



New Developments in the Formation of Nanocomposites between Starch and Clay

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Abstract

Biodegradable polymers, like Polycaprolactone (PCL), have recently received a lot of attention in the science establishment because of the growing global interest in non - petroleum-based polymeric materials. 3-amino - 4 - ((3-hydroxyphenyl) diazenyl) - N(pyrimidine-2-yl) benzenesulfonamide (AZO) one of the organic materials used to reconfigure natural clay (sodium montmorillonite). The clay particles were modified by stirring them in an aqueous medium of AZO-MMT, which increased the wavelength from 1.27 to 2.04 nm. The reconfigured clay would have been used to make PCL/corn-starch mixture nanocomposites. They were created by combining 0.5–5% AZO-MMT. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) were utilized to characterize the interaction of the modifier in the clay layer. The nanocomposites were prepared by solution casting method the reconfigured clay and a PCL/corn-starch mixture at a weight ratio of 80/20, which leads to an increase in the scope of tensile strength which that considers the biggest blend. The results of survey electron microscopy, transmission electron microscopy, and XRD was proved the creation of nanocomposites materials. Additionally, that PBS/corn-starch reconfigured clay nanocomposites exhibit that superior thermal stability significantly and a great increase over the PCL/corn-starch mixture.

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Key Words: Sodium Montmorillonite, 3-aminophenol, Polycaprolactone, Corn-starch, Nanocomposite, Glycerol.

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Introduction

PCL is among the most promising biodegradable prepared polymer aspirants (Oishi A., et al 2006). As a result, many materials engineers and scientists have worked hard to develop, discover, and reconfigure biodegradable polymers made from renewable resources (Chieng B.W., et al 2014). In addition to its uses in the medical and textile industries, PCL is a suitable choice for the production of disposable products. Conversely, its features such as its stiffness, low molecular weight, and rise in the preparation cost are factors that specify its uses and applications. Previous studies have been carried to promote the advantage and properties of biodegradable polymers by blending and integrate them with other composites or

utilizing the low-molecular-weight plasticizers to increase flexibility and reduce brittleness (Reddy M.M., et al. 2020). Investigated the morphologies and phase behavioral patterns of a Poly(lactic acid) / butylene succinate blend (Cho H.S, et al., 2010), while evaluated its properties and chemical structures (Sugihara S. et al. 2006). The physical, biodegradation, and thermal properties of PCL were evaluated by reconfiguring it with corn-starch. Corn starch has been used to improve PCL biodegradability and properties. It has numerous advantages in the chemical industry since it is made from biodegradable, renewable, and easily available raw materials (Yu L.L. et al 2009).

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Another method for modifying a material's property balance is to incorporate organoclays into the polymer to create a nanocomposite (Thuy N. Thi and Lan P.N., 2021). Furthermore, that can be improvements of mechanical and physical advantage as well as thermal stability by adding 1/2–5% weight of organoclays to polymer in the neat form (Dean K., et al 2007). Starch is a recent, sufficient, and biodegradable polymer made up of a carbohydrate and a large glucose unit linked to it by glycosidic bonds. Starch can be obtained in several plants, including rice, wheat, potatoes, tapioca, and corn (Awale R. J, et al 2018). Due to the lack of compatibility among PCL and starch, cross-link compatibility, or coupling factor, has been used to improve their positive qualities. Since such changes are toxic, expensive, and unfriendly to the community, they have received little attention. The use of organo-modified clay in polymer/starch mixtures is currently being researched. The clay is usually hydrophilic and is adjusted by positive ion substitution with alkylammonium/phosphonium to minimize its strength (Al-Mosawy M. 2020). Combination organoclay and polymer to create a nanocomposite is a first step in modifying the polymer properties. It is important to achieve full change in thematic continuity. Incorporating 2-5 percent organoclays instead of the elegant polymer improved the physical and mechanical properties (Luzi F. et al 2019). (3-amino-4-((3-hydroxyphenyl) diazenyl)-N-(pyrimidin-2-yl) benzenesulfonamide (AZO) was used to change the montmorillonite clay in this analysis (Ou-Yan Q et al 2018). The presence of long-strings in AZO donor groups implies that AZO may be useful as a mud modification surface (Park J.W. 2002). The use of AZO reduces the amount of accreditation on the petroleum surface (Yokohara T., Yamaguchi M., 2008). In addition, the current study looks at how to set up and discuss recent polymer nanocomposite compounds (Guo J. 2020.; Kalamburand S. et al 2004) PCL/modified starch.

Experimental Section

Materials

Sodium montmorillonite has been acquired from Sigma Aldrich, Germany. PCL was sent to Malaysia via (AOTD). Local suppliers such as Nagoya, Japan, and Merck, Germany, provided chloroform (CHCl₃). J.T. provided the HCl. Baker is located in the United States. Whereas *O*-aminophenol in addition to sulfadiazine get from Fluka, Germany.

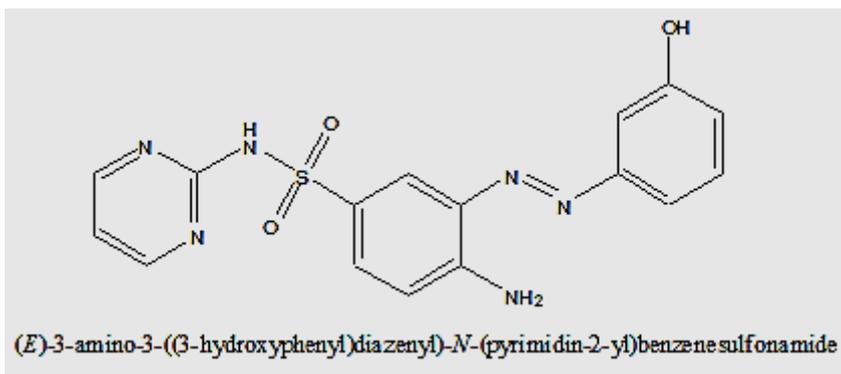
Preparation of 3-amino-4-((3-hydroxyphenyl) diazenyl)-N-(pyrimidin-2-yl) benzene sulfonamide (AZO) [10]

3 mL strong hydrochloric acid and 15 mL distilled water were used to dissolve (0.05mole) 3- amino phenol. The solution of the sample was cooled in an ice-water bath to 0-5 °C, so a solution of (0.05mole) sodium nitrite was dissolved in 5 mL distilled water and cooled to the same temperature. Dropwise, at the same temperature, this solution was added to the mixture while stirring. 0.05 mol) sulfadiazine dissolved in distilled water with sodium hydroxide 1.5 gm dissolved in 100mL distilled water, then the solution of alkaloid sulfadiazine was added slowly in to the prepared diazonium salt solution. The pH was kept at 6-7 and the temperature was kept at 0-5 °C, for 30 minutes, the mixture was mixed. The mixture was placed in the refrigerator overnight. The residue was precipitated and filtered, then washed several times with distilled water and sodium bicarbonate, then recrystallized from ethanol (yield 95%, black-brown solid).

Preparation of Organoclay [11]

Synoptically, for the preparation of organoclay; that was using a cationic exchange procedure, hence, the sodium ion in montmorillonite was replaced by the alkylammonium ion from the AZO, which was previously described in an aqueous solution in one of our previous works. To make a clay suspension, four grams of sodium montmorillonite (Na-MMT) were violently agitated with 600 mL of boiler water for one hour. Following that, specified amount of AZO compound was put to the clay suspension of the AZO compound, which was dissolved in 0.4 L of boiler distilled water and the necessary quantities of concentrated hydrochloric acid (HCl). To avoiding, finding of chloride after the vigorously agitated, that organo-clay suspension was purification by filter paper and washed with boiler distilled water for one hour at 80°C. Additionally, one mole of silver nitrate solution must be used. It was then dried for 72 hours at 60 degrees Celsius. Ou-Yan et al 2018 suggested that dry organoclay must be ground to particle size and be less than 100 m, which before was used in the creation of nanocomposite (Shamsuri A. A. and Daik R., 2020). As well as can show the structure of AZO in Scheme 1.





Scheme 1. The organizations of AZO

3. PCL/Starch/AZO-OMMT Nanocomposite Preparation

In a mass ratio of 4:0.5:3, a solution of starch, glycerol, and water was prepared. The polycaprolactone must be dissolved in 50 mL starch chloroform, and AZO-OMMT sol was pour and mixed continuously with the PCL solution. After adding the whole starch and AZO-OMM

solution to the PCL solution, the solution was mixed for 1 hour. The mixture was returned to the condenser for one hour for the changed clay (AZO-OMMT) in PCL / starch. The PCL/starch and AZO-OMMT solution were then thoroughly mixed. The dried nanocomposite was cast into Petri dishes:

Table 1. Shows the amounts of PCL/starch, AZO-OMMT, and organoclay that were used in the study

Trial	Mass of PCL (g)	Mass of Starch (g)	Mass of Organoclay (g)
1	3	1	0.00
2	2.96	0.99	0.05
3	2.92	0.98	0.10
4	2.88	0.97	0.15
5	2.84	0.96	0.20
6	2.80	0.95	0.25

1. XRD Analysis

Obviously, based on Bragg's rule ($n = d \sin$), d the wave-length intercept X-rays were dropped and intercept at the incident angle which distances among two sequential clay sheets. Moreover, galleries contain an amount chains of AZO-MMT which that causes mutate and converted hydrophilic silicate from original to organophilic silicate as well as causes raised in spacing between Na-MMT layer-to-layer (Shamsuri A.A. and Daik R., 2020). Na-MMT has a d_{001} diffraction peak at $2\theta = 6.91^\circ$, which corresponds to the interlayer distance of natural montmorillonite with a basal spacing of 1.27 nm, as determined by X-ray diffraction. Through a cation exchange method, Na-MMT was surface treated with AZO, an intercalation agent. The intercalation agent molecule's cationic head groups would preferentially reside near the surface layer, while the aliphatic tail would radiate away from the

surface. Table 2 shows that the maximum basal spacing of AZO-MMT increases from 1.27 to 2.04nm, showing that this AZO was efficaciously intercalated into the Na-MMT galleries as illustrated in the figure-1). The interlayer gap of Na-MMT forms a monolayer structure of AZO. In Scheme 1, the ammonium ion modification of clay from their nanocomposites is shown schematically. Figure 2 depicts the use of AZO and PCL/starch clay to make nanocomposite clay. For 80PCL20 starch /AZO-MMT, the basic spacing of the clay raised to 2.63 nm, as illustrated on Table 4. This clearly demonstrates that when the size of the surfactant rises, additionally raised in the basal spacing of organoclay in the polymer matrix.

These X-Ray diffraction patterns likewise imply that some of the nanocomposites are intercalated and others are exfoliated. Scheme 1. The clay modification of ammonium ions from their nanocomposites.

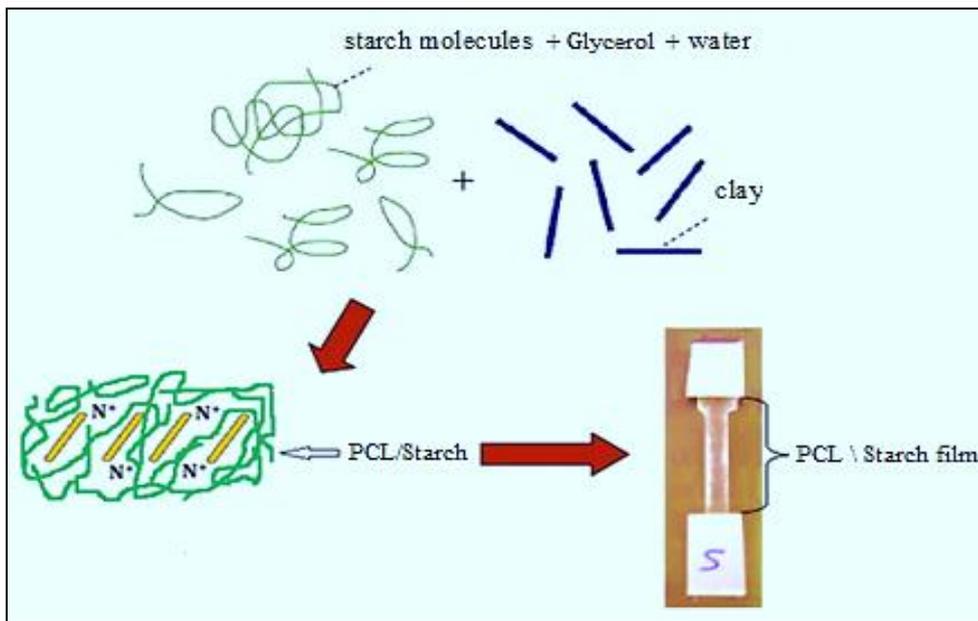


Fig. 1. Layer silicate: (a) Modified Na-MMT, (b) Na-MMT by AZO and(c) PCL/Starch nanocomposite

Table 2. Diffraction angle and basal spacing of natural clay (Na-MMT)

Sample	Exchanged cation	2 Theta degree	d-spacing .nm
Na-MMT	Na+	6.91	1.27
AZO-MMT	C16H14N6O3SNH3 AZO+	4.32	2.04
80PCL/20 STARCH-AZO-MMT	-	3.36	2.63

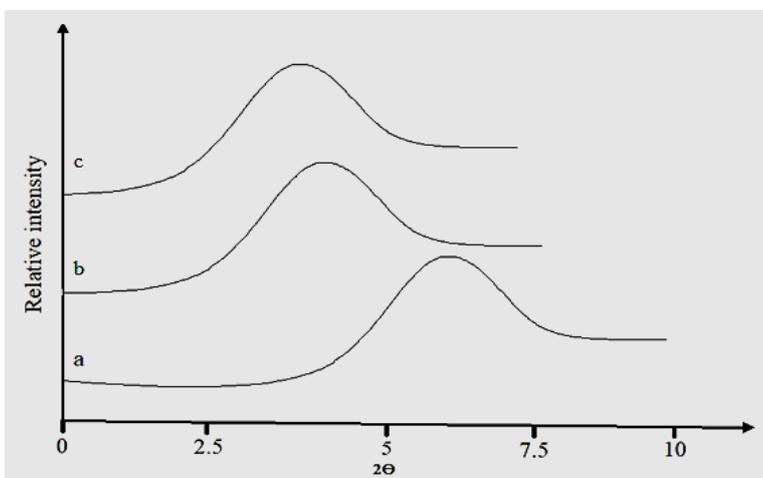


Fig. 2. Layer silicate: (a) Modified Na-MMT, (b) Na-MMT by AZO, and(c) PCL- AZO-MMT nanocomposite

2. FTIR Spectroscopy

Figures 3 and 4 show the FTIR spectra of AZO and Na (MMT), respectively. The O-H stretching, interlayer water deformation, and Si-O stretching vibrations are responsible for the peaks at 3632, 1643, and 1045 cm⁻¹ in the spectra of Na-MMT, respectively. The existence of Al-O stretching and Si-O bending, respectively, in the clay is shown by the substantial band absorption from 523 to 462 cm⁻¹. In addition to the bands of the AZO-MMT and the original Na-MMT spectra exhibit the primary

bands of AZO spectra [Ou-Yan Q et al 2018]. The presence of the ammonium ion is suggested by the bands from 1435cm⁻¹. As a result, these findings suggest that the AZO was intercalated in the Na-MMT silicate layers.



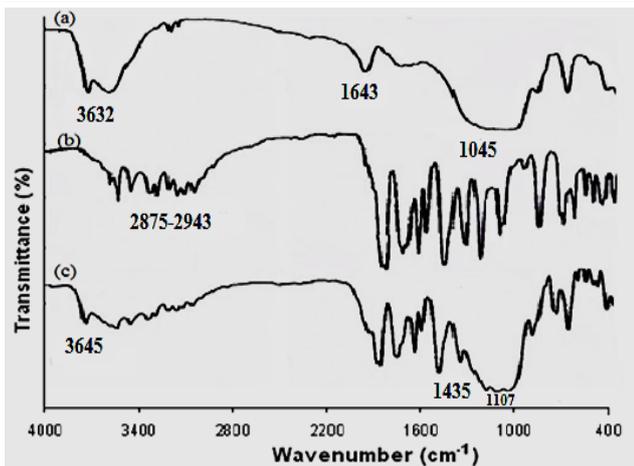


Fig. 3. FTIR spectrum about (a) Na-MMT, (b)AZO and (c)AZO-MMT

3. TGA

The majority of thermal analytical experiments give fresh information about intercalated clay structure. The weight loss steps in TGA provide data and note about of the structure form of the intercalating molecules. MMT degrades in two stages when exposed to heat. The first occurs before arrived to 200°C due to the vaporization and volatilization of the water adsorbed on the MMT's exterior surfaces and water trapped within the interlayer gap. The surfactant decomposes in the second stage at temperatures ranging from 200 to 500 degrees Celsius. In additionally, the result on the Figure 4 illustrated that weight loss curves (TGA) of the MMT and AZO-MMT. Because hydrate The existence of alkylammonium groups inside the MMT interlayer spacing decreases the inorganic

structure's surface energy, converting organophobic materials to organophilic materials. sodium (Na⁺) cations are intercalated inside the clay layers, MMT includes water. The fundamental difference between both the thermograms of unmodified clay and organoclay is that the organoclay's organic constituents decompose in the range of 200 to 500 °C, whereas the organic constituent in the unmodified clay decomposes in this range. As the temperature rose from 245 to 303 °C, the AZO disintegrated. Because of the higher breakdown temperatures of the AZO-MMT compared to pure MMT, there was a strong intermolecular contact between the alkylammonium cations and the clay. In other words, after ion exchange, the AZO is intercalated and bonded to the clay's silicate layers, raising the temperature of decomposition (Yokohara T., Yamaguchi M., 2008). To assess the influence of changed clay content in the polymer matrix on thermal characteristics, thermogravimetric investigations were performed on PCL/starch/AZO-MMT nanocomposites. The TGA results are given in Fig. 4. When comparing the PCL/starch blend (302 °C) to the PCL/starch containing AZO-MMT, the commencement of nanocomposites degradation is higher, at 324 °C. The addition of the AZO-MMT improves thermal stability, according to the data. The inclusion of uniformly dispersed silicate layers in the polymer layers reduces the permeability of volatile degradation products out of the material, which helps to postpone nanocomposites degradation.

