Original Article

Synthesis, characterization and gas permeability properties of a novel nanocomposite based on poly(ethylene-co-vinyl acetate)/polyurethane acrylate/clay

Ramesh S. a,*, Punithamoorthy K. b

a Research and Development Centre, Bharathiar University, Coimbatore 641046, Tamilnadu, India
b Department of Chemistry, Government Arts College, Kumbakonam, Tamilnadu, India

ARTICLE INFO

Article history:
Received 8 April 2018
Accepted 13 July 2019
Available online 30 July 2019

Keywords:
Ethylene-co-vinyl acetate
Urethane acrylate
Organoclay
Nanocomposites
Gas barrier properties

ABSTRACT

In this paper, nanocomposites of poly(ethylene-co-vinyl acetate) (PEVA)/polyurethane acrylate(PIUA)/clay (Cl25A) (PEVA/PUA/Cl25A) are synthesized through a novel situ method of polymerization. Isophorone-diisocyanate (IPDI) and 2-hydroxyethyl methacrylate (HEMA) are mixed with Cloisite 25A (Cl25A) nanofiller, at different percentage of weights. Organ modified montmorillonite clay like Cl25A are used with PEVA/PUA matrix for their liberal compatibility. The main characteristic peaks of the nanocomposite materials are observed in FT-IR spectra. The changes in the intensity and the position validate the strong interaction between clay and polymer. The nanocomposites were investigated by thermogravimetric analysis (TGA) and have exhibited a better thermal stability than the pure pristine PEVA/PUA. Thermal stability in the sample with 5 wt.% of PEVA/PUA/Cl25A matrix has improved up to ~60 °C. The morphology of the nanocomposites is studied by scanning electron microscope (SEM) and X-ray diffraction (XRD). The XRD results have confirmed the penetration of clay into the PEVA/PUA matrix, as the d-spacing (d60 = 4.79 Å) increases with the increase in different weight percentage of clay. The dispersion of nanoclay in PEVA/PUA nanocomposites was investigated by scanning electron microscope. The mechanical property associated with tensile strength, elongation at break and Young's modulus has showed a dramatic increase by varying Cloisite 25A, the filler loading, when compared to the pure PEVA/PUA matrix polymer. The barrier properties of the PEVA/PUA/Cl25A nanocomposite membrane with 5 wt.% of Cloisite 25A loading has decreased by 51%. The results have suggested that these nanocomposite materials have great potential for applications in packaging materials films with superior properties.

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* Corresponding author.
E-mail: ramesh.shn@rmd.ac.in (R. S.)
https://doi.org/10.1016/j.jmrt.2019.07.026
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1. Introduction

Polymer/clay nanocomposite is known as a new class of material both in the industry and in academics since last decades [1,2]. Polymer clay nanocomposites have received great interest compared to more conventional macro and micro composites because they exhibit an enhanced potential for chemical, mechanical, thermal, barrier and flame retardant properties [3–8]. Polymer clay nanocomposites are a class of multiphase materials in which one of the phases is combined with at least one dimension in size range from 1 to 100 nm. Polymer clay nanocomposites are made by dispersing one-dimensional nanoclay plateau into a polymer matrix [9].

Montmorillonite (MMT) layered clay mineral has drawn great interest due to its unique cationic changes intercalation and swelling capacities. MMT belongs to 2:1 type of phyllosilicates family with the crystal structure made up of nanometer thick layer of aluminium octahedron sheet sandwiched between two silicon tetrahedron sheets. These clay nanoparticles have more advantages over traditional macro or micro particles (e.g., glass, carbon fibres) due to their high aspect ratio, the lower amount of loading to achieve similar properties and surface area enhanced adhesion between clay and polymers [10]. Layered silicates of clay are hydrophilic in nature. Most of the organic polymer is hydrophobic. Dispersion of clays in most polymers is not easily achieved due to an intrinsic incompatibility of hydrophilic layered silicates and hydrophobic organic polymers [11]. In order to make a successful polymer clay nanocomposite, it is necessary that the surface of the natural clay minerals be modified, so that it is compatible with organic polymers [12–15]. This modification is done through ion-exchange reaction of interlayer cations with quaternary alkyl ammonium or alkyl phosphonium cations. This modification causes an increase in the d-spacing and the diffusion of the polymer into the interlayer space.

Like other polymers, ethylene-co-vinyl acetate (EVA) is also easily affected by cross-linking and main-chain scission during long term use. For several decades, the subject of research for polymer scientists, has focused on improving the properties of polyolefins [16]. Ethylene-co-vinyl acetate (EVA) is heat seal strength, flexibility, low strength and high permeability. One of the potential methods to increase the strength and control the permeability within the broad polyolefin system is to add layered nanomaterials like clay to the copolymer. The combination of ethylene-co-vinyl acetate copolymer with nanoclay has wide commercial applications such as coating, shoeing, telecommunication cable, corrosion protection and packaging industry, which depends on the main chain of the vinyl acetate (VA) content [17,18]. Therefore, our study involves the permeability values for O₂ and N₂ as media that prevent penetration through the film in food wrapping. The increasing polarity, along with increasing VA content is apparently useful in imparting a high degree of polymer–clay surface interaction. It has been reported that there is a significant rise in Young's modulus and the yield strength of the EVA base of polymer clay nanocomposites [19].

Nanocomposites based on urethane acrylate are prepared by in situ polymerization and measured UV permeability has been reported [20]. The role of clay modifier on epoxy/clay/carboxyl-terminated (butadiene-co-acrylonitrile) (CTBN) hybrid was investigated. It is found that there is a significant improvement in miscibility, thermal stability and morphology. Detailed rheological cure analysis is carried out [21,22]. The compatibilizing action of clay in polypropylene (PP)/natural rubber (NR) blends and its effect on mechanical properties have been investigated. It is found that the localization of intercalated clay platelets in the PP phase and at the interface could help in compatibilizing the polymer blends effectively [23]. Some interesting mechanical properties and morphological characteristics of EVA/montmorillonite nanocomposites are prepared by melt blending polymerization [24]. The morphology and gas barrier properties of polyethylene/clay based nanocomposite prepared by melt blending polymerization have been reported [25]. The composite EVA/Na-MMT hybrid material in its application has offered more exciting properties in the enhancement of radiation-resistant effect. The gas permeation properties for the exfoliated EVA/organo clay nanocomposites are prepared by twin screw extruders [26]. Moisture barrier characteristics of nylon 6-montmorillonite nanocomposites are prepared by melt blending [27]. EVA/clay nanocomposites are known for its interesting application, as a flame retardant and its transport properties [28,29]. The effects of nano-sized silicate layers from montmorillonite on mechanical, thermal degradation and gas permeability properties of polyurethane have been reported [30].

The gas transport properties of poly(ethylene-co-vinyl acetate)/clay nanocomposites membranes have been reported [31]. It is found that the well dispersed modified nanoclay cloisite 25A has exhibited a lower permeability to oxygen and nitrogen gases compared to the other organoclay, due to the enhanced polymer–filler interaction. The influence of loading rates on morphology and mechanical properties of clay nanocomposites based on poly(lactide) is studied [32]. A significant improvement is found in the mechanical properties of nanocomposites with the increase of clay loading, due to the addition of stiff clay nanofillers into PLA matrix. Kannan et al. [33] synthesized ester based thermoplastic polyurethane nanocomposites by melt blending a maleic anhydride grafted polypropylene which is used as a compatibilizer. They found that the nanocomposites have exhibited a better abrasion resistance and water absorption resistance than other blending systems.

In this study, for the first time, we synthesized poly(ethylene-co-vinyl acetate)/polyurethane acrylate/clay nanocomposites to be used as a gas barrier property. The effect of nanoclay is evaluated on morphology and the mechanical properties of PEVA/PUA/C125A nanocomposites. To the best of our knowledge, the role of organo modified clay on the behaviour of PEVA/PUA/C125A nanocomposites material has not been reported yet.

