Effects of clay platelets and natural nanotubes on mechanical properties and gas permeability of Poly (lactic acid) nanocomposites

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Abstract
Environmental concerns have resulted in the increased use of biodegradable polymers and their nanocomposites. We have developed a facile method for measuring the work of adhesion ($W_a$) between nanoparticles and their matrix, which we showed can be used to determine their degree of intercalation within the matrix. This method was then applied to Poly (lactic acid) (PLA) nanocomposites with either sodium montmorillonite clays (C-Na$^{+}$), organically modified clays (C-30B), resorcinol di (phenyl phosphate) (RDP) coated C-Na$^{+}$ (C-RDP), Halloysite nanotubes (HNTs) and RDP coated HNTs (H-RDP). The C-30B showed the highest $W_a$ within the PLA matrix, followed by the C-RDP, and the C-Na$^{+}$. X-ray diffraction and TEM indicated that the C-30B platelets were highly exfoliated, the C-RDP were intercalated, while the C-Na$^{+}$ were aggregated in the PLA matrix. Oxygen gas permeability measurements showed the largest decrease in permeability for the C-30B nanocomposites, followed by the C-RDP, and the C-Na$^{+}$ nanocomposites. The values of the particle aspect ratios obtained using Nielsen model were consistent with the TEM images. In contrast to clay platelets, HNTs and H-RDP were not effective in decreasing oxygen gas permeability of PLA matrix, which was in excellent agreement with the model we derived. Despite the higher degree of exfoliation, the C-30B nanocomposites had a significantly lower Izod impact than the C-RDP nanocomposites. SEM images showed numerous micro-voids on the Izod impact fracture surface of C-30B nanocomposites. On the other hand, the nanotubes were much more effective in reinforcing the mechanical properties, with RDP coated tubes having the better performance, consistent with their higher value of $W_a$ with PLA matrix. These results showed that RDP coated silicate nanoparticles can provide environmentally safe alternatives for modifying the mechanical and gas barrier properties of PLA.

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1. Introduction

In recent years the environmental concern caused by the demands on polymer waste disposal has generated an increased interest in the applications of biodegradable polymers. One of the most popular polymers in this class is Poly (lactic acid) (PLA), due to its multiple applications in consumer products, biomedical structures, and more recently additive manufacturing. PLA is a thermoplastic aliphatic polyester polymerized from lactic acid and lactide monomers which are produced from the fermentation of crops and their residues [1]. Unlike the majority of biodegradable polymers which are degraded by microbial attack, PLA primarily degrades through hydrolysis, which allows its application in food-contact packaging and biomedical implants [2]. Furthermore, in contrast to other biodegradable polymers, such as polycaprolactone (PCL), Poly (butylene succinate-co-adipate) (PBSA), the mechanical properties of PLA are comparable to those of other glassy conventional plastics. In order to develop PLA as a potential replacement, properties such as modulus, gas permeability, and rheology could be improved further. It is well documented by Masami Okamoto et al. [3–10] that organically modified montmorillonite (MMT) clays can enhance the thermo mechanical, gas barrier, and even biodegradability properties of PLA. The degree of enhancement is a function of the degree of exfoliation which in turn has been shown by numerous groups to depend on the interactions between the host matrix and the clay surface. Modification of the clay surface
energies is usually done via cation exchange with quaternary ammonium chloride salts. These salts are known to be highly toxic [11] and hence can negate some of the advantages of using “environmentally friendly” polymer technology.

We have previously shown that the surface energy of MMT-clays can also be modified using resorcinol di(phenyl phosphate) (RDP) adsorption. This technique is easy to implement and RDP is far safer than quaternary ammonium chloride salts [12]. Pack et al. [13] have demonstrated that RDP coated clays can perform better than the organoclays in conventional polymer systems, such as styrenic polymers and polyolefin. Here we explore the properties of RDP coated clays with PLA, since that would produce nanocomposites which would enable environmentally friendly manufacturing in every aspect.

The clays that we used in this study are sodium MMT-clay platelets and Halloysite nanotubes. RDP is a liquid which we have shown previously to easily adsorb onto the surface of clays. Halloysite nanotubes are a type of natural occurring minerals with the empirical formula Al₂Si₄O₁₀(OH)₄ and are expected as possible alternatives to both clays and carbon nanotubes [14]. First we show how a simple procedure which measures the Young’s contact angle can be used to determine the affinity of the nanoparticles and the host matrix. Then we use this test to determine the compatibility of RDP coated clay platelets with PLA and compare the performance relative to Cloisite 30B, quaternary amine coated MMT-clays. In addition to surface interactions, the role of particle morphology is also explored, in particular as it affects gas permeability, by comparing the performance of the RDP coated clay platelets with Halloysite nanotubes, having the same surface functionalities. Finally we derive a set of equations, where these properties are used to predict the gas permeability as well as the mechanical properties of the nanocomposites.

2. Experiment

2.1. Materials

The MMT-clays, Cloisite Na⁺ (C-Na⁺) and organoclays, Cloisite 30B (C-30B) were supplied by Southern Clay Inc. C-30B is synthesized via ion exchange between Na⁺ of the C-Na⁺ and bis (2-hydroxyethyl) methyl hydrogenated tallow quaternary ammonium cation. HNTs were supplied by Applied Minerals Inc. with the trade name Dragonite. The RDP, known as Fyrol RDXF, was a type of phosphorus flame retardant agent (FR) provided by ICL-IP Inc. Poly (lactic acid), PLA 4042D, was purchased from the Natureworks LLC with a density of 1.24 g/cm³ and molecular weight of 120,000 g/mol.

2.2. RDP coated C-Na⁺ (C-RDP) and HNTs (H-RDP) preparation

The 20 wt % of RDP was placed into a 200 mL beaker and heated on a hot plate at 70 °C. Then, the 80 wt % of C-Na⁺ or HNTs were added and stirred manually with the RDP for 10 min. The mixture was removed from the beaker and put into a plastic sample holder which was then inserted into a Thinky Mixer for further mixing. The procedure was set at 700 rpm for 5 min. After that, the mixture was taken out and put into a mortar to be ground. Finally, the mixture was removed from the shaker and poured into a beaker which was then placed in a vacuum oven at 70 °C for 24 h for moisture removal and completion of RDP coating.

2.3. Nanocomposites preparation

The PLA nanocomposites were prepared by melting blend in a CW. Brabender operated at 180 °C. PLA pellets were poured into the chamber under 20 rpm. After the pellets melted, the nanoparticles were added, then increased the speed to 100 rpm and kept for 10 min. The mixture were cut into little pieces for hot-pressure molding to fit the requirements of different characterizations. The ratios of the samples were summarized in Table 1.

2.4. Characterization methods

2.4.1. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectra of RDP oligomers and nanoparticles were directly acquired using attenuated total reflectance (ATR) sampling technique from a Perkin Elmer Frontier FT-IR spectrometer with Universal ATR Polarization Accessory.

2.4.2. Transmission electron microscopy (TEM)

Cross sections of the PLA homopolymer nanocomposites were cut by Leica UC-7 at room temperature with a diamond knife. The ultrathin films with a thickness of 80–100 nm were then floated on the deionized (DI) water and then transferred onto copper grids. The cross sections were viewed by a JEOL JEM1400 Transmission Electron Microscope at 80 kV.

2.4.3. Scanning electron microscopy (SEM)

The SEM (Jeol JSM6700F) with a Schottky electron gun was used to display the fracture surfaces of the broken impact samples. The elemental distribution of silicon, aluminum and sodium were respectively acquired using an Energy Dispersive X-ray Spectroscopy (EDXS) attachment on the SEM. All the samples were required to coat 10 nm thickness of gold on the surfaces to increase electrical conductivity.

2.4.4. X-ray diffraction (XRD)

The structure of the nanoparticles and the intercalation and exfoliation phenomena of the various clay nanocomposites were characterized using the Ultima vertical theta–theta diffractometer (Rigaku Corp.) with a 1.6 kW X-ray generator and copper anode (wavelength, \(\lambda=0.154 \text{ nm}\)). The angular scan was performed by a scintillation counter along with Bragg-Brentano optics in fixed time mode.

2.4.5. Contact angle measurements

C-Na⁺, C-RDP and C-30B monolayers were made using Langmuir–Blodgett (LB) technique under certain procedures according to the previous works [13,15] and were imaged using a VEECO/DI3000 scanning force microscope (AFM) in contact mode. Preparation of HNTs and H-RDP layers were conducted by spin casting of HNTs and H-RDP methanol dispersion on the sulfuric acid treated, hydrophilic Si wafers. The wafers with HNTs and H-RDP were annealed at 70 °C for 1 h in a vacuum oven and then detected by SEM. Little PLA pieces (around 5 mg) were located on the clay monolayers and nanotube layers in a vacuum oven set at 180 °C for 24 h to melt the pieces and form PLA droplets. The contact angles of PLA droplets on each nanoparticle layer were observed and measured using the CAM 200 optical contact angle meter (KSV Instrument Ltd., Helsinki, Finland). The contact angle value of each sample represents the average measurements of 10 PLA droplets.

2.4.6. Dynamic mechanical analysis (DMA)

TA Instruments DMA Q800 was used to perform the dynamic mechanical properties of nanocomposites under the single cantilever bend mode at the frequency of 1 Hz. The storage modulus and tan \(\delta\) were collected from 20 to 80 °C at the rate of 3 °C/min.

2.4.7. Rheology measurements

Rheology performance of nanocomposites were tested using a Bohlin Gemini HR Nano rheometer from Malverm instruments. A
constant strain amplitude (2.5%) was applied for frequency sweep from 0.01 Hz to 100 Hz in oscillatory shear mode. All the samples were measured at 180 °C on a 20 mm aluminum cup.

2.4.8. Mechanical tests

Tensile properties of nanocomposites were obtained using Instron 5542 (Instron Co., Grove City, PA) in compliance with ASTM D-638, type M with the extension rate set at 2.5 mm/min. The Izod impact tests were conducted according to ASTM D-256 test method. The measurement value for each kind of sample represents the average tests of 10 specimens.

2.4.9. Gas permeability measurements

Oxygen permeability rate of all the samples were measured at room temperature by a permeability cell apparatus (CSI-135, Custom Scientific Instruments, Inc.) under ASTM D-1434 standard. Specimens with a thickness around 750μm were prepared by hot pressing. Each result represents the average measurements of 10 specimens.

2.5. Characterization of the nanoparticles

Nanoparticle structure was characterized using X-ray diffraction, TEM imaging and FT-IR spectroscopy. X-ray diffraction patterns of clay nanoparticles are shown in Fig. 1. A single peak at 2θ = 7.66° marks the first order (001) of the interlayer spacing of C-Na + at d = 1.16 nm [16,17]. The diffraction pattern of C-RDP displays both the (001) peak 2θ = 4.34° (d = 2.04 nm) and a second order (002) peak 2θ = 8.61° (d = 1.03 nm), which is in agreement with the results of Pack et al. [13] who showed that the RDP oligomers intercalate into the interspace of the clay platelets. The diffraction pattern for C-30B is also shown in Fig. 1 where we find a strong primary (001) peak 2θ = 4.82° (d = 1.83 nm) and a very weak secondary (002) peak 2θ = 9.57° (d = 0.93 nm) indicating that these clays are uniformly coated with the quaternary amine functional groups [16,18]. TEM images of C-Na + and C-RDP displayed in Fig. 2a, b also show the difference of morphologies. Under high magnification, we can observe the closely stacking layers of C-Na +, while we can only see blurred stacking silicate layers with the incorporation of RDP. The intercalation of RDP has also been confirmed by FT-IR spectra. The RDP IR spectrum in Fig. 3a showed a distinct phosphorus-oxygen single bond characteristic peak on 961 (cm⁻¹), and a typical phosphorus-oxygen double bond characteristic peak on 1298 (cm⁻¹). In addition, three characteristic peaks on 1125 (cm⁻¹), 1259 (cm⁻¹) and 1183 (cm⁻¹) verified the existence of P-O-Ar structure. We can also identify two obviously characteristic peaks from the C-Na + spectrum on 1041 (cm⁻¹) and 3631 (cm⁻¹), corresponded to Si–O stretching vibration and O–H stretching vibration, respectively. After coating of RDP, the C-RDP spectrum demonstrated some changes on peaks. The Si–O stretching band has shifted from 1041 (cm⁻¹) to 1075 (cm⁻¹), indicating the presence of RDP oligomers in the clay galleries [13,19]. The shift of P–O peak from 961 (cm⁻¹) to 1010 (cm⁻¹) can be ascribed to the formation of hydrogen bonding between RDP and the hydroxyl groups on the platelet surface [13,20].

Both coated and uncoated nanotubes showed nearly the same X-ray pattern in Fig. 1, where we found the specific (001) peak 2θ = 11.83° (d = 0.75 nm) corresponding to the dehydration state of interlayer [14] on either pattern, which indicated that RDP oligomers were failed to intercalate into the interlayer of HNTs. The TEM images of HNTs and H-RDP were shown in Fig. 2c, d. We can observe the homogenous coating layer of RDP on the HNTs surfaces in the insert of Fig. 2d, which was consistent with Pack’s results [21]. The coating of RDP on HNTs surfaces also resulted in the change of IR spectra. From Fig. 3b, we can identify three typical characteristic peaks of HNTs, which were Si–O stretching vibration on 1030 (cm⁻¹), internal hydroxyl groups on 3623 (cm⁻¹) and external hydroxyl groups on 3698 (cm⁻¹) [22,23]. When incorporated with RDP, like the situation in clays, the P–O peak shifted from 961 (cm⁻¹) to 1009 (cm⁻¹), which implied there were hydrogen bonding formed between RDP and hydroxyl groups on the surface of HNTs.

3. Results and discussion

3.1. Microstructure of nanocomposites

In order to detect the relative affinity between PLA and nanoparticles, contact angle measurements were performed. Monolayers of the clays were lifted onto Si wafers and the clay and nanotube layers were imaged with AFM (Fig. 4a–c) and SEM (Fig. 4d, e), respectively. From the images we can see that, except for a few areas where bilayers were observed, all the clays form monolayers at the air/water interface. Furthermore, regardless of the surface functional group, all clays were lifted successfully and uniformly covered the native oxide covered silicon surfaces. The
HNTs could not be spread at the air water interface and were spun cast on the Si wafers out of a methanol solution, as described above. The surfaces were too rough to be imaged with AFM, but the SEM images indicated that in this case as well, the surfaces were uniformly covered, even though the coatings appeared to be multilayered. PLA droplets were formed by heating 5 mg pellets of PLA under vacuum at 180 °C directly on the substrates for 24 h. In this manner, the molten polymer spread on the surfaces till the equilibrium Young’s contact angle was reached at the polymer/surface/air interface. The data was then analyzed by measuring Young’s contact angle (optical images) as shown in Fig. 4f–j and the results were summarized in Table 2. From the images and the table we can see that the contact angle is decreased on all functionalized clay surfaces relative to the angle of PLA on the C–Na⁺. The contact angle measured on the HNTs surface is 48°, which is significantly higher than the value on the RDP functionalized HNTs. On the other hand, the value is still much lower than 71°, or the value observed on the C–Na⁺. Even though a reduction is expected due to the increased surface roughness, the large difference could also be attributed to differences in surface chemistry between the unmodified C–Na⁺ and the unmodified HNTs. Coating the surfaces with RDP decreases the contact angles significantly to 40° and 37° on the clays and nanotubes, respectively. In this case the small differences may be attributed to the surface roughness, since the coating chemistry is identical on the two samples. In the case of the clay platelets, we can also compare the effect of chemistry, where we see that Young’s contact angle for C–30B, 35°, is somewhat lower than 40°, the angle of the that RDP clays. Using the measured contact angles we can now derive the relative affinity between the filler particles and the polymers. The Young’s contact angle (A) is related to the surface tensions of the solid substrate, the liquid polymer droplet, and the interfacial energy between them by the following relation;

\[
\gamma_s = \gamma_I \cos A + \gamma_{\text{inter}} \tag{1.1}
\]

where \(\gamma_s\) and \(\gamma_I\) are the surface tensions of the solid and liquid phases, and \(\gamma_{\text{inter}}\) is the interfacial tension between the solid and liquid phases. The work of adhesion \(W_a\) represents the reversible work required to separate a unit area of interface between two different materials [24] where higher \(W_a\) values indicate stronger affinity between the two materials. \(W_a\) is given by:

\[
W_a = \gamma_s + \gamma_I - \gamma_{\text{inter}} \tag{1.2}
\]

Combining equations (1.1) and (1.2) we obtain an expression which is mostly dependent on the contact angle and the polymer (liquid phase) surface tension as follows:

\[
W_a = \gamma_I (1 + \cos A) \tag{1.3}
\]

where we can see that the \(W_a\) depends only on the surface tension of liquid phase and the contact angle between two phases. Substituting the contact angle values in equation (1.3), we find that both C-RDP (1.77±0.03 γI) and C-30B (1.82±0.02 γI) are much more compatible to PLA as compared to C-Na⁺ (1.32±0.06 γI). Similarly, the \(W_a\) of HNTs (1.67±0.04 γI) is significantly improved to (1.80±0.02 γI), when the HNTs are coated with RDP, illustrating the surfactant function of RDP oligomers. In order to determine whether the clays were exfoliated or intercalated, X-ray diffraction was performed and TEM images of cross sectional slices of the samples were obtained. The XRD data is shown in Fig. 5a. In the figure we can clearly observe the (001) peak at 2θ = 7.67° (d = 1.15 nm) of the C–Na⁺, which remains virtually unshifted in the PCNa5 indicating that no intercalation by the PLA chains into the clay interlayer space occurred. This result is further confirmed.

![Image](a)

![Image](b)

![Image](c)

![Image](d)

Fig. 2. TEM images of nanoparticles: (a) C–Na⁺, (b) C-RDP, (c) HNTs and (d) H-RDP.

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by the TEM images of this sample, shown in Fig. 6a, where we can see that the clay is not exfoliated, but rather distributed as C-Na\textsuperscript{+} tactoids within the polymer matrix. In the case of PCRDP5, an obvious primary (001) peak at 2θ=2.42° and a secondary (002) peak at 2θ=4.81° can be found easily. By comparing the shifts of peaks between C-RDP and PCRDP5, we find that in PLA matrix, the interlayer spacing of C-RDP has been extended from 2.04 nm to 3.65 nm, which implies intercalation of clay platelets by the PLA chains. In contrast, only one weak secondary (002) peak at 2θ=5.28° (d = 1.67 nm) is observed in the samples with C-30B, indicating that clays are mostly exfoliated \cite{25,26}. The TEM images shown in Fig. 6b, c confirm the X-ray diffraction results, where we can observe enlarged interlayer spacing indicative of a well-intercalated structure in PCRDP5, while mostly individual platelets of C-30B are observed in PC30B5. These data are consistent with the relative values in the \textit{W}_a measured for the three types of clays and the PLA matrix and provide a guide as to the magnitude of the \textit{W}_a values required for exfoliation and intercalation. From the data we see that the work of adhesion between the polymer and the clay surface has to be significantly increased in order to affect intercalation, but only a small additional increase is required to initiate exfoliation.

The X-ray scattering spectra from PH5 and PHRDP5 are shown in Fig. 5b, where we can see that the characteristic peak at 2θ=12.18° (d = 0.73 nm) of the nanotubes on both patterns. In the case of the tube morphology, neither intercalation nor exfoliation with the polymer chains is possible. Furthermore, the results indicate that the incorporation of PLA has no influence on the dehydration state of interlayer for either coated or uncoated HNTs. The TEM images of cross sectional segments from these samples are shown in Fig. 6d, e, where we can see that both types of tubes are well dispersed within the matrix, which is consistent with the relatively high \textit{W}_a between the tube surface and the PLA matrix.

### 3.2. Mechanical properties

#### 3.2.1. Tensile and thermodynamic mechanical properties

The Young’s modulus results of PLA/clay nanocomposites are plotted in Fig. 7a, where we can see that the values increase linearly with increasing clay loading. The highest slope is observed for the PC30B samples followed by the PCRDP samples, while the smallest is observed for the PCNa samples. This behavior can be understood in terms of the degree of exfoliation of the different clays in the PLA matrix. The largest reinforcement of the modulus is achieved by the C-30B platelets which have the largest degree of exfoliation. As a result for the same weight fraction, this clay produces the largest amount of polymer/platelet interfaces, and coupled with the largest \textit{W}_a, these platelets are the most efficient at reinforcing the polymer. Even though the C-RDP is only intercalated and the C-Na\textsuperscript{+} is tactoidal as shown in TEM, they are also well dispersed within the polymer with sufficient polymer clay interfaces to reinforce the modulus of PLA. The Young’s modulus results of PLA/nanotubes nanocomposites are also plotted in Fig. 7a. As shown in the figure, the length of the nanotubes and their higher intrinsic modulus than clays \cite{27,28} are very effective at reinforcing the Young’s modulus of the composite and the increase in Young’s modulus with nanotube concentration is similar to that observed with the clays and in fact even larger for the H-RDP, than the 30B clays. A lot of previous researchers have mentioned that the polymer–filler interaction is the key to improving the Young’s modulus \cite{29–33}. In this case, higher \textit{W}_a enables a higher degree of exfoliation of clays, which creates more interaction areas, and stands for higher interaction ability between polymer and filler surface. Consequently, the nanocomposites with better \textit{W}_a always show the better improvements in Young’s modulus.
In contrast to the modulus, the degree of elongation shows a linear decrease with increasing filler concentration. The degree of elongation is a reflection of the degree of “flow” of the sample when shear stress is applied. If the $W_f$ between particles and matrix is large, strong adsorption of the polymer chains occurs onto the filler interfaces which restricts their motion under stress. As a result chain scission occurs rather than flow, which reduces elongation and embrittles the samples. This can be seen from Fig. 7b where we plot the degree of elongation, and where we can see that the PC30B samples have the largest negative slope, while the other samples show similar small slopes with increasing clay concentration.

The tensile strength of the neat PLA and nanocomposites, plotted in Fig. 7c, exhibits small enhancement for all the samples except the PC30B with the increasing filler content. The increase of Young’s modulus compensates the reduction of elongation rate, which leads to the constant value of tensile strength for PCNa, PCRDP, PH and PHRDP samples. On the other hand, the reduction of elongation rate for PC30B is so large that the improvement of modulus is insufficient to compensate for it.

The storage modulus ($G’$) of neat PLA and nanocomposites are shown in Fig. 8a, where we see that, below the glass transition temperature ($T_g$), all nanocomposites have larger values of $G’$ than neat PLA due to the interaction between PLA chains and the rigid nanoparticles. In the case of PLA/clay nanocomposites, the enhancement of $G’$ for PC30B is the largest while that for PCNa5 is the smallest, which again, confirms the fact that higher degree of exfoliation for clay nanoparticles yields more polymer/platelet interfaces and results in the better reinforcement within the polymer. The largest increase in $G’$ is observed for the PH5 and PHRDP5, indicating that in addition to enhancing the static properties, the tubular nanoparticles are also more effective at enhancing the dynamical properties of the composites. In the case of the clays, the enhancement was attributed to the positive $W_f$, which scaled with the increase in the value of the modulus. Furthermore, in a strongly interacting system is also known that the $T_g$ of the polymers are affected. This has been confirmed by detecting the peak of tan $\delta$ in Fig. 8b and displayed in Table 3, where we can see that the PCNa5, PCRDP5 and PC30B5 have increased 0.5 °C, 1.2 °C and 2.8 °C of $T_g$ respectively, and both PH5 and PHRDP5 show higher $T_g$ (2.5 °C and 2.4 °C respectively). The interaction between the PLA chains and nanoparticles causes the limitation of chains’ mobility and results in the rise of $T_g$. Therefore, higher $T_g$ corresponds to higher interaction, which is perfectly agreed with the $W_f$ values of all the particles with the PLA.

The performances of rheology tests have been shown in Fig. 9, where we can find out that the $G’$ of each nanocomposites becomes less frequency dependence compared to that of neat PLA. The small slopes of PH5 and PHRDP5’s curves at low frequency indicate that the $G’$ are becoming nearly independent of frequency. We ascribe this pseudo-solid viscoelastic transition to the restraint of PLA relaxation by the present of nanotubes. Similar rheological behavior has been observed in other polymer blend systems containing tubular nanoparticles like single and multi-wall carbon nanotubes [34–36]. PLA/clay nanocomposites also perform $G’$ curves with lower slopes at low frequency, which is consistent with some previous researches [5–8]. Among them, PC30B5 shows the lowest slope due to the highest degree of exfoliation. The $G’$ of both PH5 and PHRDP5 exhibit a similar independency of frequency to the high exfoliated PC30B5 sample, which implies that nanotubes are very effective to restrain the relaxation and long-range motion of PLA chains. The reason can be ascribed to the fact that tubular nanoparticles are easy to form intersected spatial networks in polymer matrix. It is worth to mention that all the mechanical results of PHRDP samples are better than PH samples at same filler concentration. This can be ascribed to the higher $W_f$ between the RDP coated on HNTs surfaces and the PLA matrix.

