Mechanical properties and chemical reaction of 3-aminopropyltriethoxysilane of polypropylene, recycle acrylonitrile butadiene rubber and sugarcane bagasse composites

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Abstract: The mechanical and chemical properties of sugarcane bagasse (SCB) treated with 3-aminopropyltriethoxysilane (3-APS) filled polypropylene (PP)/recycled acrylonitrile butadiene rubber (NBRr) bio-composites were aim and investigated. The composites with different SCB loading from 5 wt.% to 30 wt.% were prepared using heated two-roll mill by melt mixing at temperature of 180°C. Tensile properties of composites which is tensile strength, Young Modulus and elongation at break were investigated. Increasing of treated SCB filler loading in composites have increased the Young modulus, however, decreased the tensile strength and elongation at break of the composites. The chemical properties and morphology of composites were investigated using Fourier transform infra-red analysis. These findings were supported by micrograph diagram from the morphological study. SCB filler treated with 3-APS has improved the adhesion and gave strong interfacial bonding between SCB filler and PP/NBRr matrices which results in good tensile strength of composites.

Keywords: mechanical properties; chemical reaction; 3-APS; 3-aminopropyltriethoxysilane; FTIR; Fourier transform infra-red analysis; polypropylene; PP; acrylonitrile butadiene rubber; SCB; sugarcane bagasse; composite.
1 Introduction

Natural fillers can be utilised as fillers or reinforcement in a polymer composite. The usage of natural fillers has gained a lot of attention in recent years. Research on the reinforcing materials on application of natural fillers such as cellulose fibres, sago, rubber wood powder, sisal, sugarcane, short silk fibre, oil palm, banana fibres, cotton stalk, empty fruit bunch, jute fibre, rice husk ash, hemp, sisal, jute and kenaf has been done (Tajvidi et al., 2006). In comparison with man-made fibres such as glass fibres, natural fillers have more benefits due to its biodegradable, recyclable, renewable, cheaper in cost, lower in density, properties of specific tensile which are equivalent, lower in energy usage and possesses reduced health threat (Sgriccia et al., 2008). Hence, natural fillers serve as a better substitute in comparison with other man-made fibres substitute (Gupta et al., 2016).
However, natural fillers are hydrophilic (polar) in nature and hence they are not compatible with the hydrophobic (non-polar) polymeric matrices. As a result, composites with low and poor properties are produced (Ragunathan et al., 2011). In addition, the hydrophilic nature of natural fillers tends to result in high moisture absorption, which in return will affect the mechanical properties of the resulting composites (Pang and Ismail, 2014). This problem, which results a physical and chemical interaction across the phase boundaries, is very poor, giving rise to the very weak interface. The incompatibility leads to poor adhesion and reduction in the ability of the matrices to transfer stress to the filler. Ragunathan et al. (2017a) have report the poor lower mechanical properties of polypropylene (PP), recycled acrylonitrile butadiene rubber (NBRr), sugarcane bagasse (SCB) composite. According to Ismail et al. (2010), the interaction between the PP and acrylonitrile butadiene rubber (NBR) phase is very poor, and incompatibility exists in both phases in the absence of rice husk powder as filler. This incompatibility between the hydrophilic filler particles and hydrophobic polymer matrices can be reduced by introducing coupling agent to the composites (Farahana et al., 2015).

This research work, the fabrication of PP, NBRr, SCB composite was evaluated for mechanical and chemical reaction. Therefore, the FTIR test has been run to examine the formation of inter- and intra- molecular hydrogen bonds in cellulose. The detailed database allows the establishment of strong correlation between the nature of hydrogen bonds and physical (e.g., solubility, hydroxyl reactivity and crystallinity) and mechanical properties of cellulose (Fan et al., 2012). The main aim of this study is to reduce the incompatibility of these materials with the help of appropriate coupling agent such as 3-APS.

2 Experimental

Polypropylene (PP)/NBRr/SCB composites were fabricated using heated two roll mill technique at 180°C. Dumbbell specimen according to D412 has been produces for mechanical and Fourier transform infra-red (FTIR) analysis. Universal Testing Machine model Instron 3366 has been use to evaluate the difference filler loading of SCB with and without 3-APS. The detail of preparation and experimental will be discuss in depth this section.

2.1 Material

Polypropylene (PP) Grade 6331 was obtained from Titan Pro Polymers (M) Sdn Bhd Johor with a melt flow index of 14 g/10 min at 230°C and a density of 0.9 g/cm³. NBRr with 33% acrylonitrile content was obtained from Juara One Resources Sdn Bhd, Penang. Coupling agent 3-aminopropyltriethoxysilane (3-APS) was supplied by Alfa Aesar (M) Sdn Bhd. SCB is collected from Kilang Gula Felda Perlis Sdn. Bhd. The NBRr and SCB were grinded into powder. The powder was then sieved at a particle size of 150–300 µm. The SCB was dried at 80°C for 24 h in the oven to remove the water.
2.1.1 3-APS treatment

The 3-APS treatment reaction of SCB was carried out in a mixture of ethanol and water with ratio of 95/5 volume, respectively. One hundred and fifty grams of SCB powder is soaked into the solution and stirred continuously for 1 h before the SCB was filtered out from the solution. Next, 3-APS (3 wt.% of the fillers) then mixed into the 1000 ml of 95/5 volume of ethanol and water prepared. The pH of the solution was maintained at 4 by using acetic acid. Then, the filtered SCB was added into the solutions and stirred continuously for 1 h. The treated SCB was filtered and dried in an oven at 80°C for 24 h before was further crushed in blender to ensure homogenous size of 150–300 µm.

