Effect of Filler Loading and Benzyl Urea on Tensile, Water Absorption, and Morphological Properties of Recycled High-Density Polyethylene/Ethylene Vinyl Acetate/Calcium Carbonate (rHDPE/EVA/CaCO₃) Composites

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Abstract – *Coupling of individual properties between recycled high-density polyethylene (rHDPE) and ethylene vinyl acetate (EVA) blends as polymer matrix which has different chemical structure requires coupling agent to improve their interfacial adhesion. Therefore, benzyl urea (BU) was examined to access its potential as the coupling agent in rHDPE/EVA composites. RHDPE/EVA blends with ratio of 50/50 and different loadings of calcium carbonate (CaCO₃) as filler from 0 to 25 phr were prepared by using melt blending technique Brabender Plasticorder at 190 °C and rotor speed of 50 rpm for 10 minutes. The compatibilization of rHDPE/EVA blends were enhanced by the addition of 6 phr of the BU. The tensile, water absorption and morphological properties were studied. Tensile properties such as tensile strength and Young's modulus were improved while the elongation at break was reduced by the addition of BU. The water absorption resistance was also improved due to the enhanced interfacial adhesion and intercalation between rHDPE and EVA as observed from the SEM images .**Copyright © 2015 Penerbit Akademia Baru - All rights reserved.**

Keywords: Compatibilization, Ethylene vinyl acetate, Calcium carbonate, Recycled HDPE

1.0 INTRODUCTION

Recycled high-density polyethylene (rHDPE) is one of the promising candidates due to its high portion of post-consumer waste. It is also safe during its production and while being used by the consumer [1]. Previous studies show that the properties of the rHDPE obtained from the post-consumer milk bottles was not largely different from those of virgin resin and thus could be used for various applications [2]. Also the recycled plastics are cheaper than in the virgin form, for example, rHDPE pellets and flakes are 31-34 % less expensive than the virgin HDPE.

Thus, increased use of rHDPE offers the prospect of lessening the packaging and industrial product waste disposals and reducing the product costs.

The blends of polyethylene (PE)/ethylene vinyl acetate (EVA) blends are widely used as packaging films and heat-shrinkable tubes [3]. Other industrial applications of these blends include wire and cable-insulation coatings and foams. It has been reported that EVA addition to different PE grades can improve the PE properties such as toughness, transparency, environmental stress cracking resistance, and filler-carrying capacity [4]. Khastgir and Ray have found that the composition of 50/50 EVA/LDPE exhibit a maximum tensile strength when the interfacial of these two phases are crosslinked with the aid of dicumyl peroxide (DCP) curing agent [5]. However, because of different chemical structure, PE and EVA are not compatible. Zou et al. found that the HDPE/EVA blends are partially miscible in the melt state, which could in turn lead to partial miscibility in the amorphous region in the solid state [6]. The addition of compatibilizer or coupling agent to HDPE/EVA blends to form a polymer blend with better properties has been extensively studied [7–9].

In this study, we decided to blend the rHDPE with ethylene vinyl acetate containing 50/50 (rHDPE/EVA) to couple their individual properties of both materials as polymer matrix. However, because of their different polarity, a coupling agent was used to improve the interfacial adhesion between the rHDPE and EVA. To the best of our knowledge, there has been no work reported on the polyvinylchloride-maleic anhydride (PVC-MA) as coupling agent between rHDPE and EVA. Calcium carbonate was chosen as the filler in the rHDPE/EVA blends with different loading from 0 to 25 phr. The purpose of this study was to prepare the benzyl urea modified rHDPE/EVA composites by the melt mixing method in the internal mixer and to further study the influence of the benzyl urea coupling agent and the calcium carbonate filler on the properties of the composites.

2.0 METHODOLOGY

2.1 Materials

rHDPE pellets with a melt flow index of 0.7 g/10 min (190 °C) and a density of 939.9 kg/m3 and EVA contains 6.5 wt.% VA, with melt index of 2.5g/10 min (80 °C; 2.16 kg) and density of 0.93 g/cm3 was supplied from A.R. