



Investigation of the Physico-Chemical Absorption Characterizations of Jute Polymer Clay Nanocomposites as a Function of Chemical Treatments

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Authors' contributions

This work was carried out in collaboration among all the authors. Author MFH designed the study, managed the literature searches, performed the statistical analysis, wrote the protocol and wrote the draft of the manuscript. Authors MAA, MKEZ, MMH, RZ and CMZ managed the lab facilities and analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

In this study, jute polyethylene clay nanocomposites were developed using hot press technique. The hydrophilic nature of fiber and nanoclay exhibited poor interfacial interaction to hydrophobic polymer matrix. In order to enhance the interfacial interaction among fiber, polymer, and nanofillers, the chemically treated jute (with benzenediazonium salt, propionic anhydride, and 3-isocyanatopropyltriethoxy silane) and organically modified nanoclay were used for the manufacturing of nanocomposites in this study. The effect of chemical treatments and nanoclay addition on the improvement of absorption characterizations of prepared nanocomposites against water and few chemical reagents have been investigated. It has been observed that the treated jute composites showed higher improvement in absorption properties than raw jute composite and silane treated jute composite found highest value. In addition, nanoclay filled composites showed higher improvement than composite without nanoclay and MMT-1.31PS nanoclay loaded

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nanocomposite exhibited highest improvement among five types of MMT nanoclay used in this work. The fabricated nanocomposites were resistant to all chemicals used except carbon tetrachloride.

Keywords: Jute fiber; montmorillonite; chemical treatment; nanocomposites; physico-chemical absorption.

1. INTRODUCTION

Recently, jute polymer composites have been widely considered a potential substitute for synthetic fibers in various industries [1,2]. The presence of the large amount of hydroxyl groups (-OH) and surface impurities make the fibers hydrophilic in nature, which weaken the fiber-matrix interfacial bonding in the composite system [3]. Many techniques have been used for fiber chemical treatments (alkaline, esterification, benzylation, permanganate, peroxide, and isocyanate treatments etc.) to overcome the incompatible surface polarities between the natural fiber and polymer matrix [4-6]. Thus, in order to enhance the fiber-matrix interfacial interaction, three types of chemical agents such as; benzene diazonium salt (BDS), propionic anhydride (PA) and 3-isocyanatopropyl triethoxysilane (silane) have been used in this study. On the other hand, the matrix phase plays an important role in the performance of polymer composites. Thermoplastics offer many advantages over thermoset polymers, because of their low processing costs and design flexibility. Most of the work has been reported so far deals with polymers such as polyethylene, polypropylene, polystyrene, and polyvinylchloride. Polyethylene (PE) with outstanding properties like low density, low cost, good flex life, excellent surface hardness, scratch resistance and excellent electrical insulating properties was chosen as matrix materials [7]. It had been reported that the chemically treated natural fiber reinforced polymer composites have shown remarkable improvement in mechanical and thermal properties [8]. Hence, polyethylene (PE) matrix have been used for the manufacturing of composites in this study.

In addition, montmorillonite (MMT) nanoclay as nanofiller in polymeric composites and their laminates have been used by many researchers for its low cost, availability, well-known intercalation/exfoliation chemistry, high surface area, and high surface reactivity [9]. Generally, MMT nanoclay is hydrophilic in nature [10]. In order to achieve an enhanced compatibility with polymer matrices, organically modified clay is used for the manufacturing of nanocomposites.

The addition of a small quantity of nanoclay can significantly improve the composite properties [11]. Higher clay loading above a certain threshold value can increase the viscosity of the matrix and a higher value can also be the cause of air bubble during the mixing process. It had been reported that the alkali treated jute-polyester/nanoclay bio-composites showed a considerable improvement in thermo-mechanical properties [12]. Thus, in this work, different wt% of chemically modified MMT nanoclay used for the optimization of clay content, and five types of MMT nanoclay have been used to identify the suitable nanofillers for manufacturing of nanocomposites.

The composite materials are largely used in many industrial applications that range from the petroleum industry to common household goods [13,14]. The fiber-reinforced composites are finding many applications in the manufacture of chemical reagents and water storage tanks. Thus, it is very urgent to examine the water and chemical absorption profiles of fiber polymer nanocomposites. It is also noted that the physico-chemical absorption behaviors of prepared nanocomposites have not been reported yet. Therefore, the aim of this study is to investigate the effect of chemical treatments and nanoclay content on the physico-chemical absorption characterizations of prepared nanocomposites.

2. EXPERIMENTAL

2.1 Materials

Jute fibers (*Corchorus olitorius*) were collected from Bangladesh Jute Research Institute (BJRI), Dhaka, Bangladesh. Polyethylene (PE) granules, used as matrix material, were supplied by Siam Polyethylene Company Limited, Bangkok 10110, Thailand. Chemicals used in this study such as NaNO₂ (sodium nitrite), C₆H₅NH₂ (aniline), CH₃OH (methanol), NaOH (sodium hydroxide), HCl (hydrochloric acid), H₂SO₄ (sulfuric acid) and CH₃COOH (acetic acid) propionic anhydride (PA), and 3-isocyanatopropyl- triethoxy silane (95%) were supplied by Merck, Germany. Montmorillonites such as: MMT-1.28E, MMT-

1.30E, MMT-1.31PS, MMT-1.34TCN, and MMT-1.44P were supplied by Sigma-Aldrich (USA).

2.2 Chemical Treatment of Jute Fiber

In this research, three types of chemical agents namely: benzenediazonium salt (BDS), propionic anhydride (PA), and 3-isocyanatopropyl triethoxysilane (silane) have been used for the fiber surface treatment. Jute fibers were mercerized using NaOH initially, and then submerged approximately for 1 hour individually with freshly prepared BDS solution, PA solution containing few drops of conc. H₂SO₄, and methanol-water (90/10 w/w) containing 2% silane solution, respectively. Then the fibers were taken out, washed well with distilled water and dried in an oven at 80°C for 12 hours. The fibers were then trimmed approximately into 3 mm in length for composite fabrication.

2.3 Fabrication of Composites and Test Specimens

Jute fibers, PE granules and MMT were mixed thoroughly in different weight fractions according to Table 1. The mixture was then settled in a mold and performed hot press technique for 1

hour at 180°C under the pressure at 7 MPa. The mould was then air cooled at room temperature and the prepared composites were collected from mold for characterization.

2.4 Characterization

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

The infrared spectra was recorded to determine the functional groups of jute fibers as a function of treatment using a Shimadzu FTIR 81001 Spectrophotometer taking scanned for 32 times from 4000 to 500 cm⁻¹.

2.4.2 Tensile test

To study the mechanical characterization of prepared composites, tensile tests were conducted using a Universal Testing Machine (Model: MSC-5/500, Shidmadzu Company Limited, Japan) at a crosshead speed of 5 mm/min according to ASTM D 638. The five rectangular dog bone specimens with dimension of 115 mm x 6 mm x 3.1 mm were tested in each case and the average value was reported.

Table 1. Different composition of jute, PE and MMT for composites fabrication

Specimen name with treatment method		Composition by weight (wt.%)		
		Jute	PE	MMT
Raw jute polyethylene composites (RJPEC)	5	95	--	
BDS treated jute polyethylene composites (BDSJPEC)	10	90		
PA treated jute polyethylene composites (PAJPEC)	15	85		
Silane treated jute polyethylene composites (SJPEC)	20	80		
PA treated jute polyethylene MMT-1.30E-1% nanocomposites (PAJPENC-1%)	5	94	1	
	10	89		
	15	84		
	20	79		
PA treated jute polyethylene MMT-1.30E -1.5% nanocomposite (PAJPENC-1.5%)	5	93.5	1.5	
	10	88.5		
	15	83.5		
	20	78.5		
PA treated jute polyethylene MMT-1.30E -2% nanocomposite (PAJPENC-2%)	5	93	2	
	10	88		
	15	83		
	20	78		
PA treated jute polyethylene MMT-1.30E -2.5% nanocomposite (PAJPENC-2.5%)	5	92.5	2.5	
	10	87.5		
	15	82.5		
	20	77.5		
Silane treated jute polyethylene MMT-1.28E nanocomposites (SJPENC-1.28E)	5	93	2	
Silane treated jute polyethylene MMT-1.30E nanocomposites (SJPENC-1.30E)	10	88		
Silane treated jute polyethylene MMT-1.31PS nanocomposites (SJPENC-1.31PS)	15	83		
Silane treated jute polyethylene MMT-1.34TCN nanocomposites (SJPENC-1.34TCN)	20	78		
Silane treated jute polyethylene MMT-1.44P nanocomposites (SJPENC-1.44P)				

2.4.3 Water absorption test

Water absorption test was conducted to determine water absorptivity as per ASTM D570-99. The test specimens were immersed in a beaker containing 100 mL of deionized water at room temperature (27°C) up to 552 hours (23 days). The weight of the samples was determined initially. After 24 hours, samples were taken out from the beaker, wiped and dry, weighted immediately. The percentage of water absorbed (w_{ab}) by the samples was calculated using the following formula. Three samples were tested for each set and were averaged.

$$w_{ab} = \frac{w_t - w_0}{w_0} \times 100$$

Where,

w_0 and w_t are the specimen weight before and after an immersion time t respectively.

2.4.4 Chemical absorption test

Chemical absorption properties were studied to find out whether these composites can be used in making chemical storage tanks that are resistance to chemicals in which more weight gain indicates the materials are less chemically resistant [15]. The chemical absorption of manufactured composites was tested according to the ASTM D543-87. The effect of some solvents, acids and alkalis on raw and treated jute composites with and without nanoclay were studied. In each case, five samples were weighed and dipped in the respective chemical reagents for 24 hours. They were then removed and immediately washed with distilled water and dried by pressing them on both sides with a filter paper at room temperature. The samples were then weighed and the percentage of weight gain/loss ($W_{g/l}$) was determined using the following formula.

$$W_{g/l} = \frac{W_f - W_i}{W_i} \times 100$$

Where,

W_i and W_f are the initial and final weight before and after immersion respectively.

2.4.5 Scanning Electron Microscopy (SEM)

The surface morphology of the prepared composites was examined using a table top

Scanning electron microscope (TM3030) supplied by JEOL Company Limited, Japan. To study the interfacial adhesion between fiber, clay and polymer matrices, the images were taken from the fracture surface. The samples were coated with gold and the images were taken at a magnification of 500x.

3. RESULTS AND DISCUSSION

3.1 FTIR Study

In order to reduce hydrophilicity, raw jute fiber was chemically treated using three different chemical agents such as: propionic anhydride (PA), benzene diazonium salt (BDS), and silane. Upon chemical treatment, the agents broke the OH groups at C-2 and/or C-3 and C6 positions of the cellulose in the jute [16]. Due to the steric effect, the hydroxyl group at C-3 did not undergo chemical reaction with the bulky diazobenzene group of the salt but the remaining two agents can react with the OH groups at C-2, C-3 and C-6. Fig. 1 show the FTIR spectra of untreated and treated jute fibers. The characteristic features of the spectrum are due to its constituent lignin, hemicelluloses and α -cellulose. In this study, in each treatment, the reactions were carried out in alkaline medium or jutes were pre-treated with 5% NaOH solution which removes a certain amount of lignin, hemicellulose and some impurities from fiber. A broad common absorption band in the region of 3600-3200 cm^{-1} is characteristic of hydrogen bonded O-H stretching vibration [17]. The intensity of O-H stretching vibration shifted to lower value due to the chemical treatment of jute fibers and the lowest value observed for silane treated fiber. The C-H stretching vibration of methyl and methylene groups in cellulose and hemicelluloses was observed at 2902 cm^{-1} . It decreased may be due to the pre-treatment of fibers with NaOH [18].

The band near 1751 cm^{-1} is assigned to the C=O stretching of the carboxyl and acetyl groups in hemicelluloses of the jute fiber that was prominent in raw jute fiber [19]. This band further decreased and became weak after chemical treatment, which is mainly due to the removal of acetyl group present in hemicelluloses. The bending vibration at 1641 cm^{-1} indicated the absorbed water in crystalline cellulose which disappeared after fiber chemical treatment. The band at 1512 cm^{-1} and 1359 cm^{-1} are considered to the presence of aromatic rings in lignin and C-H bending in hemicellulose and lignin,

respectively [20]. The band 1048 cm^{-1} , which is indicated C–O deformation for primary alcohol in lignin, was found with higher absorption intensity in raw jute compared to treated jute fibers [21]. It had been conducted by the researchers that the chemical treatment reduced the hydrophilic -OH groups resulting in increased interfacial bonding between the fiber and PE matrix in the composites [22], which is reflected on tensile values and absorption characteristics discussed below.

3.2 Optimization of Fiber Loading

Optimization of fiber loadings has been studied through the tensile behavior of the prepared composites. The tensile strength (TS) and tensile modulus (TM) of raw and treated jute reinforced polyethylene composites against different fiber loading are presented in Fig. 2, wherein A, B, C, and D belong to TS and A', B', C', and D' belong to TM values, respectively. It was observed that both the TS and TM increase continuously up to 15% fiber loading and then decrease after further addition of jute fiber. The 15 wt% jute content was the optimum composition. The effect of fiber loading on the tensile properties of composites is explained by the homogeneity of fiber and wettability of polyethylene matrix [23]. As the fiber content increases, the stress is more evenly distributed and the strength of the composites increases up to 15 wt% jute content. The

composite reveals a decrement after 15% fiber content due to the fiber agglomeration [24]. Significant improvement in tensile properties were observed for treated composites compared to raw one. This is due to the chemical treatment which reduced the hydrophilicity of jute fiber resulting in increased interfacial bonding between the fiber and PE matrix into the composite system [21]. As a result, tensile properties of the treated jute composites were improved. The highest improvement observed for silane treated jute composites (SJPEC) followed by PAJPEC, BDSJPEC, and RJPEC. It was observed that at optimum fiber content (15 wt%), the BDS, PA and silane treated jute composites exhibited improvements in TS by approximately 20%, 22% and 24%, and TM by 37%, 41% and 44% respectively over the raw composites.

3.3 Water Absorption

Fig. 3 shows the water absorption behavior for raw and treated jute composites as a function of time. During the experiment the composites absorbed water with different profiles. It has been mentioned that the hydroxyl group is responsible for the water absorption characteristics [22]. The number of -OH groups in the composite increased with fiber loadings which increases the value of water absorption. The untreated composite continued to absorb water up to 456 hours (19 days), and then the values remained

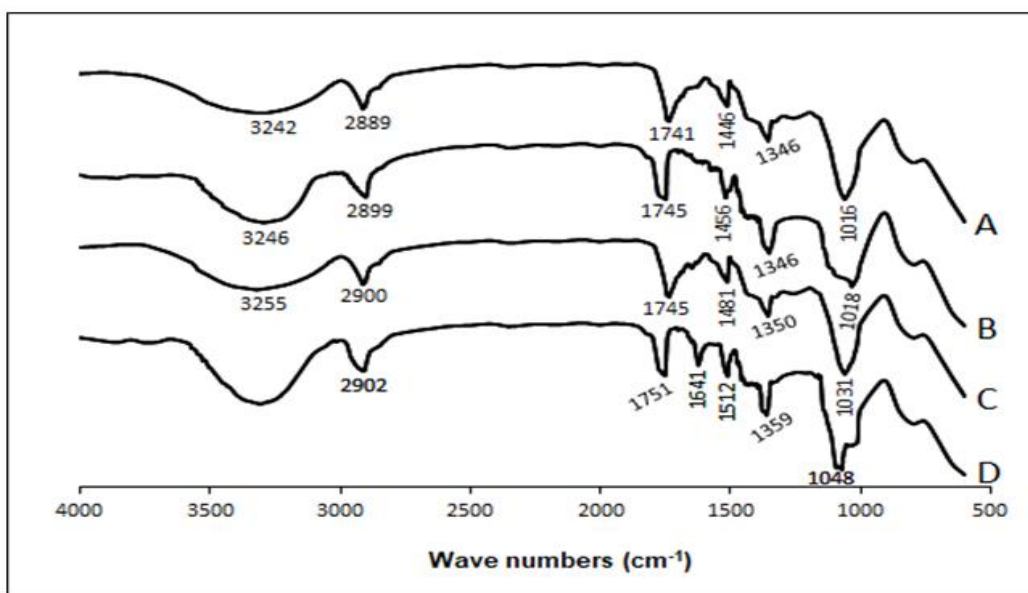


Fig. 1. FTIR spectra of (A): Raw jute fiber, (B): BDS treated jute fiber, (C): PA treated jute fiber, and (D): Silane treated jute fiber

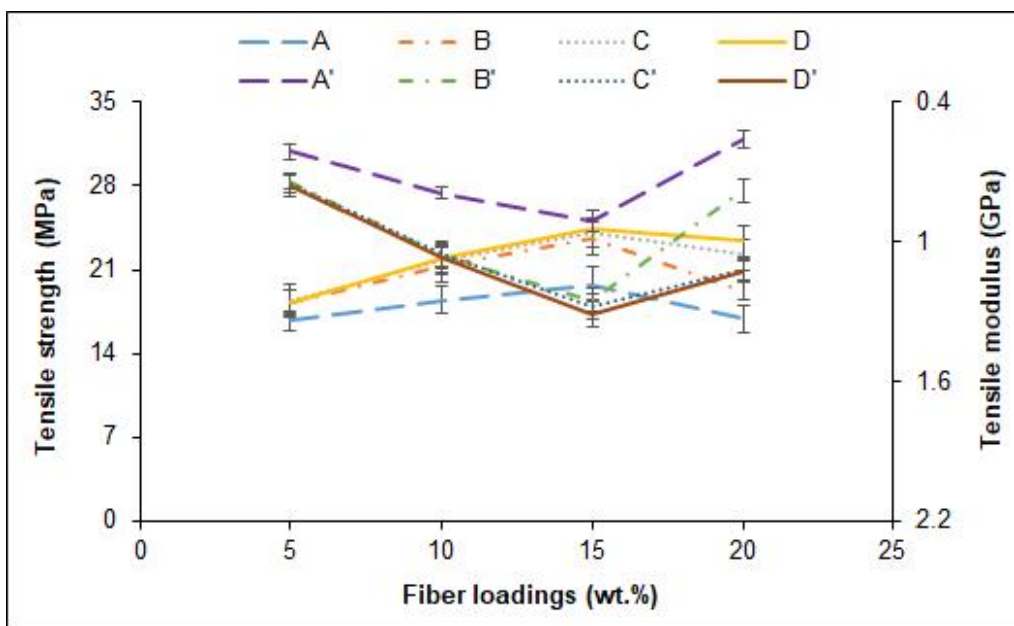


Fig. 2. Variation of TS and TM for A/A': RJPEC, B/B': BDSJPEC, C/C': PAJPEC, and D/D': SJPEC

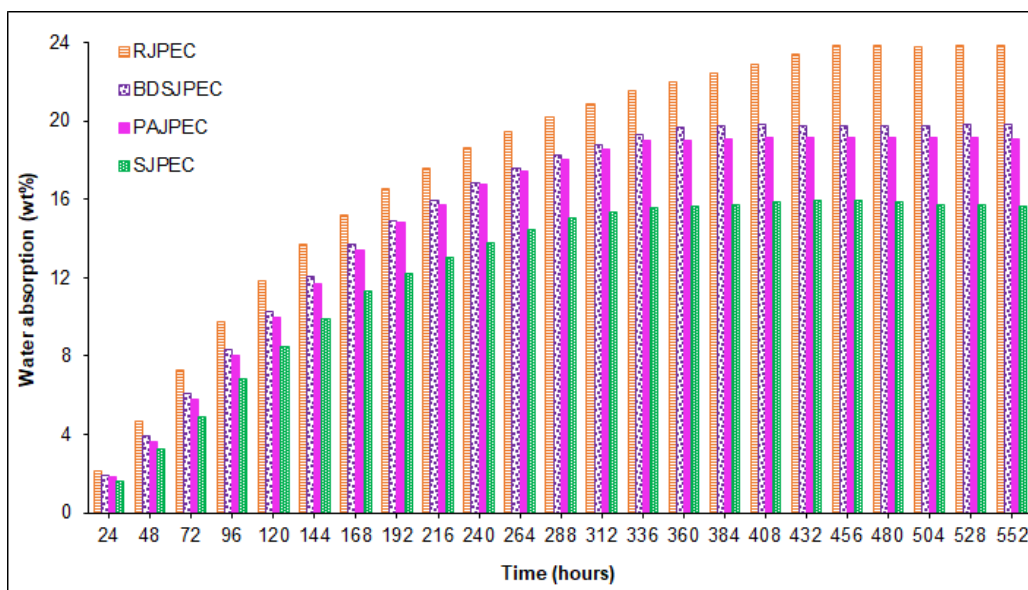


Fig. 3. Water absorption profile for RJPEC, BDSJPEC, PAJPEC, and SJPEC

constant. Water absorption was considerably lower for treated composite than raw composite. It can be seen that after 552 hours (23 days) of experiment, the lowest amount of water (approximately 16%) was taken up by the silane treated jute composite, SJPEC followed by PAJPEC (19%), BDSJPEC (20%), and RJPEC (24%). The reduced water uptake of the treated

composite compared with the untreated one is due to the fact that the chemical treatment reduces the -OH groups from the fiber which significantly reduces the water absorption of the composites [25]. It had been reported that the water uptake was considerably higher for untreated fiber composites, compared with that of their esterified cellulose ones [26].

