Biodegradable blends from plasticized soy meal, polycaprolactone, and poly(butylene succinate). *Mac. mol. Mat. and Eng.* (297)455–463(2012). <http://dx.doi.org/10.1002/mame.201100203>.
- [4] Cho H. S., Moon H. S., Kim M., Nam K., Kim J. Y., Biodegradability and biodegradation rate of poly(caprolactone)-starch blend and poly(butylene succinate) biodegradable polymer under aerobic and anaerobic environment. *Was. Manag.*, **31**, 475–480(2010). <http://dx.doi.org/10.1016/j.wasman.2010.10.029>.
- [5] Sugihara S. , Toshima S. K., Matsumura, New Strategy for Enzymatic Synthesis of High-Molecular-Weight Poly (butylene succinate) via Cyclic Oligomers. *Mac. molec.Rap.Comm.* **7** 203–207(2006).<http://dx.doi.org/10.1002/marc.20050723>.
- [6] Yu L. L., Cheng J., Qu W. L., Mechanical properties of poly(butylene succinate) (PBS) biocomposites reinforced with surface modified jute fibre. *Composites Part A: Appl. Sci. and Manuf.*, **40**(669-674) (2009).
- [7] Thuy N.Thi and Lan P.N., Investigation of the Impact of Two Types of Epoxidized Vietnam Rubber seed Oils on the properties of poly lactic acid . *A. in Polymer Technology*; **9**(2) (2021).
- [8] Dean K., Yu L., Bateman S., Wu D. Y., Gelatinized starch/ biodegradable polyester blends: Processing, morphology, and properties. *J. of App. Polym. Scie.*, **103**(2) 802–811(2007).
- [9] Awale R. J., Ali F. B., Azmi A.S., Puad N. I. M, Anuar H. and Hassan A., Enhanced Flexibility of Biodegradable Poly(lactic Acid/Starch Blends Using Epoxidized Palm Oil as Plasticizer, *Polymers* , **10**(9) (2018).
- [10] Al-Mosawy M.G.A.A., New Biopolymer Nanocomposite Based Poly Polybutylene Succinate (PBS)/Corn Starch Modified Clay., **10** (1-7)(2020) .
- [11] Luzi F. , Torre L. , Kenny J. M. , and Debora Puglia., Bio- and Fossil-Based Polymeric Blends and Nanocomposites for Packaging: Structure–Property Relationship., *Materials (Basel)*. Feb; **12**(3): 471 (2019).
- [12] Ou-Yan Q. , Guo B. and Xu J., Preparation and Characterization of Poly(butylene succinate)/Polylactide Blends for Fused Deposition Modeling 3D Printing. *American Chemical Society* **3** (10) 14309–14317(2018).
- [13] Shemmari F. A., Rabah A. A. A., Comparative study of different surfactants for natural rubber clay nanocomposite preparation. *Rend. Linc. Sci. Fis. e Nat.*, **25**(409-413) (2014). <http://dx.doi.org/10.1007/s12210-014-0307-z>.
- [14] Park J. W., Im S. S., Phase behavior and morphology in blends of poly(L-lactic acid) and poly(butylene succinate). *J. of Appl. Polym. Sci.*, **86** 647-655(2002).
- [15] Yokohara T., Yamaguchi M., Structure and properties for biomassbased polyester blends of PLA and PBS. *Eur. Polym. J.*, **44** 677-685(2008).
- [16] Kim D. J., Kim W. S., Lee D. H., Modification of Poly(butylene succinate) with Peroxide: Crosslinking, Physical and Thermal Properties, and Biodegradation. *J. of Appl. Polym. Sci.*, **81** (5) 1115–1124(2001).
- [17] Cui Li. , Rundong Z., Yahui W., Chuanjie Z. and Yi G. , Effect of plasticizer poly(ethylene glycol) on the crystallization properties of

- stereocomplex-type poly (lactide acid) *J. of Natural Sciences* (**22**) 420–428(2017).
- [18] Jariyasakoolroj P., Rojanaton N. and Jarupan L. Crystallization behavior of plasticized poly(lactide) film by poly(L-lactic acid)-poly(ethylene glycol)-poly(L-lactic acid) triblockcopolymer., *Polymer Bulletin*,(5)(2020).
- [19] Kulinski Z., Piorkowska E., Crystallization, structure and properties of plasticized poly(l-lactide). *Polym.* **46** (2005)10290–10300 (2005).
- [20] Ren Z., Dong L. ,Yang Y. Dynamic mechanical and thermal properties of plasticized poly(lactic acid). *J. Appl. Polym. Sci.* **101** 1583–1590 (2006).
- [21] Fama L., Rojas A. M. and Goyanes S., Mechanical properties of tapioca-starch edible films containing sorbates. *Food Sci. Technol.*, **38**(6): 631-639(2005).
- [22] Iqbal M., Mensen C., Qian X. and Picchioni F. Green Processes for Green Products: The Use of Supercritical CO₂ as Green Solvent for Compatibilized Polymer Blends., *Polymers*.,10(11), 1285 (2018).
- [23] Luo Q. , Chen J. , Gnanasekar P. , Ma X. , Qin D. , Haining Na., Zhu J. and N. Yan, A facile preparation strategy of polycaprolactone (PCL)-based biodegradable polyurethane elastomer with a highly efficient shape memory effect., *New J. Chem.*, **44**, 658-662(2020).
- [24] Kaboorani A. Gray N. Hamzeh Y. Abdulkhani A. and Shirmohammadli Y., Tailoring the low-density polyethylene - thermoplastic starch composites using cellulose nanocrystals and compatibilizer., *Polymer Testing*., 93, (1), 107007(2021).
- [25] Yang J. , Ching Y. C. , Chuah C. H. , and Nai-Shang Liou Preparation and Characterization of Starch/Empty Fruit Bunch-Based Bioplastic Composites Reinforced with Epoxidized Oils., *Polymers*.**13**(1): 94(2021).
- [26] Guo J. , Wang J. ,He Y. , Sun H. , Chen X. , Zheng Q. , Xie H. Triply Biobased Thermoplastic Composites of Polylactide/Succinylated Lignin/Epoxidized Soybean Oil., *Polymers (Basel)* **12**(3):632(2020).
- [27] Kalamburand S. B. ,Rizvi, S. S. H. Starch-based nanocomposites by reactive extrusion processing *Polym. Int.*, **53**, 1413 (2004).
- [28] Shamsuri A. A. and Daik R., Mechanical and Thermal Properties of Nylon-6/LNR/MMT Nanocomposites Prepared Through Emulsion Dispersion Technique., *J. of Advanced Research in Fluid Mechanics and Thermal Sciences*., **73**(1) 1-12(2020).