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Evaluation of water repellency in bentonite filled polypropylene composites via physical and mechanical methods

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Abstract

With the advent of polymeric materials having dimensional stability, outdoor applications for polymer composites are increasing expeditiously. The employment of durable material in wet environments is the most effective means of water repellency. Silane modification was applied to bentonite clay for the donation of hydrophobicity on its surface. Surface functionalities of powder surfaces were confirmed by FTIR-ATR spectroscopy and SEM techniques. Polypropylene composites involving pristine and modified bentonite powders were produced in bulk and film forms at three different loading ratios. Water permeability of bulk and film samples was evaluated via water absorption test. In addition to water uptake values, optical microscopy was utilized in order to visualize the structural deterioration of composite samples after water immersion. Mechanical behaviours of composite materials before and after water absorption test were reported in order to analyze the effect of water aging. Based on the findings, in-depth discussions were performed by comparison with basic models postulated regarding migration of water molecules into polymer structure.

1. Introduction

Polymers found usage in numerous products of modern life from medical devices to automotive parts. The effectiveness of polymeric materials for specific applications is highly depend on its stability and durability in various environments. Several factors including humidity, heat or solar radiation can give rise to break polymer chains. To overcome to degradation and maintain the structural stability of polymers, several protection activities applied mainly during their production. Estimation of the degree of aging is another important point in order to adress a selective preservation route to avoid prolonged degradation of polymer [1–3].

The recyclability and practical processing characteristics of polypropylene (PP) are the main advantages over other polymers. Besides other polyolefins, PP is susceptible to various kinds of degrading activity occurs in its amorphous regions [4, 5]. In a recent study, Zhang et al demonstrated the initial aging of PP using confocal microscopy. They postulated that early-stage detection of degradation in PP structure plays key role to avoid several accidents from reactor discharge to shuttle explosion [6]. PP gains impressive mechanical and thermal resistance thanks to inclusion of additives. However, its stabilization against aging should be established by execution of specific efforts. Natural clays are favoured as additives for PP because of having low cost and ease of processing characteristics besides improvement numerous performances of neat polymer [7–10]. Nevertheless, their tendency to absorb water provokes reduction in desired properties and dimensional stability of polymeric composites in the case of exposure in hydrolytic environments [11, 12].

In this experimental study, silane modification was applied to bentonite (BNT) to enhance its interfacial adhesion to PP matrix in addition to obtain hydrophobic surface. PP-based composites were produced in bulk and film forms to investigate appropriate results in large-scale and packaging applications. It is aimed to evaluate the effect of water immersion to structural and mechanical properties of PP/bentonite composite system.
Another target is to visualize dimensional stability of PP and relevant composites before and after water absorption test by the help of optical microscopy observations.

2. Experimental

2.1. Materials
Polypropylene was supplied from Petkim, Turkey with the trade name of Petoplen EH-251. Bentonite powder was obtained from Eczacibasi Esan, Turkey under trade name of EBNT SA. Na-activated BNT has specific gravity and average particle size of 2.2 g cm\(^{-3}\) and 7.8 μm, respectively.

2.2. Surface silanization of bentonite
BNT clay was subjected to surface treatment according to similar silanization routes in the literature [13, 14]. BNT powder was mixed in 2 wt% APTES/ethanol solution for 2 h at room temperature. After drying process, silanized sample was named as Si-BNT.

2.3. Fabrication of composites
PP pellets and BNT powder were dried under vacuum at 85 °C for 8 h to remove moisture content prior the compounding. Composites were fabricated using micro-extruder (MC15HT, Xplore). Concentrations of BNT in PP matrix were 1, 5, and 10% by weight. PP film samples were produced via lab-scale hot-press (AtsFaar). The dog-bone shaped test specimens with dimensions of 7.6 × 2.0 × 80 mm\(^3\) were prepared by injection molding (Daca).

2.4. Characterization techniques
FTIR measurements in ATR mode were carried out by IR-spectrometer (Bruker VERTEX70). The measurements were taken at resolution of 2 cm\(^{-1}\) with 32 scans.

Water absorption test was performed by immersing samples in water bath at room temperature in accordance with ASTM D570 procedure (figure 1). Test samples were periodically taken out from the water, wiped with paper to avoid their surface water, weighed and put back into the water bath repeatedly during 9 days’ period. SEM photographs were taken at 5000 × magnification using FEI Quanta 400F. Computer-controlled optical microscope (Veho VMS-004D) was utilized for the characterizations of the thickness of composites in bulk and film forms. Digital photographs were taken at 200× and 400× magnifications. Tensile tests were conducted using Lloyd LR30K tensile-testing instrument. The crosshead speed of 5 cm min\(^{-1}\) was applied according to ASTM D-638 standard.

3. Results and discussion

3.1. Surface functionality of BNT clay
Surface characteristics of neat and silane-modified BNT are represented with their FTIR spectra given in figure 2. The characteristic absorption bands correspond to oxygen functionalities are located at 900 and 1200 cm\(^{-1}\) which are stem from C–O stretching. Other oxygen-related peaks can be seen around 1600 and 3300 cm\(^{-1}\) are attributed to COO-asymmetric-stretching and O–H stretching, respectively [15]. The intensities of these bands are found to be higher for Si-BNT with respect to BNT. The indicative peaks in the range between 2800 and 2900 cm\(^{-1}\) due to stretching vibrations of –CH\(_2\) and –CH\(_3\) groups display higher intensities for Si-BNT since the presence of propyl segment in silane coupling agent [16]. The shoulder peaks between 500 and 800 cm\(^{-1}\)
represent the Si–O vibrations [17]. These bands are common for both BNT samples due to SiO₂ content of bentonite. According to FTIR spectrum of Si-BNT, silane covering on BNT surface leads to increase for intensities of Si–O related peaks. The chemical changes on clay surface after silane modification are confirmed by these findings.

Neat BNT particles tend to form agglomerate due to particle-particle adhesion; on the contrary, silane layer on modified BNT surface restricts formation of agglomerates as confirmed by SEM micrographs of BNT samples in figure 3.

3.2. Water uptake measurements
Water absorption values of bulk and film samples are represented in figures 4 and 5, respectively.

According to figure 4, PP reaches its maximum water uptake capacity by absorbing less than 0.1 wt% of water in 2 days. Addition of BNT with the lowest loading level leads to significant increase for water absorption of PP. Nearly 8-fold improvement is observed for 5% BNT containing composite with respect to unfilled PP. Water uptake of PP raise by a factor of 12 with inclusion of the highest amount of BNT (10%). Composite involving silane treated BNT yields significant reduction in water absorption. Nearly 3-fold decrease is observed for Si-BNT containing sample compared to the same amount of unmodiﬁed BNT.

Figure 5 indicates that BNT additions cause similar trend with bulk samples. In comparison, water absorption values of film samples are found to be higher than bulk samples since films have higher speciﬁc surface area concerning exposure to water. Therefore, film samples are obtained as more susceptible to water aging compared to bulks. The addition of BNT shifts water uptake tendency of PP film to higher levels likewise its bulk form.

Water absorption is mainly related with hydrogen bonding of water molecules to the hydroxyl groups present on clay surface. Another factor affecting water uptake is interfacial adhesion between polymer and reinforcing material. Because of weak additive-matrix adhesion, formations of gaps or micro-cracks cause penetration of water through the pores in the composite structure with suction effect [18]. The diffusion of water molecules into film and bulk forms lead to rise in weight of material associated with single phase diffusion model.
of Fick’s law [19]. Correspondingly, silanized clay addition restricts water penetration in either way of donating hydrophobicity to clay surface and enhancing BNT-PP interface adhesion.

### 3.3. Physical observation of water aging

The influence of water immersion of bulk and film composite samples to their dimensions is demonstrated with optical photographs. The thickness values of bulk samples before and after (WA) of water absorption test in 9 days period are indicated in figure 6.

According to figure 6, water absorption test makes notable differences in thickness of bulk samples with the exception of unfilled PP. PP retains its structure thanks to its lower amount of water uptake. The thickness values of composites are extended with increase in BNT concentration. Conversely, Si-BNT composite exhibits identical values before and after water immersion. Nearly 2.8% increase in thickness of PP/BNT 5 sample is completely disappear with Si-BNT addition. Another observation from optical photographs of composites is measurement of different thickness values on some points which is related with the nonhomogeneous dispersion of agglomerated BNT regions responsible from water absorption. High BNT loadings enforces the formation of agglomerates in the structure similar to other particulate additives [20–22].

Figure 7 shows that thickness changes of film samples are observed for 5 and 10% BNT filled composites. These increments are found to be lower compared to bulk samples. Despite the fact that film samples yield higher percent water uptake values, their thickness are obtained as almost identical after water immersion owing to higher specific surface area relative to bulk samples This result is regarding structural difference of bulk composite samples in accordance with the various models suggested the time-dependent diffusion of water molecules into polymer structure based on molecular interactions approaches [23–25].

### 3.4. Mechanical characterization

Tensile test curves of bulk samples are given in figure 8.

The characteristic stress–strain curves and tensile test data of samples after water absorption test (WA) and prior to test are represented in figure 8. BNT additions cause remarkable reduction for elongation of unfilled PP regardless of loading ratio. Among composites, only Si-BNT reinforced composite reaches to tensile strength

![Figure 4. Water uptake values of bulk samples.](image)

![Figure 5. Water uptake values of film samples.](image)
level of PP. PP and composite samples give higher strain values after water immersion. The increase in elongation of PP is found to be smaller amount compared to composites. Sample containing 10% amount of BNT exhibits the highest improvement for strain after water aging. This result is related with the plasticizing effect of water immersion of polymeric materials [26–28]. The increase of strain is found to be in narrow range for Si-BNT loaded sample since composite gains water repellency after silane treatment. In the case of stress parameters, it can be said that water aging causes no obvious change for tensile strength of composites.

Figure 6. Micrographs of bulk samples.
4. Conclusion

FTIR study proves that silicon functionality of BNT surface is increased by silane treatment. Agglomerate formation tendency of neat BNT is confirmed by SEM micrographs. Water uptake values of composites extend up with the amount of BNT whereas silane treated BNT gives lower water absorption due to its hydrophobic nature. The particle-particle adhesion tendency of BNT causes reduction of dimensional stability. Film samples retain their thickness after water immersion in contrast to bulk samples. Silane covering on the surface of BNT leads to increase in water repellency and mechanical strength thanks to enhancement of polymer-additive adhesion. Results are found to be in accordance with related water diffusion models. Silane modified BNT
containing PP exhibits the best performance among composites and it is remarked as the most suitable candidate for outdoor applications of PP-based composites.

Data availability statement

Any data that support the findings of this study are included within the article.

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