

Water Absorption Behavior of Palm Kernel Shell Filled Polypropylene / Recycled Acrylonitrile Butadiene Rubber Composites: Effects of γ -Methacryloxypropyltrimethoxysilane

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ABSTRACT

Effects of γ -methacryloxypropyltrimethoxysilane on water absorption behavior, mechanical and morphological properties of palm kernel shell filled polypropylene/recycled acrylonitrile butadiene composites were studied. Water absorption was found to increase with increasing filler loading while γ -MPS treated PKS filler composites were found to have lower water absorption due to the better adhesion between polymer matrix and natural filler. Mechanical properties of γ -MPS were also found to be higher compared to that of untreated filler. SEM micrographs showed that there were less gaps, pull out and voids in the γ -MPS treated PKS filler composites.

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1. Introduction

Thermoplastic elastomers (TPEs) belong to a class of materials that combine the physical properties of thermoplastics and elastomers. Among different types of TPEs, those prepared by the physical blending of a polyolefin and an elastomer have gained considerable attention due to the simple method of preparation and easy attainment of the required technical properties. Because of its excellent processability and good mechanical properties, polypropylene (PP) has been widely used [1-3].

Elastomer such as recycled acrylonitrile butadiene rubber (NBRr) or known as nitrile gloves has gained increasing attention of the researchers. Currently, Malaysia is the world's largest exporter and producer of both nitrile and natural rubber gloves. After its use, NBRr is generally left as garbage which is very difficult to biodegrade [4-6]. TPEs with natural fillers is one of the most promising routes to create filler reinforced polymer composites.

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The utilization of fillers from various sources into TPEs composites has been an accepted route to achieve an enhancement in material properties or cost saving possibilities, or both. Over the past two decades, organic or natural fillers have become a strong competitor to inorganic fillers [7]. Natural fillers like palm kernel shell, cotton, wood fiber, jute, pineapple leaf, sisal, flax, kenaf, and so on have been used by researchers to replace the inorganic fillers [8]. At the present, around 6.89 million tons of PKS are produced annually and this amount is expected to increase rapidly in the coming years [9,10]. A few research have been done to study the waste of palm oil as natural filler [11-13].

However, one of the most important characteristics of natural filler reinforced TPEs is the water absorption behavior of the composites exposed to environmental conditions. It is important to study in detail the water absorption behavior in order to estimate not only the consequences of the absorption of the composites, but also how this water uptake can be minimized in some way. In order to solve this problem, silane coupling agent was used in this study [14-16].

Silane coupling agent has been found to improve the compatibility between the hydrophilic natural filler and hydrophobic matrix polymer. γ -methacryloxypropyltrimethoxysilane (γ -MPS) has been used in this study. To our knowledge, no study has been made on the water absorption and mechanical properties of PP/NBRr/PKS composites with γ -MPS. The effect of filler loading and a coupling agent, γ -MPS, on water absorption and mechanical properties of PP/NBRr/PKS composites were investigated.

2. Methodology

2.1 Matrix Polymer

The thermoplastic polymer, polypropylene (PP), was supplied by Titan Pro Polymers (M) Sdn.Bhd. Isotactic PP as grade 6331 with melt flow index at 230°C of 14 g/10 min and density 0.9 cm³ was used. The elastomer matrix, recycled acrylonitrile butadiene rubber (NBRr) was supplied by Juara One Resources Sdn.Bhd, Penang, Malaysia. NBRr was masticated to particle size < 150 μ m by using a two roll mill.

2.2 Natural Fillers

Palm kernel shell (PKS) was used as the natural fillers in the composite with particle size < 150 μ m. The PKS was supplied by Solid Orient Holdings Sdn.Bhd, Kedah, Malaysia. Before being ground to obtain that particle size, PKS was dried under the hot sun for 24 hours and continued with oven dried at 90°C for 3 hours to remove the moisture content. Chemical compositions of palm kernel shell are cellulose 33,04%, hemicellulose 23,82%, lignin 45,49% and extractives 9,89%.