2. Materials and methods

2.1. Materials

All reagents are used as an analytical grade. EVA copolymer (PILENE 1202, VA content 12 wt.%, MFI 8.0 g min⁻¹, density
0.92 g m\(^{-3}\)) was purchased from National Organic Chemical Industries Ltd. 2-hydroxyethyl methacrylate (HEMA) and azoisobutyronitrile (AIBN) were procured from Fluka, India. Isophorone-diisocyanate (IPDI) has been purchased from Sigma–Aldrich, India. Dibutyltin-dilaurate (DBTDL) is obtained from Fluka. Cloisite 25A (sodium montmorillonite modified with dimethyl hydrogenated tallow, 2-ethylhexyl quaternary ammonium cation) was received from southern clay, USA. Initially, clay was dried in a hot air oven at 80 °C for 6 h to remove moisture content. Chloroform (Merck, India) was used as such without further purification.

2.2. **Synthesis of PEVA/PUA clay nanocomposite**

The PEVA/PUA clay nanocomposite is prepared as described earlier in the literature[28]. 6 g of ethylene-co-vinyl acetate was taken in a three-necked reaction kettle and dissolved in chloroform. After swelling of EVA in chloroform, the calculated quantity of cloisite 25A (1 wt.% regarding the monomer) and (0.02 mol L\(^{-1}\)) 2-hydroxyethyl methacrylate (HEMA) is added slowly to a reaction vessel. IPDI (0.01 mol L\(^{-1}\)) is added drop wise which form urethane acrylate adduct. AIBN is used as a radical initiator. The reaction mixture is heated up to 80 °C under the nitrogen atmosphere for 4 h. PEVA/PUA/Cl25A nanocomposites film is obtained by pouring the emulsion into a Teflon mould. The experiment is repeated with 3, 5, and 7 wt.% of clay and the prepared composite material is dried. It is characterized by various analytical techniques. The reaction procedure and the structure of PEVA/PUA/Cl25A nanocomposites synthesized in this study are given in Fig. 1.

The codes and composition of the nanocomposite are given in Table 1.

2.3. **Measurements**

The FT-IR spectra of clay nanocomposite are analyzed using a Nicolet impact of 400 FT-IR spectrometers. The X-ray diffraction (XRD) measurements of the clay and nanocomposites are taken with the Rigaku Miniflex diffractometer (30 kV, 10 mA) with Cu Kα radiation (λ = 1.54 Å) at a scanning rate of 2 °C min\(^{-1}\) at room temperature. The spectra are recorded in the 2θ range 0–15°. The basal spacing of the nanocomposites is calculated using Bragg’s equation. The composite specimens are analyzed by X-ray diffraction using films of 2 mm thickness that are obtained at 180 °C compression moulding. The thermal stability of the polymer clay nanocomposites is performed on Perkin Elmer, Thermal Gravimetric Analysis (TGA) system at a 20 °C min\(^{-1}\) heating rate in N\(_2\) atmosphere. The samples are heated at room temperature to 800 °C. Scanning electron microscopic images of fractured surfaces of tensile specimens are carried out using JEOL JEM-5800 with an acceleration voltage of 20 kV. Mechanical studies are measured using a UTM Universal Testing Machine (Instron-3369, UK). A load of 100 N is applied at a crosshead speed of 50 mm min\(^{-1}\). The dumb-bell shaped specimens with 15 mm wide at the two ends and 10 mm wide at the neck with the thickness ranging from 1.1 to 2.9 mm are used to carry out the test as per ASTM D: 638 test procedure. The permeation study is done at constant pressure method using membrane separation unit.


### Table 1: Composition and codes of poly(ethylene-co-vinyl acetate)/polyurethane acrylate/clay nanocomposites.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Composition</th>
<th>NCO/OH ratio</th>
<th>UA (wt.)</th>
<th>EVA (wt.)</th>
<th>Clay (wt.%)</th>
<th>Hard segment (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEVAPUA</td>
<td></td>
<td>1.0</td>
<td>75</td>
<td>25</td>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>PEVAPUA/Cl25A-1</td>
<td></td>
<td>1.1</td>
<td>75</td>
<td>25</td>
<td>1</td>
<td>21</td>
</tr>
<tr>
<td>PEVAPUA/Cl25A-3</td>
<td></td>
<td>1.3</td>
<td>75</td>
<td>25</td>
<td>3</td>
<td>22</td>
</tr>
<tr>
<td>PEVAPUA/Cl25A-5</td>
<td></td>
<td>1.5</td>
<td>75</td>
<td>25</td>
<td>5</td>
<td>23</td>
</tr>
<tr>
<td>PEVAPUA/Cl25A-7</td>
<td></td>
<td>1.7</td>
<td>75</td>
<td>25</td>
<td>7</td>
<td>24</td>
</tr>
</tbody>
</table>