On the other hand, the addition of nanoclay in the composites system also influences the water absorption behavior. Fig. 4 shows the water absorption test for PA treated jute composites without and with different amount (wt%) of MMT nanoclay. Water absorption was lower for nanoclay loaded composites than the composite without nanoclay. It was also observed that after 552 hours (23 days) of experiment, the lowest amount of water (approximately 14%) was absorbed by the 2 wt% MMT loaded nanocomposites, PAJPENC-2% followed by PAJPENC-2.5% (15%), PAJPENC-1.5% (16%), PAJPENC-1% (18%), and PAJPEC (19%). The reduced water uptake of the nanoclay loaded (upto 2 wt%) composites compared to that without nanoclay is due to the nanoclay acted as a barrier to retard water absorption into composites. The higher concentration of nanoclay (above 2 wt%) are poorly dispersed inside the composite system forming air bubble and agglomerations [16,27] which can be the cause of higher water absorption.

In addition, the nanocomposites with different types of nanoclay absorbed water with different profiles. Fig. 5 shows the water absorption behavior for the silane treated jute composites without and with various types of MMT nanoclay. Water absorption was lower for nanoclay loaded composites than composite without nanoclay and lowest water absorption was observed for MMT-1.31PS loaded nanocomposite. This is due to the nanoclay which acted as a barrier to retard water absorption into composites. It was seen that after 552 hours (23 days), the lowest water absorption was observed for SJPENC-1.31PS (approximately 8%) followed by SJPENC-1.34TCN (9%), SJPENC-1.28E (10%), SJPENC-1.30E (12%), SJPENC-1.44P (14%), and SJPEC (16%). The considerable improvement in water absorption for MMT loaded nanocomposites is due to the hydrophilicity of MMT nanoclay. The hydrophilicity of MMT nanoclay decreases as the carbon number of modifier increases which decreases the water absorptivity of materials [12]. It had been stated that the MMT-1.31PS nanoclay was modified by organic modifier with highest number of carbon among five types of MMT.

3.4 Chemical Absorption

Chemical absorption properties were studied to find out whether these hybrid composites can be used in making water and chemical storage tanks that are resistance to chemicals. More

weight gain indicates the materials are less chemically resistant [15]. In this study, the chemical absorption of raw and treated jute reinforced composites were examined. Fig. 6 shows the percentage of weight gain/loss for 15 wt% (raw and treated) jute fiber loaded composites immersed in solvents, acids and alkalis. It was clearly observed that weight gain was observed for almost all the chemical reagents except carbon tetrachloride. The composites have weight loss in carbon tetrachloride because the cross-linked polymers are easily attracted by chlorinated hydrocarbons [28]. The composites were also resistant to water. The hydrophilicity of natural fibers is the cause of weight gain for water and aqueous solutions [29]. From the results, it was seen that the weight gain is higher for raw jute composite compared with treated ones. The lowest weight gain was observed for silane treated jute composite, SJPE followed by PAJPE, BDSJPE, and RJPE. The improvement of chemical absorption as well as chemical resistance is due to the fact that the chemical treatment reduces the hydrophilicity of fibers which lead to better improvement in interfacial interaction between treated fiber and polymer matrix into the composite [30]. It had been reported by other researchers that the alkali treated biodegradable fibers hybrid composites exhibited better improvement in chemical resistance compared with untreated ones [31].

The addition of nanoclay in the composites system also impacts the chemical absorption behaviour. Fig. 7 shows the percentage of weight gain/loss for PA treated jute composites without and with different amount (wt%) of MMT nanoclay immersed in different chemicals. It was also observed that weight gain was observed for almost all the chemical reagents except carbon tetrachloride. Weight gain was lower for nanoclay loaded (up to 2 wt%) composites than the composite without nanoclay. The lowest value was observed for PAJPEC-2%, followed by PAJPEC-2.5%, PAJPEC-1.5%, PAJPEC-1%, and PAJPE. This is due to the addition of nanoclay that increases the interfacial adhesion between treated fiber and polymer matrix [12]. The higher concentration of nanoclay (above 2 wt%) are poorly dispersed inside the composite system forming air bubble and agglomerations which can be the cause of higher chemical absorption [16,27].

On the other hand, the nanocomposites with different types of nanoclay absorbed chemicals

with different profiles. Fig. 8 shows the chemical absorption behaviour for the silane treated jute composites without and with various types of MMT nanoclay. It was clearly observed that weight gain was observed for almost all the chemical reagents except carbon tetrachloride. Weight gain was lower for nanoclay loaded composites than composite without nanoclay and lowest value was observed for MMT-1.31PS loaded nanocomposite. The lowest chemical

absorption was observed for SJPEC-1.31PS followed by SJPEC-1.34TCN, SJPEC-1.28E, SJPEC-1.30E, SJPEC-1.44P, and SJPE. The considerable improvement in chemical absorption as well as chemical resistance for MMT loaded nanocomposites is due to the hydrophilicity of MMT nanoclay. The hydrophilicity of MMT nanoclay decreases as the carbon number of modifier increases which decreases the water absorptivity of materials.