2.3 PKS Surface Modification

First, PKS was immersed in the 5% sodium hydroxide (NaOH) solution for 24 hours at a temperature of 45 °C to remove the lignin. After immersion, the fillers were washed with running tap water and then immersed in distilled water containing 1% acetic acid to neutralize the remaining unreacted NaOH. These fillers were dried in an oven at 45 °C for a period of 24 h. This was followed by a silane treatment.

5 % by weight of γ -MPS (weight of silane relative to the weight of PKS loading) then diluted in a 80/20 solution of ethanol/water. pH of the solution was maintained at 4 to 5 using acetic acid. The

fillers were immersed in the solution for 4 hours at a room temperature and washed with distilled water before being dried in the oven at 45 °C for 24 hours.

2.4 Sample Preparation

The matrix polymers, PP and NBRr, were melted and mixed with the untreated and γ -MPS treated PKS fillers. A Heated two-roll mill was employed to compound the PP/NBRr/PKS composites. The formulations of PP/NBRr/PKS composites (70/30/0, 70/30/5, 70/30/10, 70/30/15 and 70/30/30 phr) were used. Compounding was performed at 180°C at a speed of 15 rpm. Polypropylene (PP) was first charged into the heated two roll mill and melted for 4 minutes prior to NBRr addition. PKS was then added into the compound after 6 minutes of mixing. The compound was allowed to further mix for another 3 minutes to mixed homogeneously.

The composites were then compressed and molded into a 1 mm sheet for preparing test samples using hot press model GT 7014 A 6895 kPa at 180°C. The composites were preheated for 7 minutes at 180°C, compressed for 2 minutes and then cooled for 2 minutes. The 1 mm thin sheet was further cut into a dumbbell shaped using wallace die cutter model (S6/1/6.A).

2.5 Water Absorption

Water absorption test was carried out by immersing the samples in distilled water at room temperature (25°C). Five repetitive of specimens were prepared with dimensions of 30mm x 5mm x 1mm and weighed by a Sartorius balance Model: BS224S with a precision of 1 mg. The samples were placed in distilled water and kept at room temperature. The samples were removed from water, wiped, weighed and placed back into water. Weight gains after exposure were recorded every day for 60 days. The moisture content at any time t, M_t (%) as a result of moisture absorption was calculated by using Equation (1):

$$M_t = 100 \times (W_t - W_o) / W_o \quad (1)$$

where W_o and W_t are original dry weight and weight after exposure, respectively.

2.6 Mechanical Properties

The mechanical properties were tested using a universal tensile machine Instron machine Model: 5569 at a cross-head speed of 5 mm/min at room temperature. According to ASTM D-638 Tensile strength, tensile modulus, and elongation at break of the each sample were obtained from the average of five dumbbell specimens.

2.7 Morphological Properties

The tensile 1 mm fracture surface at failure mode was analyzed by using JOEL JSM-6460 LA Scanning Electron Microscopy (SEM). SEM micrographs were taken at 200x magnification for morphological evaluation. All samples were mounted on aluminum stubs and sputter coated with a thin layer of gold to avoid electrostatic discharge during the examination.

3. Results and Discussion

3.1 Water Absorption

Figure 1 shows water absorption of PP/NBRr/PKS composites with untreated PKS filler. With the increase in PKS filler loading, higher water absorption was recorded. This may be due to more OH functional groups from the PKS filler. These free OH groups come in contact with water and form hydrogen bonding which results in weight gain the composites [17]. Mishra and Verma [18] reported the similar finding in polypropylene/wood flour foamed composites.