![Fig. 2 – FT-IR spectra of neat PEVAPUA.](image)

**3. Results and discussion**

#### 3.1. Fourier transform infrared analysis

The structural characteristic of polyurethane acrylate and PEVAPUA/Cl25A nanocomposites are carried out using FT-IR analysis [34]. FT-IR spectroscopy provides information about the functional groups. FT-IR spectra of the described samples are carried out in the region 4000–500 cm⁻¹ at room temperature. The infrared spectrum of the PEVAPUA and PEVAPUA/Cl25A nanocomposite is given in Figs. 2 and 3. The presence of the characteristic peak at 1543 cm⁻¹ is assigned to the NH bending vibration of urethane acrylate which is produced by the reaction of the NCO and OH group. The following absorption bands of 3754 cm⁻¹ (O–H stretching), 3394 cm⁻¹ (hydrogen-bonded water), and 1642 cm⁻¹ (O–H deformation) are shown by PEVAPUA spectrum. The characteristic bond at 1721 is ascribed to the C=O stretching frequency of acetate ions. In addition, distinct bands are observed at 660 cm⁻¹ (CH out of plane bending), 1156 cm⁻¹ (C–O stretching), 1390 cm⁻¹ (CH bending), 1458 cm⁻¹ (CH₂ plane scissoring), 2953 cm⁻¹ (CH₂ symmetric stretching) respectively. The bands occur around at 1050–1300 cm⁻¹ that correspond to the C–O stretching vibration of the ester group.

![Fig. 3 – FT-IR spectra of PEVAPUA/Cl25A-nanocomposite.](image)

The characteristic absorption bands of poly(ethylene-co-vinyl acetate)/polyurethane acrylate/clay for the nanocomposites are revealed. The following are characteristic bands 660 cm⁻¹ (C–H vibration of aromatic ring), 2975–2888 cm⁻¹ (CH stretching), 1088 cm⁻¹ (Si–O asymmetric stretching), 1259,
1088, 1018 cm$^{-1}$ (C–O stretching vibration of ester group) respectively.

In order to investigate the presence of hydrogen bonding in the PEV A/PUA/Cl25A nanocomposites the FT-IR spectra are studied at wavelength ranges from 2460 to 2980 cm$^{-1}$. The vibrations related to CH stretching observed at a range of 2888–2975 cm$^{-1}$, are found to be more intense with the increasing percentage of clay in the nanocomposites as compared to neat PEV A/PUA. The presence of carbonyl (urethane C=O and C–O stretching vibration of ester group) was also observed at vibration ranges from 1018 to 1259 cm$^{-1}$ which is due to the urethane part of the PEV A/PUA/Cl25A nanocomposite. Thus, the organomodified clay acts as a shield, which prevents the formation of hydrogen bonds between urethane (NH–COO) groups.

3.2. **X-ray diffraction analysis**

XRD analysis is used to examine the type of dispersion of nanoclay in the polymer matrix as well as the change in crystal form of PEV A/PUA with the presence of nanoclay. The wide-angle XRD patterns of pure clay and PEV A/PUA/Cl25A nanocomposite of different wt.% is shown in Fig. 4. Polymer/clay nanocomposites are formed by the insertion of polymer chains between the clay layers with increased gallery space. The XRD measurement is used to calculate the basal spacing ($d_{001}$) at peak positions according to Bragg’s law [35]. A shift in the $d_{001}$ peak of clay in the XRD spectrum is associated with the formation of intercalated structure, while the disappearance of this peak is indicative of an exfoliated structure in nanocomposites [36]. The basal spacing of organomodified MMT clay, i.e., Cl25A, shows a (001) characteristic peak at 20°=4.79°, that corresponds to the silicate-interlayer spacing value of 18.3 Å.