### 3.2.2 Impact resistance

In Fig. 7d, we plot the impact strength as a function of clay loading. From the figure we can see that it also drops linearly with increasing clay concentration. The slope of the PCRDP samples is smaller than that of the PCNa samples, while the slope of the PC30B samples is the largest. Comparing the rate of decrease in elongation with the rate of decrease of the impact strength one can see that the impact strength decreases much faster for all the PLA/clay nanocomposites. These differences are a consequence of the fact that the

<table>
<thead>
<tr>
<th>Parameters</th>
<th>PLA on C-Na</th>
<th>PLA on C-RDP</th>
<th>PLA on C-30B</th>
<th>PLA on HNTs</th>
<th>PLA on H-RDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact Angle</td>
<td>71.49±3.51°</td>
<td>39.86±2.34°</td>
<td>35.23±2.16°</td>
<td>47.92±2.94°</td>
<td>36.94±2.25°</td>
</tr>
</tbody>
</table>
Impact force in the Izod test is applied much faster than the ability of the chains in the entangled polymer to flow.

Nanoparticle inclusions in matrices can generate internal stresses, which result in local crack formation. When an external stress, $\sigma_s$, is applied, the stress generated at the tip of the particle, $\sigma_{\text{max}}$, is a function of the particle aspect ratio as follows [37].

$$\sigma_{\text{max}} = \sigma \left(1 + \frac{2a}{b}\right)^2$$  \hspace{1cm} (2.1)

Where, $a$ and $b$ are the length and width of the volume occupied by the particle. This volume can be estimated from the TEM images shown in Fig. 6 for each type of particle. From the figures we can see that the average aspect ratio, $r = a/b$, of C-Na + tactoids is around 1 to 5. In contrast for the PC30B samples, the platelets are fully separated and each platelet propagates the external force $\sigma$. From equation (3.1), $r$ is around 10 to 150, which results in a much larger stress applied to the matrix at the tip of the particle for the exfoliated vs. the tactoidal structures. This large concentration of energy cannot be easily dissipated and can result in cracks forming around the clay platelets. For low clay concentrations, the cracks would be small and localized around the particles, but as the number of platelets increases with increasing clay concentration, percolation

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**Fig. 5.** X-ray patterns of nanoparticles. (a) PLA/clay nanocomposites and (b) PLA/nanotube nanocomposites. The dots lines indicate the exact location of (001) peaks for every nanocomposites.

**Fig. 6.** TEM images of nanocomposites: (a) PCNa5, (b) PCRDPS, (c) PC30B5, (d) PH5 and (e) PHRDPS.
of the cracks is expected to occur, rapidly decreasing the impact resistance of the nanocomposite. In contrast, the number of the non-exfoliated particles is much smaller while the distance between particles is much larger, making propagation of the cracks more difficult, and resulting in a much smaller decrease with increasing clay concentration.

This can be seen in the SEM images obtained from the fracture surfaces of the specimens broken after the Izod impact tests. From Fig. 10a, f we can see that the PLA surface shows elongated fibrils which formed prior to fracture. Even though these fibrils are absent from the PLA/clay nanocomposites, large differences are observed between the exfoliated and non-exfoliated compounds. On the fracture surface of the PCNa5 one can see many steps and protruding clay tactoids (Fig. 10b). Closer observation of the tactoids, shown in Fig. 10g, indicates that they appear nearly oblong and are surrounded by a delaminated region, which resulted from the weak $W_t$ with the PLA matrix and the high internal stress at the tip of the tactoid ($\sigma_{\text{max}}$ can be as high as $11\sigma$). But since the particles are far apart, they remain isolated. In the case of the intercalated CRDP, the stronger $W_t$ suppresses delamination at the periphery of the particle. On the other hand, from Fig. 10h we find that the crack occurs in the middle of the tactoidal particle. In this case, the strong $W_t$ prevents the delamination at particle surface. Instead, the polymer in the interstices of the clay weakens the structure and makes it more prone to cracking under stress. The EDAX in the insert shows that the bright areas surrounding the cracks are rich in Si, or parts of the tactoidal structure. This different cracking mode is not much to be found on the fracture surface, and leads to the smoother surface appearance shown in Fig. 10c, which is consistent with the small decrease rate of the PCRDP samples in impact strength. A very different images are observed for the PC30B samples. From the high magnification image in Fig. 10i we see that the cracks decorate the individual clay platelets where the length of the cracks is consistent with the dimensions of the clay platelets obtained from the TEM images. Even though the $W_t$ of C-30B with the PLA matrix is very strong, the cracks are initiated by the extremely high internal stress at the tip of the platelet ($\sigma_{\text{max}}$ can be as high as $300\sigma$). Since the concentration of platelets is high, even at the low weight fraction (5%) shown in Fig. 10d, regions are already formed where the cracks percolate forming much larger fissures, consistent with the large embrittlement measured with increasing concentration. SEM images of samples where the C-30B concentration was increased to 15% are also shown. The lower magnification image in Fig. 10e shows large cracks that run parallel across the sample surface and are oriented in a direction where the impact forces were applied (red arrow). Higher magnification image in Fig. 10j of this sample shows large cracks that are forming as the smaller cracks which surround the clay particles converge and propagate the force in the direction of the applied stress. These cracking mechanisms of all the PLA/clay nanocomposites are summarized in the illustration shown in Fig. 11.

In Fig. 12a, b we show the fracture surfaces following the impact testing of the PLA/nanotube nanocomposites at lower resolution. The surfaces of the composites are more similar to the neat PLA, than to the PLA/clay nanocomposites, indicating that with nanotubes, some flow was able to occur. In Fig. 7d we plot the impact strength as a function of nanotube concentration, where we can see that even though the impact strength is somewhat smaller than that of neat PLA, the rate of decrease is significantly smaller than that observed for the PLA/clay nanocomposites, consistent with the appearance of the surface i.e. lack of steps or cracks, after fracture.

Fig. 7. Mechanical properties of neat PLA and nanocomposites: (a) Young’s modulus, (b) Elongation at break, (c) Tensile strength and (d) Impact strength.
The relative low aspect ratio and good $W_a$ with the matrix of HNTs and H-RDP are able to prevent the delamination under external force, which is further confirmed by the lack of voids around the nanotube/polymer interfaces. In addition, as shown in Fig. 12c and d, the erected tubes and voids on the fracture surface indicate an extraction or pull out process during the impact, which contributes to the impact resistance of composites. Similar to the results in tensile and thermodynamic tests, PHRDP samples always perform better than PH samples in impact resistance at same filler loading, which can be also ascribed to the higher $W_a$ of H-RDP with the PLA matrix.

3.3. Oxygen gas permeability

3.3.1. Platelets

It has been established by multiple groups that layered silicates provide efficient barriers towards gas diffusion by increasing the tortuosity of their diffusion pathways within a polymer, i.e. PLA matrix [5–7,9,10,38,39]. In order to determine the influence of $W_a$ and particle structure on the permeability, we plot the relative oxygen permeability as a function of filler concentration in Fig. 13a, where we can clearly see that the reduction in permeability is highest for the PC30B, or where the exfoliated particles provide the largest total barrier surface area. The data can be fit with the Nielsen model [40] which assumes that gas molecules travel through a tortuous pathway composed of rectangular platelets of width ($L$) and thickness ($W$), oriented in a direction which is perpendicular to the gas diffusion direction, as shown in the schematic of Fig. 13b. The relative oxygen permeability within the nanocomposites can then be given by

$$\frac{P}{P_0} = \frac{1}{1 + \frac{a^2}{2\phi}}$$ (3.1)

Where $P$ and $P_0$ are the gas permeability of polymers with and without nanoparticles respectively. $\phi$ is the volume fraction of the nanoparticles and $a=L/W$ is the aspect ratio of the platelets. If we fit the data with $a$ as the only free parameter, the best fits are obtained in Fig. 13a with the values listed in Table 4, where we can see that the values are somewhat lower than the centroid of the distributions observed in the TEM images, but this can be explained by introducing a tilt angle of platelets caused by random array in real situation as shown in Fig. 13c. The values obtained for the C-Na+ and C-RDP are much lower and clearly not related to the dimensions of the MMT platelets. But the values for $a$ obtained are similar to those for $r$, or the aspect ratio of the tactoids, which was used to determine the impact stress concentration. In this case, the lower permeability is an even more sensitive measure of both the number as well as the aspect ratio of the tactoids, and clearly

![Fig. 8. Dynamic mechanical curves of neat PLA and nanocomposites: (a) Storage modulus ($G'$) vs temperature and (b) $\tan \delta$ vs temperature.](image)

![Fig. 9. Storage modulus ($G'$) vs frequency curves of neat PLA and nanocomposites at 180 °C.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
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<tr>
<td>PLA</td>
<td>65.3</td>
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<td>PCNa5</td>
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<td>PCRDP5</td>
<td>66.5</td>
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<tr>
<td>PC30B5</td>
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<td>67.8</td>
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<tr>
<td>PHRDP5</td>
<td>67.7</td>
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Table 3  
Glass transition temperature ($T_g$) of neat PLA and nanocomposites from $\tan \delta$ curves.
Fig. 10. SEM images taken on the fracture surfaces of the neat PLA and PLA/clay nanocomposites, low magnification: (a) PLA, (b) PCNa5, (c) PCRD5, (d) PC30B5 and (e) PC30B15. High magnification: (f) PLA, (g) PCNa5, (h) PCRD5, (i) PC30B5 and (j) PC30B15.
sensitive to the reduction in size produced by the increased value of $W_a$ for the C-RDP relative to the C-Na$. The low gas permeability observed in all cases and especially for the PC30B is also consistent with the observation that the voids shown in Fig. 10i are a result of the shock of the impact. If the voids were generated by processing strains at the particle interface [41], increased, rather than decreased, permeability values would have resulted.

3.3.2. Nanotubes

The influence of the PLA/nanotube composites on the oxygen gas permeability is plotted in Fig. 14a as well, which clearly shows that for the same volume fractions, the tubes appear to have a much smaller influence on the gas permeability, even at high loadings. The cylindrical structure of the nanotubes is not well approximated by the schematic shown in Fig. 13b and c, and hence a modified version of the Nielsen model had to be developed, using the schematic shown in Fig. 14b. The evenly dispersed nanotubes with diameter $(2R)$ are first presumed to be arranged in an array perpendicular to the gas diffusion direction. The permeability coefficient ($P$) equals to the product of the diffusion coefficient ($D$) and sorption coefficient ($S$) [28].

$$P = DS$$

(3.2)

Since $D$ is affected by the tortuosity ($\varphi$):

$$D = \frac{D_0}{\varphi}$$

(3.3)

Where $D_0$ is the diffusion coefficient of polymer matrix, and $S$ is dependent on the volume fraction ($\varnothing$):

$$S = S_0(1 - \varnothing)$$

(3.4)