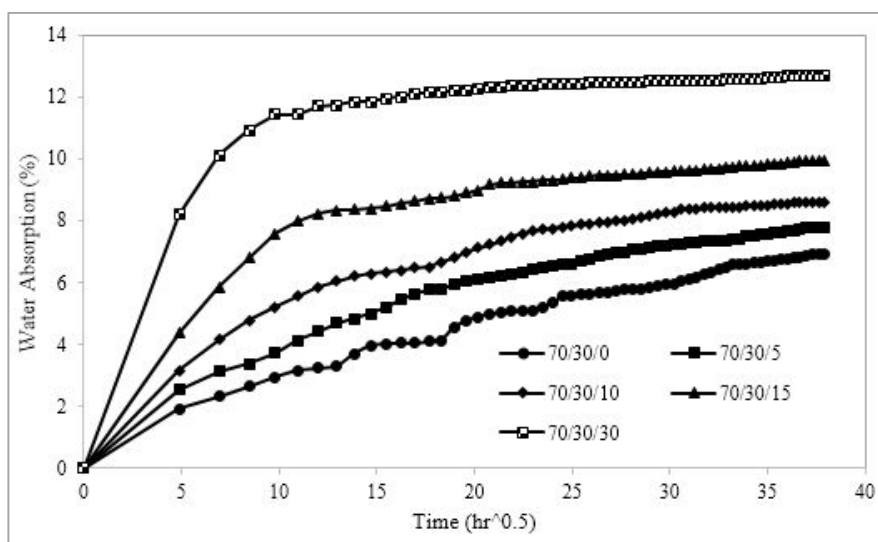


Fig. 1. Water absorption of PP/NBRr/PKS composites with untreated PKS filler

Figure 2 shows water absorption of PP/NBRr/PKS composites with γ -MPS treated PKS filler. The γ -MPS treated filler absorbed less water compared to the untreated filler. This could be possible due to the better adhesion or interfacial bonding between polymer matrix and cellulosic materials, the velocity of the diffusion processes decreases since there are fewer gaps in the interfacial region and also more hydrophilic groups as hydroxyls are bonded by the coupling effect.

Less water absorption could be due to the change of the crystallinity of composites coupled by the γ -MPS silane. As the crystalline regions are impermeable to the penetrant, the water absorption is less in the coupled composites [19-21]. Ismail [21] reported similar observation on silane coupling agent treated bamboo filler in natural rubber composites which exhibits lower water absorption.

From both untreated and γ -MPS treated filler composites, it is clear that the water absorption increased with the increase of immersion time, reaching a maximum value at saturation point.

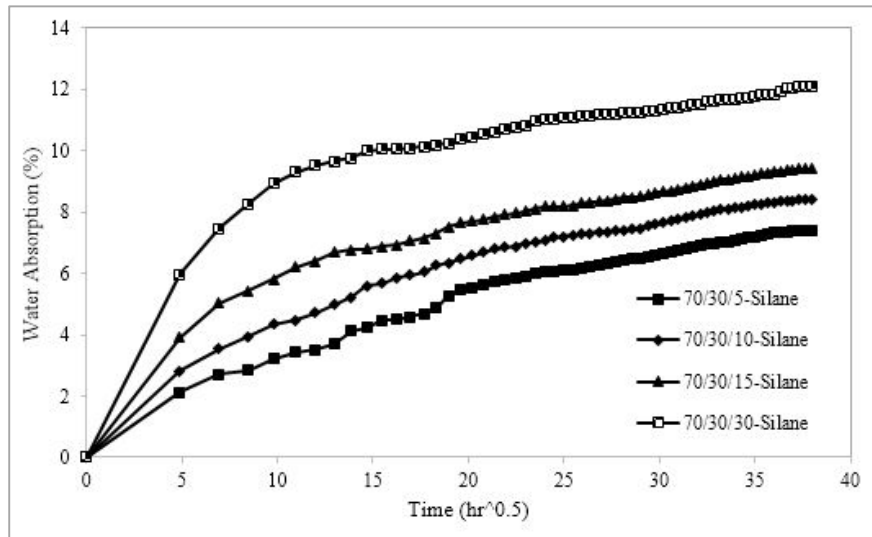


Fig. 2. Water absorption of PP/NBRr/PKS composites with γ -MPS treated PKS filler

3.2 Mechanical Properties

Figure 3 shows the tensile strength of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler. It can be seen that the tensile strength decreases with increasing of PKS filler loading for both composites.

