Mechanical and Thermal Properties of Natural Rubber/Poly Lactic Acid/dioctadecyldimethylammonium bromide Modified Clay Nanocomposites

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Abstract. This paper tackles a melt blend of polylactic acid/natural rubber with dioctadecyldimethylammonium bromide (DODAB) modified clay. The study investigated mechanical, thermal and morphological properties of polylactic acid/natural rubber and nanocomposites. The paper also examined Montmorillonite clay with alkyl ammonium ion of (DODAB). The studied parameters, PLA/NR nanocomposites revealed larger enhancements in mechanical properties in comparison to PLA/NR blend because of high polymer blend matrix shear forces exerted on clay aggregated during mixing polymer-clay. The original MMT with Na+ action leads to weak improvements in mechanical properties in comparison to organoclays. It is noted that the strength of tensile, modulus, and the nanocomposite samples can be improved with 4% of clay loading. The optimum sample morphology and chemical structure were tested by X-ray diffraction and FT-IR spectroscopy respectively. This paper denotes that polylactic acid/natural rubber-toughened nanocomposites with a higher modulus and in this way, thermal stability could be made.

1. Introduction:

Nanotechnology field has witnessed a great surge of developments especially Polymer nanocomposite, which is one of the latest steps towards this new field of science. Polymer nanocomposites attract research institutions’ and industries attention and interest as well. Several studies have been conducted to find out the appropriate enforcement filler for polymer nanocomposite [1,2]. Polylactic acid (PLA) is identified as a biodegradable thermoplastic polymer with a wide potential applications that has gained a lot of commercial attention because the polymer is made by a fermentation process from 100% annually renewable resources [3]. Generally, PLA is considered one of the most promising plastics as its tensile strength and stiffness is similar to polystyrene polyethylene terephthalate. Moreover, its processing properties are alike but it has low impact toughness. The lack of toughness limits its use in the applications that need plastic deformation at higher level of stress[4].Rasal et al.
(2010) have probed PLA advantages and their limitation [5] that is referred to as eco-friendly, biocompatibility, possible high strength and high modulus. High fragility, poor toughness, slow corrosion rate, hydrophobicity and lack of reaction side-chain groups that are PLA limitations. In order to overtake these limits, PLA was mixed with another polymer known polymer mixture that is employed various synthetic polymers as a second polymer. These include poly (ethylene) [6], polycaprolactone[7]. These polymers depended on petroleum to be replaced with renewable resource polymer to decrease negative impact on the environment[8].

Natural rubber (NR) is a unique elastomer that is utilized as an impact modifier to strengthen brittle polymers like polystyrene [9]. The excellent strengthening influence is due to its very low glass transition temperature (Tg) (-70°C) and the ability to apportion a small field in the polymer matrix [10]. Nevertheless, the immiscible issue between NR and PLA matrix is a challenge that should be taken into consideration to gain a good interfacial adhesion of PLA/rubber blends and optimal rubber particle dispersion in PLA matrix [11]. Ishida et al. proposed that elastomer with a high polarity as epoxidized natural rubber (ENR) (Tg -25 to -45 °C) could be an appropriate alternative as a PLA impact modifier. NR is flexible with low strength and modulus. In respect to their complementary characteristics, mixing PLA with NR is an alternative choice to improve the properties of PLA as toughness and elongation at the break without compromising its biodegradability [12]. On the opposite side, the epoxidized natural rubber (ENR) can be described as a chemically modified form of the cis-1,4-polyisoprene rubber with epoxide groups that are randomly situated along the polymer backbone [5]. The fusion of ENR into rubber blends offers many advantages as enhanced processing, toughness, flexibility in addition to outstanding oil resistance, decreased air permeability, sound damping and wet grip performance [13].

Clay can be used as a natural rubber filler for many years, but the reinforcing capability of clay is very low because of its large particle size and poor surface activity. The clay particles are only disseminated on the microscale in the polymer matrix even though the clay composed of silicate layers of 1 nm thick planar structure. The layers cannot be dissolved from each other by general polymer processing methods [14- 16].

Other earlier papers of synthetic rubber and natural rubber/clay composites that are cured by sulfur or peroxide have been investigated by several researchers. Pongtanayut et al. [17] showed that acrylonitrile butadiene rubber (NBR) cured by sulfur in which only 10 phr organoclay was necessary to attain tensile strength in comparison to compounds loaded with 40 phr carbon black. Beatrice Coltelli et al. [18] observed that entirely diverse tear morphology of acrylonitrile-butadiene rubber/clay nanocomposites cured with peroxide. The natural rubber/organoclay intercalated nanocomposites were effectively prepared through a melt mixing method, which is proven by the XRD pattern and TEM images. The physical and mechanical properties of radiation-induced crosslinking of natural rubber organoclay composite developed because of the existence of nanosize intercalated silicate layers in the natural rubber matrix [19].

The study has revealed that the incorporation of NR into PLA at a blend ratio of 20 phr had a plasticizing effect on the polymer blend [PLA/NR (60/40)]. The blend thermal stability was lower than that of the unblended PLA. A further study of the properties of the blends is ongoing.
2. Methods and Materials

2.1. Materials

Sodium montmorillonite was bought from Kunimine Ind. Co. Japan. Dioctadecyldimethylammonium bromide was got from Acros Organics, USA. Polylactic acid was bought from Japan. Natural rubber known as pureprena with the chemical name cis-1,4-polyisoprene was supplied by the Malaysian Rubber Board. Hydrochloric acid HCl was bought Sigma – Aldrich, Germany.

2.2. Organoclay Preparation

Through the exchange process it is prepared by a cation in which Na+ in the montmorillonite is substituted with alkylammonium ion in a solution. A definite quantity of sodium montmorillonite (Na-MMT) is moved strongly in 600 ml of hot distilled water for 1 hr. to make a clay suspension. Then, the preferred quantity of surfactant (dioctadecyldimethylammonium bromide) is being melted in 400 ml of hot water and preferred quantity of condensed acid hydrochloride (HCl) is appended to clay suspension (dioctadecyldimethylammonium bromide). After an hour stirring strongly for at 80 °c, the suspension of organoclay is purified and bathed in distilled water till no chloride is identified in 1.0 m silver nitrate solution. Then dried it up for three days at 60 °c. The dried organoclay (DODAB-MMT) is ground till the magnitude of the particle is less than 100 μm before the nanocomposite preparation.

2.3. PLA/NR–Clay Nanocomposites Preparations by Melt Blending

An internal mixer was used to prepare PLA/ NR blends of 60/40 ratio using diverse conditions of blending temperature, speed and time so as to study the optimal circumstances that were 170 °C, 75 round per minute and 10 mins. respectively. In order to make a sample of the compound, 20 g of PLA was first dissolved and blended comprehensively with 20 g of NR for 2 min. Different quantities of organoclays were combined into the blend in the third minute. Different quantities of organoclays (1, 2, 3, 4, 5, 6 and 7 pphp) are combined in mixture in 3rd min. That blend is compress-molded to a 1 mm thickness sheets under100 kgcm-1 compression in a standardized hot press at 150 °C along fifteen minutes with cold pressed method along ten min. to get an appropriate mixture film [20]. The quantity of PLA, NR and the organoclays employed are shown in table1.
Table 1. The amount of PLA/NR and organoclay for melt blending

| Sample Identity | Weight of PLA (g) | Weight of NR (g) | Weight of Organoclay |
|-----------------|------------------|------------------|---------------------|
| 6PLA 4NR        | 24.00            | 12.00            | 0.00                |
| 6PLA 4NR mod1   | 23.76            | 15.84            | 0.40                |
| 6PLA 4NR mod2   | 23.52            | 15.68            | 0.80                |
| 6PLA 4NR mod3   | 23.28            | 15.52            | 1.20                |
| 6PLA 4NR mod4   | 23.04            | 15.36            | 1.60                |
| 6PLA 4NR mod5   | 22.80            | 15.20            | 2.00                |
| 6PLA 4NR mod6   | 22.56            | 15.04            | 2.40                |
| 6PLA 4NR mod7   | 22.32            | 14.88            | 2.80                |
| 6PLA 4NR mod9   | 21.84            | 14.56            | 3.60                |

3. Results & Discussion

3.1. Analyzing elements

A quantity of surfactant that was inserted inside the clay galleries designed depending on the analysis of the element of the changed clays. These quantities of atomic carbon and nitrogen of sample clay are analyzed by the analyzer of elements. It is discovered that Na-MMT contained 0.46% carbon, and 0.15% nitrogen. Table 2 showed the quantities of C, N in Na_MMT, DODAB-MMT. The maximum adsorbed amount of DODAB-MMT is nearly corresponding to the cation exchange volume. As clay was denoting, which Na⁺ in clay could be simply substituted by the alkylammonium ion as shown in table 3.

Table 2. Amounts of C, N in Na_MMT, DODAB –MMT

| Element | Amount of element presence in clay (%) |
|---------|----------------------------------------|
|         | Na-MMT | DODAB-MMT |
| C       | 0.46   | 33.1      |
| N       | 0.15   | 2.1       |

Table 3. Amount of surfactants presence in the clay layers

| Organoclay       | Amount of intercalant intercalated in the modified clay |
|------------------|--------------------------------------------------------|
|                  | Calculation based on atom C (mmol/g) | Calculation based on Atom N (mmol/g) |
| DODAB-MMT        | 1.51                           | 1.39                                 |
3.2. Fourier Transform Infrared (FTIR) Spectroscopy

Figure 1 shows the FTIR spectra of the DODAB-MMT, PLA/NR or PLA/NR nanocomposites. The PLA/NR nanocomposites spectrum shows that the peaks are at 2997 cm\(^{-1}\) and 2944 cm\(^{-1}\) because of the C-H distending. C=O bending peak was observed in 1751 cm\(^{-1}\). The C-O bending peak is in 1184 cm\(^{-1}\). The Si-O peak is stretching in 460 cm\(^{-1}\) [21-22].

![Figure 1. FTIR spectra of (a) DODAB-MMT, (b) PLA/NR and (c) PLA/NR DODAB-MMT by melt blending](image)

3.3. Analysis of Thermogravimetric TGA

Analysis of Thermogravimetric (TGA) simply is a mass change quantitative dimension for a material that subjected to the controlled temperature program. Moreover, it displays the weight loss region temperature and the decomposition extreme temperature. TGA finds one or several steps of loss from the room temperature to 1000 °C. The purpose of the measurement was to define the sample thermal stability. The mass loss of the sample is because of the degraded by-product volatilization, which was observed like temperature role. Inorganic materials were considered more thermally constant also have resistance in comparison with these organic materials. Therefore, the inorganic particles introduction would significantly develop these organic materials to be thermally stable [23]. The NR decomposition commences about 242 °C. Above this temperature, The decomposition is speedy and it finishes at 530 °C. A total of weight loss was about 98.41% detected in NR decomposition. The TGA curve of NR in Figure 2a displays a single peak at 359 °C. This decomposition resembles to the NR total dissolution. While PLA begins decomposing about 268 °C and it finishes at 482 °C. The PLA decomposition displays a greater
level of volatile formation and a greater level of series scission than NR that displays a single peak of TGA curve at 420 °C (Figure 2b)[24].

The decomposition of PLA/NR, as shown in figure 2C, starts about 290.14 °C and finalizes in 391.21 °C. PLA/NR nanocomposites TGA curve, as shown in (figure 2c), is a single peak at 342.15 °C. When PLA blended with NR, thermal PLA decomposition in the mixture changes to a greater temperature zone. Figure 2d shows TGA thermogram of PLA/NR-DODAB-MMT nanocomposites. The nanocomposites degradation temperature increases with the addition of DODAB-MMT for the PLA/NR mixture. PLA/NR-DODAB-MMT nanocomposites decomposition begins about 299.51°C and concludes at 398.51°C. The PLA/NR-DODAB-MMT nanocomposites DTG curve in (Figure 2d) denotes a single peak at 349.24 °C.

![TGA thermograms of (a) NR, (b) PLA, (c) PLA/NR, and (d) PLA/NR-DODAB-MMT](image)

**Figure 2.** TGA thermograms of (a) NR, (b) PLA, (c) PLA/NR, and (d) PLA/NR-DODAB-MMT

### 3.4. X-Ray Diffraction XRD

The peak 20 of 7.48 and 2.82 of XRD pattern of MMT and DODAB-MMT corresponds to the basal spacing 1.17 nm and 3.11 nm respectively (Figure 3). In the melt blending process, the XRD of PLA/NR with 1,2,3,4, and 5php of DODAB-MMT indicate a change to a lower angles between 20 of 2.78-2.51, which resemble the basal spacing between 32.25-35.76 (Table 5). It is discovered that PLA/NR/DODAB-MMT nanocomposites with organoclay in melt mixing loading 4% render the maximum basal spacing (35.76). The previous results show that there is PLA/NR insertion inside the interlayers of the organoclay arranged by melt mixture. The increase of organoclay content decreases the basal spacing interlayer spacing due to the increment of organoclay content, which will minimize the quantity of polymer inserted in the galleries of the silicate layers [20]. Furthermore, it is associated with the surface accessibility in
which the closer packing of the silicate coatings was harder for the polymer chains pierce. According to the above mentioned results, inserted nanocomposites followed that method to prepare it in this study.

Table 4. Diffraction angle and basal spacing of montmorillonite and modified montmorillonite with DODAB.

| Sample               | 2Ѳ (˚) | d(001) spacing (Å) |
|----------------------|--------|---------------------|
| Montmorillonite      | 7.48   | 11.7                |
| DODAB modified       | 2.82   | 31.1                |

Figure 3. The XRD patterns (a) Na-MMT (b) DODAB-MMT

Figure 4. XRD patterns of PLA/NR with various ratio of DODAM-MMT

Table 5. XRD of PLA/NR-DODAB-MMT

| Organoclay content | 2Ѳ (degree) | d(001)- spacing (Å) |
|--------------------|-------------|---------------------|
| 1%                 | 2.78        | 32.25               |
| 2%                 | 2.74        | 32.73               |
| 3%                 | 2.71        | 33.09               |
| 4%                 | 2.51        | 35.76               |
| 5%                 | 2.58        | 34.75               |
| 6%                 | 2.59        | 34.62               |

3.5. Tensile strength

The optimal ratio of tensile strength and modulus properties of PLA/NR mixture was 60/40 \(^{25}\). Thus, the 60/40 ratio is employed for additional experiments. The polymeric materials tensile properties could be enhanced in diverse degrees if nanocomposites were shaped with layered silicates. The tensile strengths of hybrid films with diverse OMMT contents are displayed in Figure 5. The Figure shows that the
maximum tensile strength percentage is obtained at (4 wt%) of OMMT. This is the best ratio of organoclay that increased by about 20% respectively in comparison to PLA/ NR. In addition, the increase of the DODAB-MMT inclusions does not considerably alter the blend tensile strength. The greater clay concentration, organoclay wasn't evenly dispersed in the matrix. The accumulation of clay leads to split-up of phases [25].

![Tensile Strength](image)

**Figure 5.** Tensile strength of 60PLA40NR, with various contents of DODAB-MMT

### 3.6. Young’s modulus

It is displayed in figure 6 Young's modulus of PLA/NR nanocomposites with different OMMT percentages. The result showed that Young's modulus maximizes with an increase in the amount of OMMT. A maximum outcome is realized at 4 wt% of OMMT, which increased by 20%. The modulus improvement is because of high OMMT modulus with the good dispersal of OMMT inside the PLA/NR matrix. Young's modulus at higher OMMT concentration, which is at 5,6 wt% reduced because of an increase of localized clusters or accumulation of OMMT in the matrix, which can reveal in our SEM analysis of the composites at the levels of higher concentration.
3.7. Morphological Examination

3.7.1. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) shows the morphology of PLA/LNR and PLA/NR-DODAB-MMT nanocomposites at 4% OMMT loading, which shows the dispersal abilities of OMMT in the PLA/LNR matrix. Figure 7 (a) displays the SEM micrograph of the PLA / NR matrix. Figure 7 (b) indicates the good dispersal of 4wt% of OMMT inside PLA/NR. This discloses that the OMMT existence as a filler improved dispersal and interfacial adhesion of the polymer matrix. This remark corresponds to the greater value of tensile strength throughout the tensile test once OMMT was appended to composites.

Figure 6. Young’s modulus of PLA/NR nanocomposites at different OMMT loading

Figure 7. SEM micrographs of (a) PLA/NR, (b) PLA/NR with 4% DODAB-MMT
3.7.2. Transmission electron microscope (TEM)

Figure 8a explains the TEM micrographs of PLA/NR pure while in Figure 8b, the TEM PLA/NR/4% DODAB-MMT images displayed that the OMMT layers had aggregated at 4 phr OMMT content consistent with XRD analysis earlier. It can be the possible reason for the drop in the impact strength observed for PLA/NR with 4 phr of OMMT. The decrease in impact strength still was not acute because of the well-dispersed NR particles, which compensated the loss of toughness due to OMMT accumulation.

Figure 8. TEM micrographs of (a) PLA/NR, (b) PLA/NR/4% DODAB-MMT

4. Conclusions

DODAB-MMT reinforced PLA/NR nanocomposites have been made by melt blending method. The mechanical tests display that the tensile strength and Young's modulus are enhanced considerably at 4 wt% of OMMT in comparison to PLA/NR. X-ray diffraction (XRD) which indicates the method can be employed to synthesize PLA/NR clay nanocomposites. FTIR results display that DODAB-MMT is intercalated with the polymer. The OMMT homogeneous dispersal throughout PLA/LNR matrix and strong interfacial adhesion between OMMT and matrix realized through applying the ultrasonic energy method as confirmed by SEM and TEM images and proposed to be responsible for the significant properties enhancement. An additional amount of organoclay can cause brittleness of nanocomposites.
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