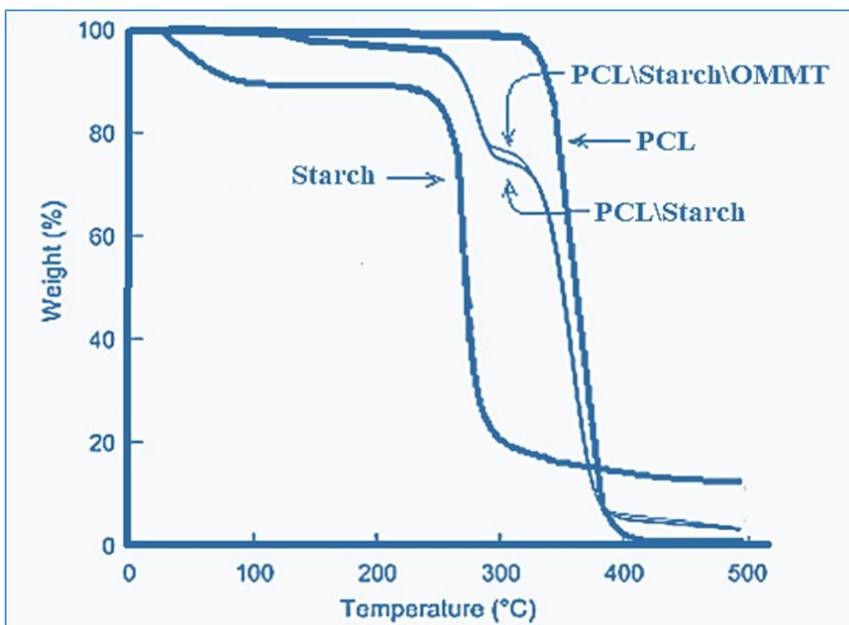


Fig. 4. TGA thermograms of PCL, Starch, PCL/Starch blend, and PCL/ starch-OMMT nanocomposite



TEM

The original Na-MMT stack morphology was fully preserved with Starch/PCL due to the incompatible nature of both constituents (Fig. 5) (Guo J. 2020). TEM micrographs of the Starch/PCL composites show that the original Na-MMT stack morphology was fully preserved with Starch/PCL due to the incompatible nature of both constituents. The thickness of the separate clay layers or agglomerates is represented by the dark lines (tactoids, stacks). The original layered structure of the organoclay is not visible. Intercalated lamellae, tactoids made up of a variable number of lamellae, and tactoids aggregates are all terms for the same thing. The TEM micrograph of the PCL/Starch/AZO-MMT reveals a higher degree of intercalation and the presence of certain exfoliated zones.

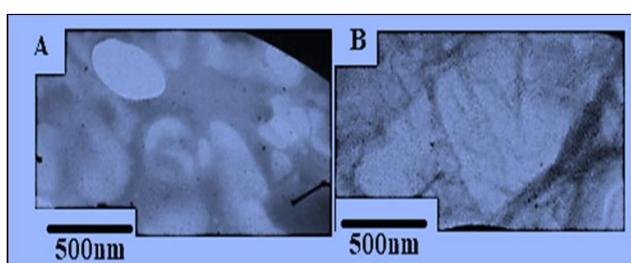


Fig. 5. TEM micrographs of (a) AZO-MMT, (b) PCL/Starch/MMT

Conclusion

New biopolymer nanocomposites were created in this study by treating starch-plasticized PCL-modified MMT with AZO. By adding 2% of AZO-MMT, PCL/Starch-clay nanocomposites were created. The produced nanocomposites were intercalated with partially exfoliated types, according to TEM examination (AZO-MMT). Since, they have outstanding thermic characteristics and ability to process and treated are made from renewable, ecologically acceptable biodegradable, and readily obtainable basic ingredients, these nanocomposites are a viable contender for producing disposable packaging. Biopolymer nanocomposites generated in this work are a good contender for producing disposable packaging, as well as their uses in the different sectors as textile and medical fields.

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