The characteristic peak of cloisite 25A is absent up to a 4° angle. PEVA/PUA/Cl25A, a nanocomposite which suggests that the cloisite 25A has nearly an exfoliated effect in the PEV A/PUA matrix. It appears from the results that the clay contents are homogeneously exfoliated and randomly dispersed in the PEV A/PUA matrix.

3.3. **Thermogravimetric analysis (TGA)**

The TGA thermograms of PEV A/PUA and PEV A/PUA/Cl25A, with different wt.% of clay nanocomposites, at 20 °C under nitrogen are illustrated in Fig. 5. The values of PEV A/PUA and PEV A/PUA/Cl25A are given in Table 2. The thermal degradation temperature undergoes two stages for PEV A/PUA/Cl25A nanocomposite [37]. The first stage is attributed to the elimination of acetate groups, which occurs at the degradation temperature range up to 300–400 °C. In other words, these nanocomposites have excellent thermal stability up to 270 °C. The second stage is the degradation of the main chain.

The PEV A/PUA and PEV A/PUA/Cl25A nanocomposites have shown no weight loss under 270 °C, and all the samples undergo decomposition that commences at around 300 °C. This result has revealed that the highly cross-linked PEV A/PUA is completely anhydrous and possesses a relatively good thermal stability. Moreover, it is found that the PEV A/PUA/Cl25A nanocomposites exhibit a slightly higher thermal decomposition temperature, i.e., 355 °C when compared to PEV A/PUA adduct 348 °C, respectively. The PEV A/PUA/Cl25A nanocomposite samples have left a residue of about 20% at 800 °C whereas the PEV A/PUA adduct has left a residue of about 16% at the same temperature. Such results indicate that 80% of the initial clay added is quantitatively introduced into the PEV A/PUA adduct. Therefore, the samples prepared are stable up to 500 °C, and the residual weight of the obtained

**Table 2 – Thermal behaviours of PEV A/PUA/Cl25A nanocomposites.**

<table>
<thead>
<tr>
<th>Nanocomposites with various clay content (wt.%)</th>
<th>PEV A/PUA</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$ (°C)</td>
<td>307.38</td>
<td>338.75</td>
<td>371.36</td>
<td>376.88</td>
<td>351.28</td>
</tr>
<tr>
<td>$T_2$ (°C)</td>
<td>416.44</td>
<td>457.43</td>
<td>475.07</td>
<td>480.59</td>
<td>435.92</td>
</tr>
<tr>
<td>Residue wt.%</td>
<td>17.24</td>
<td>19.47</td>
<td>22.87</td>
<td>24.57</td>
<td>20.62</td>
</tr>
</tbody>
</table>
nanocomposites films has increased as a result of the addition of clay to the PEVA/PUA.

\( T_{20} \) and \( T_{60} \) is the decomposition temperature at 20% and 60% of the weight loss, respectively. The temperature for pure PEVA/PUA is \( T_{20} = 307 \) °C and \( T_{60} = 416 \) °C, while PEVA/PUA/Cl25A nanocomposites have increased the temperature from 376 °C and 480 °C, respectively. Thus, the highest percentage of clay is successfully achieved at the highest decomposition temperature. Finally, the TGA results imply that the mobility of the polymer segments and clay at interfaces are partially suppressed by the interaction between them, resulting in a delay in polymer degradation. The thermal stability of the nanocomposites has improved when compared to that of pure PEVA/PUA that confirms a positive structural changes.

### 3.4. Scanning electron microscopy analysis (SEM)

The scanning electron microscopy (SEM) is used as a first step to evaluate the dispersion of the modified clay in the PEVA/PUA nanocomposites. The SEM photographs of PEVA/PUA with different clay weight content are displayed in Fig. 6. Significant differences between the SEM images of pure PEVA/PUA and PEVA/PUA/Cl25A nanocomposites are observed under this magnification and the clay particles are seen evenly dispersed within the PEVA/PUA matrix structure in the presence of small agglomerates. The size of these clay particles is in the range of 0.5–10 µm. Better clay dispersion is observed within the PEVA/PUA matrix due to the presence of stronger interactions between modified clay and this polymer.