2.1.2 Sample preparation

Formulation of PP/NBRr/SCB composites is given in Table 1. The mixing process was carried out by using heated two roll mill machine at 180°C. PP was allowed to melt for 4 min, followed by NBRr and adding of SCB filler after 6 min with total mixing time of 9 min. The PP/NBRr/SCB composites are prepared in 1 mm sheets by using compression-moulding. The hot-press machine was preheated for 6 mi at 180°C, 3 min of compressing and 2 min of cooling down the sample composite. The total preparation time is 11 min. After the compression process, the composite moulded into square shape with the thickness of 1 mm thin. The moulded composite was cut into dumbbell shape according to ASTM 412 using a Wallace die cutter S6/1/6A and the samples were ready for the testing.

Table 1 Formulation of PP/NBRr/SCB composites

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compositions (wt%)</th>
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<tbody>
<tr>
<td>PP</td>
<td>70</td>
</tr>
<tr>
<td>NBRr</td>
<td>30</td>
</tr>
<tr>
<td>SCB</td>
<td>5, 10, 15, 20, 25, 30</td>
</tr>
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</table>

*(wt%)-weight percent.
*Similar composites but without 3-APS treatment were also prepared.

3 Results

3.1 Mechanical properties

Tensile test was conducted on several samples for each series of the prepared composites according to ASTM 412. The test was conducted using Universal Testing Machine model Instron 3366 at room temperature. The initial jaw separation distance of the tensile tester was 50 mm and the testing was carried out at a crosshead speed of 5 mm/min. The data recorded are tensile strength, elongation at break (Eb) and Young’s Modulus. Figure 1 shows the dumbbell shape of sample.
3.2 **FTIR analysis**

FTIR analysis was done to examine the chemical composition of raw materials PP, NBRr and SCB. Besides that, it is also conducted to investigate the chemical interaction that occurs in the composites. In the case of powder specimen, ~5 mg of the specimen was mixed with 95 mg of potassium bromide (KBr) prior to compacting into thin pellets with a hydraulic press using 8 tons of force and maintain for 3 min. For sample in solid or sheet form, the sample was cut into small rectangular sheet and use directly with the transmission mode. FTIR spectra are recorded by plotting wavelength against observance. The spectrum resolution is 4 cm⁻¹ and the scanning range is from 550 to 4000 cm⁻¹ for 20 cycles of scanning.

**Figure 1** Dumbbell shape of sample

![Dumbbell shape of sample](image)

3.3 **Morphological examination**

The failure mode of the fractured tensile specimens was examined using Field Emission Electron Scanning Microscope (SUPRA-ZEISSVP36). Prior to the scanning electron microscope (SEM) micrographs were taken at various magnifications for fracture and other observations. Prior to the SEM observations the fractured ends of the specimens were mounted on aluminium stubs and were sputter coated with a thin layer of gold to avoid electrical charging during examinations.

4 **Discussion**

4.1 **Mechanical properties**

Figure 2 shows tensile strength of PP/NBRr/SCB composites with and without 3-APS treatment on SCB. From the results, it can be observed that matrix filled with SCB tends to reduce the tensile strength. This due to the poor adhesion between polar SCB and non-polar PP matrix. However, PP/NBRr/SCB composite treated with 3-APS coupling agent shows comparatively higher tensile strength compared with the untreated SCB. This due to the presence of 3-APS coupling agent which significantly improved the adhesion of the filler and matrix interface (Ragunathan et al., 2011). Stronger interfacial bonding provides higher tensile strength to the resulting composites (Ling and Ismail, 2012).
Figure 2  Tensile strength of PP/NBRr/SCB composites with and without 3-APS treatment on SCB

![Tensile strength graph]

Figure 3 shows tensile modulus of the untreated and treated PP/NBRr/SCB composites. The increasing addition of SCB filler has increased the tensile modulus of composites for both with and without 3-APS treatment. This due to increase in rigidity and increase stiffness of the composites at higher filler loading. The stiffness of the filler is higher than of the polymer matrix therefore increasing the stiffness of the composites resulted. Overall, the trend of the Young Modulus of the 3-APS treated PP/NBRr/SCB composites is much better than untreated one. The better adhesion between filler and matrices is due to better chemical interactions between SBC filler and PP/NBRr matrices. Good adhesion and enhance undeformed capacity of the matrix in the elastic zone. Thus increasing the Young Modulus of the resulting composite (Ragunathan et al., 2011). The addition of SCB filler into the PP/NBRr matrices also reduces the PP chains mobility and making the composites more rigid.

Figure 3  Young modulus of PP/NBRr/SCB composites with and without 3-APS treatment on SCB

![Young modulus graph]
Figure 4 shows the elongation at break of PP/NBRr/SCB composites with and without 3-APS. From the figure, it can be seen that the incorporation of SCB into the PP/NBRr composites resulted in continuously reduction of elongation at break. The $E_b$ of the composites decreased as the SCB filler loading increased. However, at a similar filler loading, the $E_b$ for PP/NBRr/SCB composites with 3-APS treatment was lower than the composites with the untreated filler. It also means that the treatment composites have improved the elongation at break ($E_b$). This due to the presence of the coupling agent, which enhances the matrix and filler interactions. The similar finding was supported by Metin et al. (2004) in the application rice husk ash as filler in polypropylene on effect titanate, zrconate and silane coupling agent.

**Figure 4** Elongation at break of PP/NBRr/SCB composites with and without 3-APS treatment on SCB

4.2 FTIR analysis

Figure 5 shows the FTIR spectra corresponding to SCB filler, NBRr, untreated PP/NBRr/SCB composite and 3-silane treated PP/NBRr/SCB composite. Based on the figure, all the spectra show different bands around 3200–3500 cm$^{-1}$ and 1740 cm$^{-1}$ which represent the stretching of OH group and C=O group, respectively (Ghani et al., 2016). As for SCB which composed mostly of cellulose, hemicelluloses and lignin, the cellulose backbone C–OH is represent by the peaks of 1050 cm$^{-1}$ and 1048 cm$^{-1}$, respectively (Ragunathan et al., 2017b). The 3-APS intense band around 1174 cm$^{-1}$ and 1105 cm$^{-1}$ in treated composite was assigned to the stretching of the –Si–O–Cellulose bond and –Si–O–Si– bond, respectively (Tee et al., 2013; Wang et al., 2014). The large band around 1050 cm$^{-1}$ found on SCB filler was attributed to the –Si–OH group which later this band disappeared after the surface modification (Abdelmouleh et al., 2007).
Figure 5  FTIR spectra corresponding to SCB filler, NBRr, untreated PP/NBRr/SCB composite and 3-APS treated PP/NBRr/SCB composite (see online version for colours)
4.3 Morphology

Figure 6(a) and (b) shows SEM micrographs of PP/NBRr/SCB composites untreated and treated SCB with 3-APS at filler loading of 30 wt.% with magnification of 100×. Based on the SEM micrographs, it shows that poor adhesion between SCB filler and PP/NBRr matrix. The incorporation of SCB filler into the PP/NBRr matrix has contributed to the rigidity of the material thus reducing the ductility of the composites (Ragunathan et al., 2011). However, the Figure 6(b) shown in the composites attachment and dispersion between SCB filler and PP/NBRr matrix were improved in the present 3-APS coupling agent. The better attachment can be observed as the filler was rather broken under stress. The use of 3-APS as a coupling agent proved to be effective in enhancing dispersion, attachment and compatibility of the hydrophilic filler and hydrophobic matrix through modification of polymer-filler interface (Ifuku and Yano, 2015).

5 Conclusion

In this study, the effect of 3-APS treatment on PP/NBRr/SCB composites was conducted. Tensile strength and elongation at break of the PP/NBRr/SCB composites decreased with increasing SCB filler loading. This is due to poor adhesion of filler with matrices in higher SCB filler loading. However, the treated SCB filler composites shown the higher tensile strength but lower elongation at break. At 70/30/15 loading of composites the tensile strength increment by 13.2% compared with untreated SCB. Meanwhile, the elongation at break reduced by 21.5% at same loading. This was due to strong attachment of SCB filler with PP/NBRr matrices in the presences of 3-APS coupling agent. This results significant with research by Pang and Ismail (2014) using polypropylene/waste tyre dust/ kenaf composites. At the same loading 70/30/15, the increment of tensile strength 15.4% and the elongation at break is 18.7%. The FTIR test shows different bands around 3200–3500 cm⁻¹ and 1740 cm⁻¹ which represent the stretching of OH group and C=O group, respectively. As for SCB which composed mostly of cellulose, hemicelluloses and lignin, the
cellulose backbone C–OH is present by the peaks of 1050 cm⁻¹ and 1048 cm⁻¹, respectively. The 3-APS intense band around 1174 cm⁻¹ and 1105 cm⁻¹ in treated composite was assigned to the stretching of the –Si–O–Cellulose and –Si–O–Si– bond, respectively. The large band around 1050 cm⁻¹ found on SCB filler was attributed to the –Si–OH group which later this band disappear after the surface modification. SEM micrographs examined shows small gap with good attachment between the filler and matrices at lower filler loading. Overall, PP/NBRr/SCB composites treatment with 3-APS on SCB showed better performance when compared with the untreated PP/NBRr/SCB composites.

References