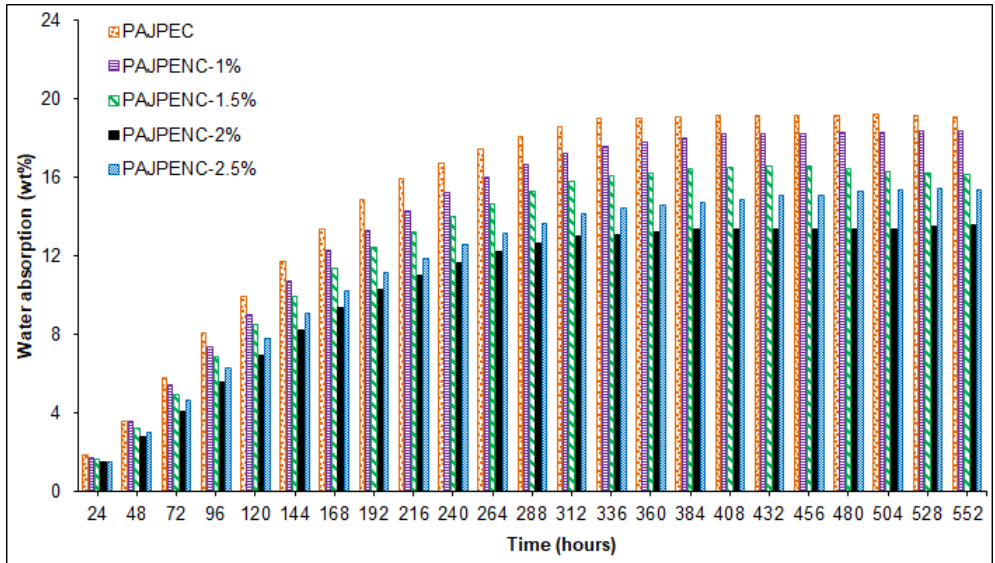


Fig. 4. Water absorption profile for PAJPEC, PAJPENC-1%, PAJPENC-1.5%, PAJPENC-2%, and PAJPENC-2.5%

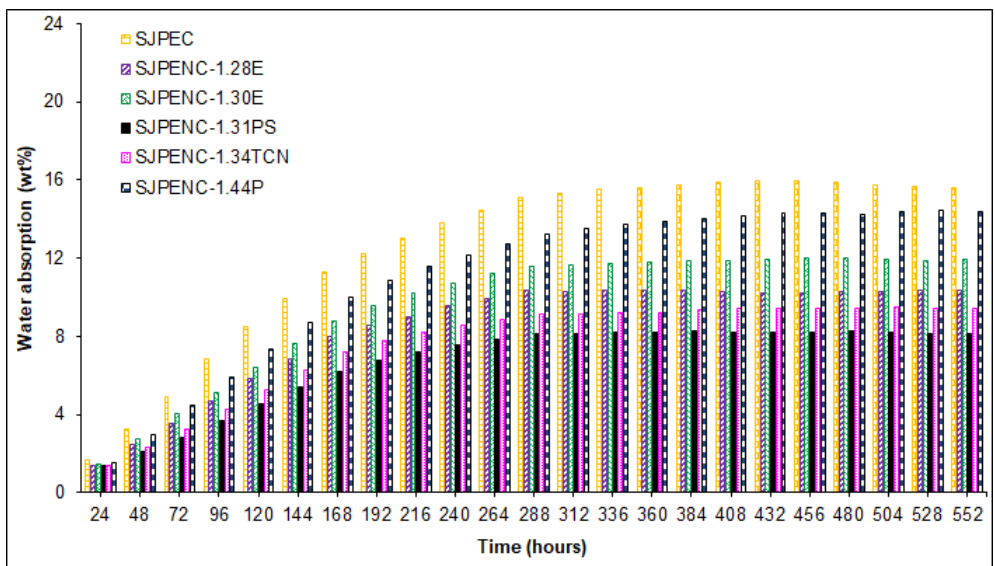


Fig. 5. Water absorption profile for SJPEC, SJPENC-1.28E, SJPENC-1.30E, SJPENC-1.31PS, SJPENC-1.34TCN, and SJPENC-1.44P

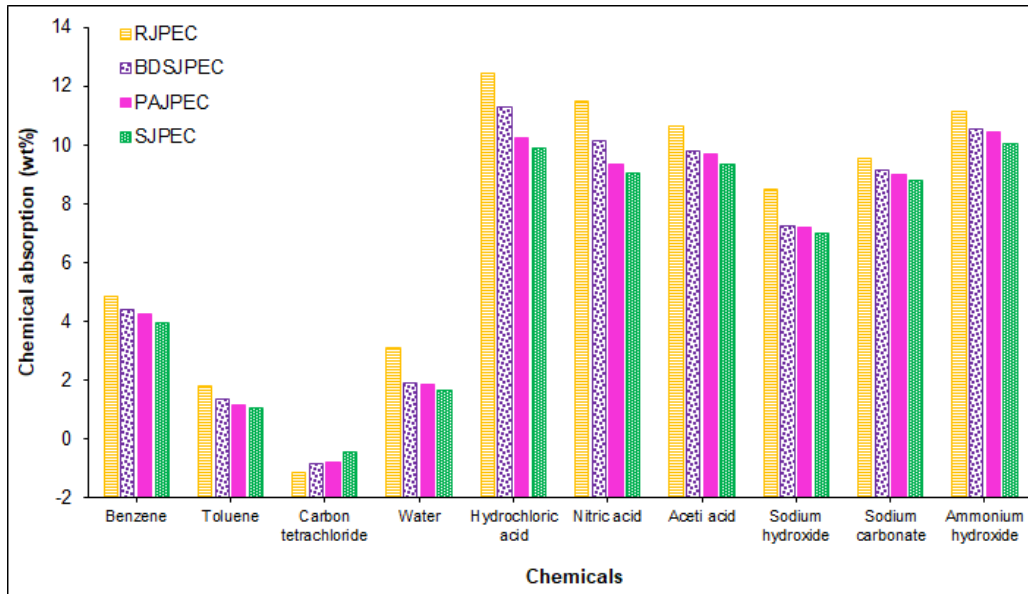


Fig. 6. Chemical absorption profile for RJPEC, BDSJPEC, PAJPEC, and SJPEC

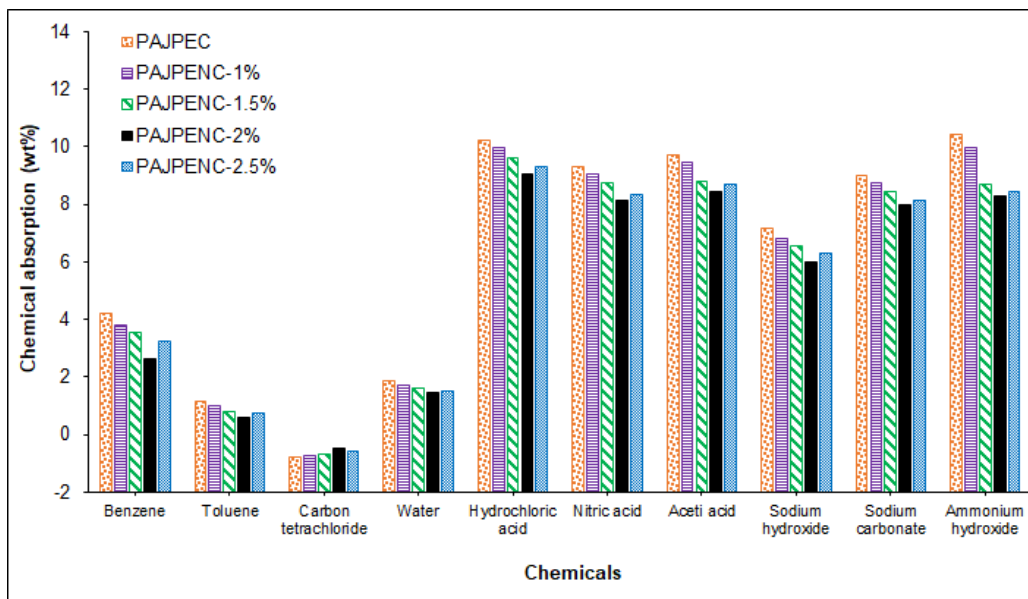


Fig. 7. Chemical absorption profile for PAJPEC, PAJPENC-1%, PAJPENC-1.5%, PAJPENC-2%, and PAJPENC-2.5%

3.5 SEM Study

SEM images of raw and silane treated jute composites without and with optimized nanoclay (2 wt% MMT-1.31PS) at 15 wt% fiber loading were investigated and the images are presented in Fig. 9. The figure indicates that there appear considerable differences in the interfacial interaction between fiber and polymer matrix in

the composite system. The SEM image of raw composite (RJPEC) shows the pullout traces of fiber with rough surfaces and voids as well as agglomeration (Fig. 9A). This feature indicates that there was poor dispersion and weak interfacial bonding between fiber and matrix [19]. On the other hand, the treated jute composite (SJPEC) shows better dispersion of filler throughout the matrix which in turn improved

interfacial interaction between fiber and matrix (Fig. 9B) [3]. The improvement of interfacial adhesion between jute and PE is due to the chemical modification that enhanced the hydrophobicity of jute fiber [22]. In addition, the clay incorporated nanocomposite (SJPEC) showed less fibers pull out from the fractured

surface (Fig. 9C), which is due to the MMT particles that increased the interaction between PE matrix and jute fiber [11]. As a result, the significant improvement in physico-chemical absorption behaviors have been observed for SJPEC which is also evident from tensile properties.