The SEM images are used to study the nanocomposites film surfaces and to calculate the size of clay filler agglomerates on the film surfaces. The SEM images reported in Fig. 6 points out the film surfaces of PEVA/PUA and PEVA/PUA with 1%, 3%, 5% Cl25A nanocomposites as having the best results in terms of filler dispersion in PEVA/PUA matrix as shown by XRD spectra. The phenomenon of exfoliation, intercalation, and aggregation is challenging to study from SEM conclusively, which is easily reflected in XRD studies. Fig. 6a has shown that 0 wt.% organo clay is smooth and compact, with no evidence of pores, whereas in Fig. 6b, the surface of PEVA/PUA nanocomposites with 1 wt.% of organo clay is completely rough, which is attributed to the homogeneous distribution of the organoclay aggregate in the polymer matrix. During in situ polymerization, the high viscous and cross-linking of the dispersed phase, may produce an uneven surface. Fig. 6c shows a micrograph of 3 wt.% of organoclay with the best dispersion of the organoclay. SEM images of PEVA/PUA nanocomposite containing 5 wt.% Cl25A are shown in Fig. 6d, which shows a higher ratio of agglomerates.

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Fig. 6 – Scanning electron micrographs of (a) PEVA/PUA, (b) PEVA/PUA/Cl25A-1, (c) PEVA/PUA/Cl25A-3, and (d) PEVA/PUA/Cl25A-5 nanocomposites.
Fig. 7 – Tensile strength and elongation at break versus organoclay in PEV/PUA/Cl25A nanocomposites.

| Table 3 – Mechanical data of PEV/PUA/Cl25A nanocomposites. |
|-------------------|-------------------|-------------------|
| Sample code       | Tensile strength  | Young's modulus   | Elongation at break (%) |
|                   | (MPa)             | (MPa)             |                             |
| PEV/PUA           | 8.2               | 15.2              | 693                         |
| PEV/PUA/Cl25A-1   | 9.6               | 19.4              | 752                         |
| PEV/PUA/Cl25A-3   | 12.1              | 21.7              | 785                         |
| PEV/PUA/Cl25A-5   | 14.5              | 24.3              | 968                         |
| PEV/PUA/Cl25A-7   | 13.3              | 22.1              | 918                         |

3.5. Mechanical properties

The tensile test shows the film strength and elasticity which are determined according to the strength at break. A clear advantage of nanocomposites in comparison with conventional composites is the improvement in the strength by adding fillers. These results are mainly due to the high surface area of fillers, which create interaction with the matrix in nanoscale. The mechanical properties of PEV/PUA/Cl25A nanocomposites are summarized in Fig. 7. Tensile strength (TS) and percent elongation at break (EB) test results are listed in Table 3.

The tensile strength and elongation at break increase with an increase in the clay content up to 5 wt.% are shown in Fig. 7. In general, mixing Cloisite 25A with PEV/PUA has resulted in the diffusion of polymer chains into modified organophilic silicate layers and strong interfacial interactions. Hence it is expected that nanocomposite would tolerate more external load in comparison to the pure PEV/PUA. The tensile strength has changed to 14.5 MPa, which has shown an 80% increment when 5 wt.% of clay is added to PEV/PUA in comparison with pure PEV/PUA. This is due to the toughening and strengthening of PEV/PUA by the insertion of homogeneously dispersed clay in PEV/PUA matrix. The TS and EB begin to decrease in composites containing 7 wt.% due to the aggregation of clay content, causing a weak interaction between the PEV/PUA and clay layers. Young’s modulus of the nanocomposites, with different clay wt.% is shown in Fig. 8. Such results indicate that the incorporation of clay might reduce the molecular mobility of polymer chains, resulting in a less flexible material with a high Young’s modulus. The results have proved that the homogeneously dispersed clay particles in the polymer matrix have shown the maximum surface of the filler clay for the interactions with the polymer matrix. This large amount of interface between the clay and PEV/PUA chains has formed shear zones that probably stops the development of cracks and enhance the tensile strength and percentage elongation of nanocomposites.