Decreasing in tensile strength properties, at the higher filler loading, thought to be caused by several possibilities. The first is the characteristic of the natural filler which is easy to agglomerate. The presence of these agglomerates results in the generation of flaws and voids between filler and matrix polymer. Second, it is difficult to achieve a homogeneous mixture in the mixing process that uses a roll-mill for high filler loading. The third is weak interfacial area between filler and matrix increased [20,22,23].

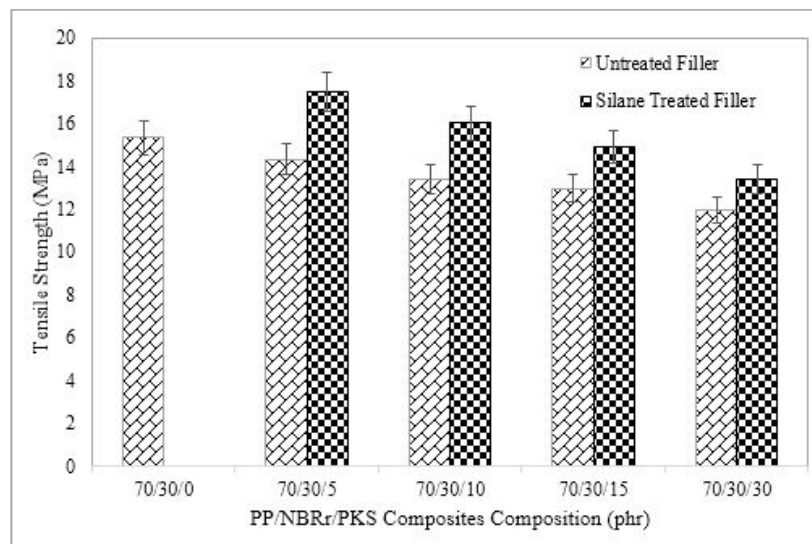


Fig. 3. Tensile strength of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler

The tensile strength of PP/NBRr/PKS with γ -MPS treated PKS filler was found to be higher than untreated fillers. The incorporation of silane coupling agent improves chemical compatibility, interfacial adhesion and stress distribution between filler and matrix. The presence of hydroxyl groups on the surface of the natural filler can promote the establishment of strong interactions between the coupling agents and the filler, while the non-polar part of the coupling agents interacts with the polymer matrix [10,21]. Ragunathan *et al.*, [5] have reported similar findings using rice husk powder treated γ -APS Silane.

Figure 4 shows the Young's modulus of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler. It is clear that young's modulus increases with increasing of PKS loading for both composites. The presence of the filler reduced the ductility of the polypropylene composite and increased its modulus. The incorporation of PKS into thermoplastic restrains the movement of its chains, thereby increasing its modulus [24].

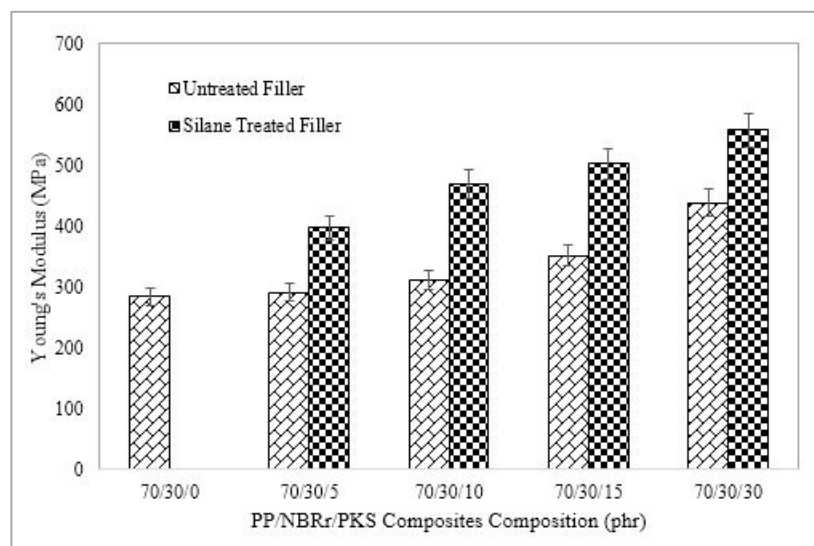


Fig. 4. Young's modulus of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler

γ -MPS treated PKS filler reinforced PP/NBRr composites are found to show higher values of Young's modulus. The presence of silane coupling agent reduces the chain mobility and increase rigidity of the composites. It has been reported that crystallites possess higher modulus compared those of amorphous substances. Better interaction between treated PKS and PP matrix reduces the matrix mobility, giving stiffness of the composites [10,25].

The effect of filler loading on elongation at break (Eb) of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler is shown in Figure 5. A significant decrease of elongation at break with increasing filler loading was observed. The decrease in elongation at break of the composites in the presence of filler indicates hindrance by filler to molecular mobility or deformability of PP/NBRr/PKS composites. Increasing in filler loading stiffens and hardens the compounds and cause reduction in its flexibility [26].

However, the incorporation of γ -MPS was found to be lower compared to composites with untreated filler. This may be due to the presence of coupling agent enhances the matrix and filler interactions resulting in lower elongation at break. Similar findings were observed by Hong *et al.*, [27] in PP and jute fiber composites. It was reported that silane treatment of natural fiber yielded a stronger interfacial adhesion, resulting in low elongation at break in composites.

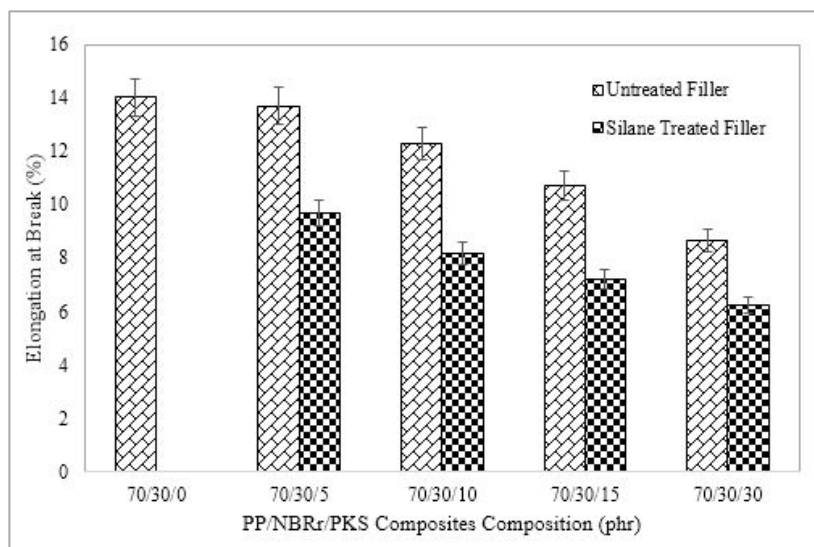


Fig. 5. Elongation at break of PP/NBRr/PKS composites with and without γ -MPS treated PKS filler

3.3 Scanning Electron Microscopy (SEM)

SEM micrographs of PP/NBRr/PKS composites without γ -MPS treated PKS filler at 70/30/15 and 70/30/30 are shown in Figure 6. It can be observed that poor adhesion of PKS filler to the polymer matrices is the main factor of reduction of the tensile strength with increasing of filler loading. The incorporation of filler increases the rigidity of the material, thus reduces the ductility of the composites [28]. The presence of pulled out, hole and gaps between the filler and matrices proves the weak interfacial adhesion.