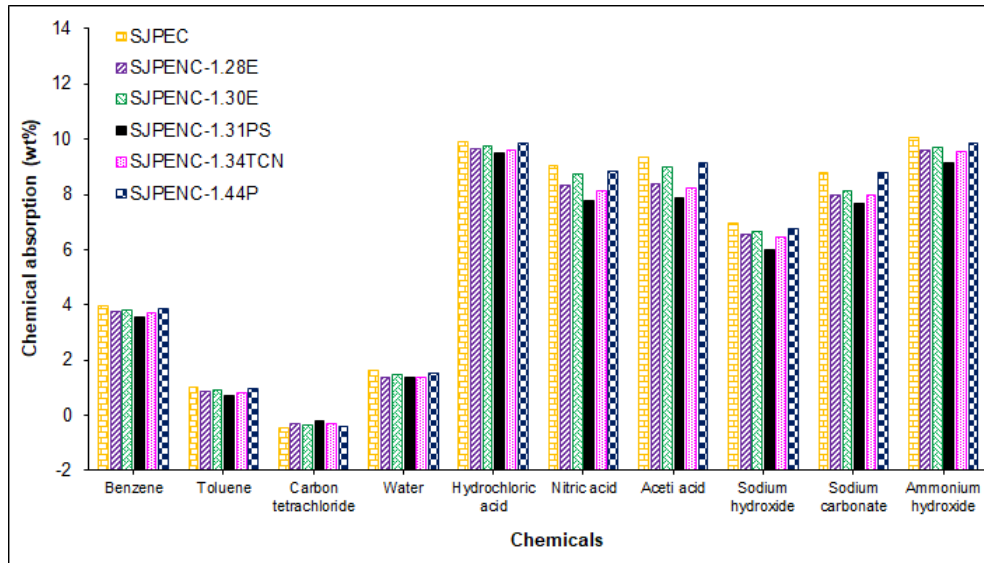


Fig. 8. Chemical absorption profile for SJPEC, SJPEC-1.28E, SJPEC-1.30E, SJPEC-1.31PS, SJPEC-1.34TCN, and SJPEC-1.44P

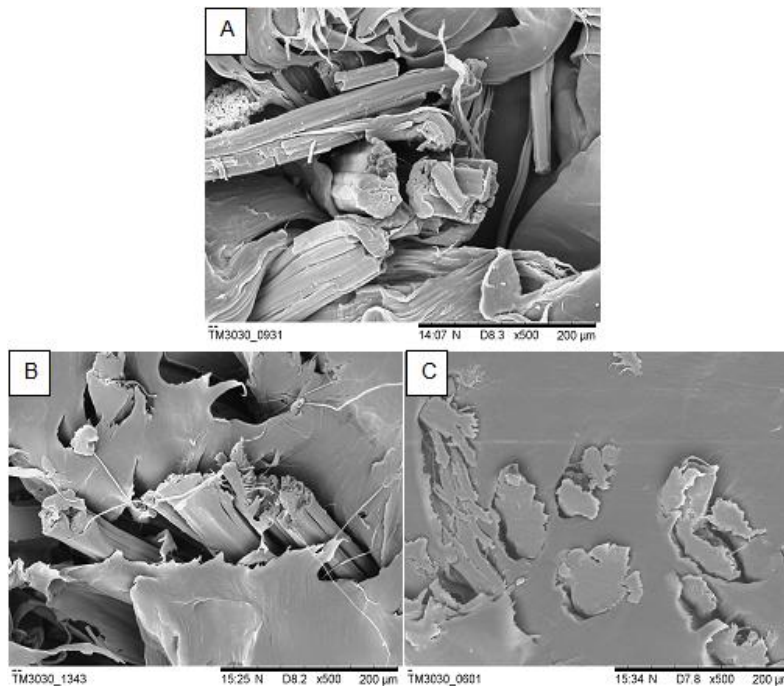


Fig. 9. SEM micrographs for 15 wt% raw and treated jute composites without and with MMT nanoclay where; A: RJPEC, B: SJPEC, and C: SJPEC

4. CONCLUSION

In this paper, the effect of chemical treatments and addition of MMT nanoclay on the physico-chemical absorption behaviors of prepared composites were studied. The tensile testing, and water and chemical absorptions have been carried out to evaluate optimum fiber loading and physico-chemical performance of jute fiber reinforced polyethylene composites without and with MMT nanoclay, respectively. It was observed that the fiber loading is optimized at 15% by weight. It was also observed that the treated jute composites showed higher tensile values than raw one and silane treated jute exhibited highest value. On the other hand, the absorption characterizations of prepared nanocomposites in terms of water and chemical absorptions has been investigated. It was seen that the percentage of water absorption increased with fiber loadings. The treated jute composite showed lower water absorption than untreated composite and silane treated jute composite exhibited lowest value. The chemical absorption study clearly suggested that the composites are resistant to all chemicals except CCl_4 , which may cause of the cross-linked polymers are easily attracted by chlorinated hydrocarbons.

Thus, it is stated that the treated jute composite exhibited considerable improvement in physico-chemical absorptions compared to raw one and silane treated jute composite showed highest improvement among three treatments performed in this research. It was also seen that the nanoclay filled nanocomposites showed higher improvements in physico-chemical absorptions than the composite without nanoclay and the MMT-1.31PS loaded nanocomposite obtained highest improvement among five types of MMT nanoclay used in this study. The results stated above are due to the chemical treatments of fiber and the carbons number of modifier of MMT nanoclay. According to the findings, it is concluded that, among the three chemical treatments and five nanoclays used in this research, the silane chemical treatment and MMT-1.31PS is the most suitable for the preparation of nanocomposites. The development of nanocomposites properties in terms of interfacial adhesion among fiber, polymer matrix, and nanoclay has become more favourable due to the chemical modification and nanoclay as nanofiller into the nanocomposite system. The manufactured nanocomposites can be suggested for interior and exterior

applications, and can also be recommended for storage tanks (chemicals and water) applications.

DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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