Where $S_0$ is the sorption coefficient of polymer matrix, the permeability coefficient equation can be expressed as:

$$\frac{P}{P_0} = 1 - \frac{\varnothing}{\varphi}$$

(3.5)

$\varphi$ is defined as the specific value of the gas diffusion path ($l'$) with the existence of nanotubes over the path ($l$) without:

$$\varphi = \frac{l}{l'}$$

(3.6)

The contribution of each nanotube to prolong the gas diffusion path is $R l' \frac{\pi^2 R - R}{8}$ on the average, and assume the mean number of nanotubes influenced gas diffusing is $C$, then:

$$l' = l + C \left( \frac{\pi^2 R - R}{8} \right)$$

(3.7)

And since $C$ can be written as:

$$C = \frac{l \varnothing}{2R}$$

(3.8)

Combine equation (3.7) and (3.8):

$$\varphi = \frac{\pi^2 - 8}{16} \frac{\varnothing}{\varphi} + 1$$

(3.9)

The relative oxygen permeability equation of nanocomposites with tubular additives is then:

$$\frac{P}{P_0} = \frac{1 - \varnothing}{1 + \frac{\pi^2 - 8}{16} \varnothing}$$

(3.10)

The equation (3.10) shows that the gas permeability of nanocomposites with tubular additives is independent of the tube diameter and hence the effectiveness of tubular nanoparticles on reduction of gas permeability in polymer matrix is much lower than that of platelet nanoparticles, in agreement with the experimental observation. The gas permeability for the nanotubes calculated from equation (3.10) is also plotted as a function of tube concentration in Fig. 14a where we can see that the actual data lies slightly above the curve, but no significant difference is discerned between the HNTs and H-RDP. The model proposed to derive equation (3.10) assumed an oriented array of tubes. The more realistic situation is shown in the lower panel of Fig. 14c, where the nanotubes are randomly oriented within the matrix. An exact equation for this case is more difficult to derive, but a simple approximation could be applied where the effective diffusion pathway of the tubes is assumed to be slightly elliptical, rather than spherical. This is further reducing the tortuosity of the gas diffusion pathway, and resulting in further, though slight, increase of the gas
permeability, and improving the agreement with experiment, as shown.

4. Conclusions

We have shown that contact angle goniometry was a good

![Figure 12](image1)

**Fig. 12.** SEM images taken on the fracture surfaces of the neat PLA and PLA/nanotubes nanocomposites, low magnification: (a) PH5 and (b) PHRDP5. High magnification: (c) PH5 and (d) PHRDP5.

![Figure 13](image2)

**Fig. 13.** (a) Relative oxygen permeability of nanocomposites with different volume fraction of clays. The black scatter lines represent the fitting results of each PLA/clay nanocomposites according to the Nielsen model. (b) The effect of parallel arrayed platelets on the oxygen diffusion inside polymer matrix. (c) The effect of random arrayed platelets on the oxygen diffusion inside polymer matrix.

<table>
<thead>
<tr>
<th>Samples</th>
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<td>PCNa</td>
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</tr>
<tr>
<td>PCRD5</td>
<td>6.60</td>
<td>1.5–15</td>
</tr>
<tr>
<td>PC30B</td>
<td>30.34</td>
<td>10–150</td>
</tr>
</tbody>
</table>

**Table 4**
Aspect ratio $a$ of each clay fitted from Nielsen model and aspect ratio $r$ of each clay observed from TEM images.
technique for determination of $W_a$ between nanoparticles and their matrix. The $W_a$ then can be used to determine the degree of intercalation of coated or uncoated clay platelets in the polymer matrix as well as the gas permeability, and the mechanical properties. The highest $W_a$ within the PLA matrix was determined for the C-30B platelets, followed by the C-RDP, and the uncoated C-Na++. X-ray scattering and TEM indicated that the C-30B exhibited a high degree of exfoliation, while the C-RDP were intercalated, and the C-Na+ platelets were aggregated into large tactoids. Consequently the C-30B showed the largest decrease in permeability to oxygen gas, followed by the C-RDP and the C-Na++. Using a modified Nielsen model developed to fit the permeability data, we obtained values of the particle aspect ratios consistent with the TEM images. Extending our model to the clay nanotubes we showed that in contrast to platelets, they would not be effective regardless of the $W_a$. This prediction was in excellent agreement with experiment.

The mechanical response of the nanocomposites was more complex. C-RDP minimized the reduction of the impact strength, while addition of C-30B significantly decreased it. SEM images indicated that the Izod impact created micro-voids at the clay/polymer interface. The voids were largest for the 30B sample, reducing its ability to withstand the shock. On the other hand, both RDP coated and uncoated nanotubes showed better performance in mechanical properties than clays especially in dynamic mechanical tests, with H-RDP always showing slightly better results consistent with the TEM images. The results above indicate that RDP absorption can be a much safer alternative method for cation exchange in functionalizing silicate surface nanoparticles. Platelet nanoparticles with high aspect ratio can efficiently improve gas barrier property but weaken the toughness of host matrix. In contrast, tubular nanoparticles are superior mechanical enhancers but have insignificant influence on gas permeability of host matrix.

Acknowledgment

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References

[12] MSDS-FYROLFLEX RDP.