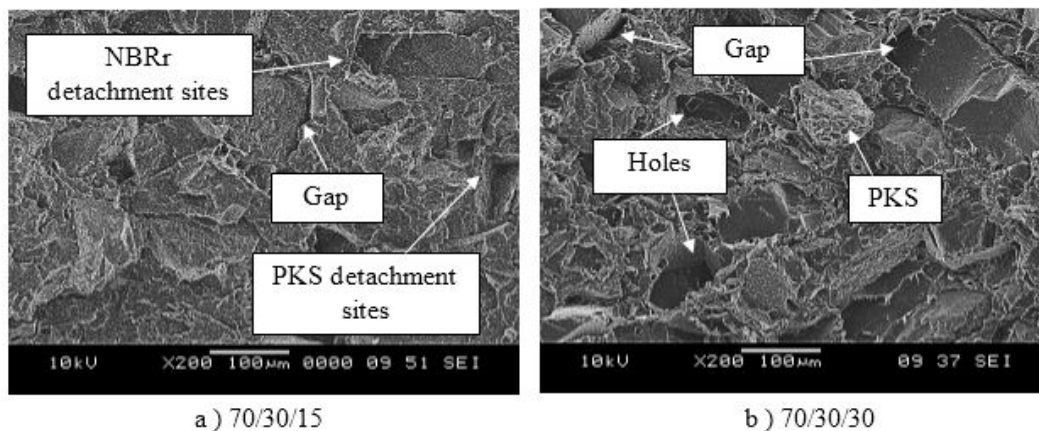


Fig. 6. SEM micrographs of the tensile fractured surface at 70/30/15 and 70/30/30 for composites with untreated filler

Figure 7 shows the SEM micrographs of PP/NBRr/PKS composites with γ -MPS treated PKS filler. It can be seen that good attachment between the filler and matrix and improves the interfacial adhesion between them. Less pull out, gap and holes were observed due to improvement of interfacial adhesion which is caused by the addition of γ -MPS silane. While, agglomeration of the fillers was observed with incorporation 30 phr of PKS filler.

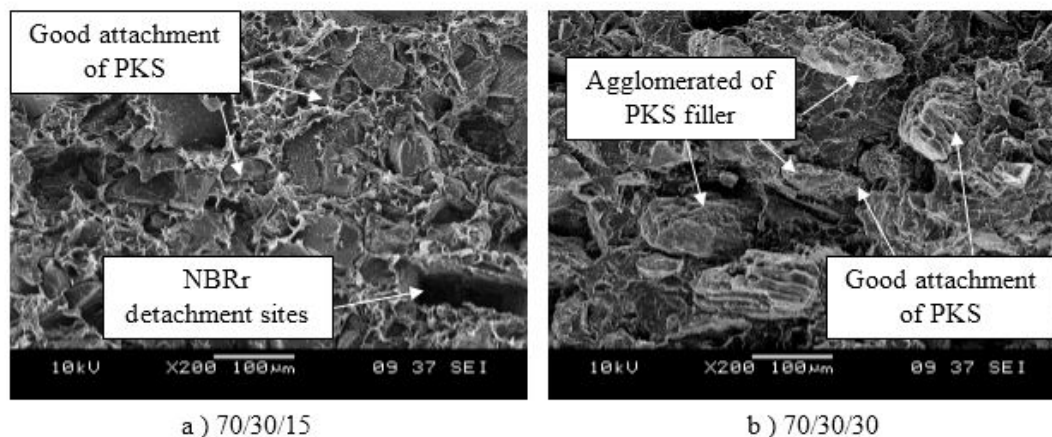


Fig. 7. SEM micrographs of the tensile fractured surface at 70/30/15 and 70/30/30 for composites with γ -MPS treated filler

4. Conclusion

Water absorption increases with increasing the filler loading due to the presence of OH groups contact with water and resulting in the weight gain of composites. However, γ -MPS treated PKS filler composites have resulted in lower water absorption approximately 5% compared to untreated filler due to better adhesion between filler and matrix. Mechanical properties of γ -MPS treated PKS filler have found to be higher compared to untreated filler. It can be shown by SEM micrographs that there are less gaps, pull out and voids in the γ -MPS treated PKS filler composites.

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