3.6. Gas permeability adsorption study

The oxygen permeability values of PEV/PUA/Cl25A nanocomposites are listed in Table 4. The permeation study is done at constant pressure method using membrane separation unit. The PEV/PUA membrane is sealed within the two pressure cells. High pressure oxygen (1.5 bar) is kept in one cell, and the other cell is maintained at atmospheric pressure. The amount of gas transported through the membrane is determined from the following tortuous path model or Nielsen model equation.

\[
P/P_0 = \frac{1 - \psi_c}{1 + (A_c \tau_c) \psi_c} \tag{1}
\]

where P is the gas permeability of nanocomposite, \(P_0\) is the gas permeability of polymer, \(\psi_c\) is the volume fraction of clay, and \(A_c\) is the average aspect ratio of clay, respectively. The oxygen permeability decreases for PEV/PUA nanocomposite film with increasing clay loading, and it indicates that the organoclay enhances the oxygen barrier of the PEV/PUA. The diffusion coefficient of gases depends on

Fig. 8 – Effect of clay concentration on young’s modulus in PEV/PUA/Cl25A nanocomposites.

| Table 4 – Oxygen permeability coefficient of PEV/PUA/Cl25A nanocomposites. |
|-------------------|-------------------|
| Sample code       | O₂ permeability coefficient (cm³ mm⁻¹ m⁻² 24 h atm⁻¹) |
| PEV/PUA           | 164.8±10.8        |
| PEV/PUA/Cl25A-1   | 125.4±9.2         |
| PEV/PUA/Cl25A-3   | 95.2±8.3          |
| PEV/PUA/Cl25A-5   | 87.3±7.5          |
| PEV/PUA/Cl25A-7   | 91.8±9.3          |
the molecular size of the gas, rigidity and mobility of polymer chains and condensability of oxygen gas. Oxygen promotes high solubility in the polymer as the condensability of O₂ is 107 K. The oxygen permeability is reduced by 51% with 5 wt.% of clay. The barrier property is reduced when the clay loading is above 5 wt.% The relative permeability for different clay stack numbers (N) is calculated using the clay platelet dimensions. The typical value for MMT the aspect ratio of the clay platelets is assumed to be 218 nm. The steady-state diffusion of solutes through many layer membranes loaded with monodispersed fillers is aligned in a regular array via the following equation [38].

\[
P = \frac{1 - \phi}{1 - \phi + \alpha(N^2)\phi^2}
\]  

(2)

Nelson’s tortuous model Eq. (1) predicts that the stack number for PEVA/PUA nanocomposites is around 2, as shown in Fig. 9. The primary assumption made during the development of Eq. (2) is that the clay platelets are monodispersed and are aligned in a regular array.

4. Conclusions

PEVA/PUA nanocomposites are prepared successfully by in situ polymerization method. The interaction between the clay and ethylene vinyl acetate/urethane acrylate has proved the potential application of composite material to enhance oxygen permeability. FT-IR results have confirmed that successful complexation and strong interaction between clay and polymer. XRD and SEM analysis have indicated that the prepared nanocomposite is exfoliated and homogeneously dispersed in the polymer chain. The results of TGA have exhibited that the nanocomposite has higher thermal stability when compared to PEVA/PUA polymer. Mechanical studies have also revealed that tensile strength and elongation at break increases with increasing clay content, while Young’s modulus also increases. The PEVA/PUA nanocomposites films have shown better barrier properties to oxygen than PEVA/PUA due to the formation of the exfoliated nanostructure. The oxygen permeability coefficient of the PEVA/PUA has decreased after it was incorporated with clay. This enhancement in the barrier property is attributed to the clay content, which is well dispersed in the polymer chain and has to improve the oxygen permeability by 51%. It is concluded that the incorporation of clay has successfully enhanced the barrier properties of PEVA/PUA/G125A nanocomposites, whereby this improvement may aid in packaging materials.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

The authors would like to acknowledge the Research and development centre Bharathiar University for support and Central Leather Research Institute (CLRI) for all the analysis.

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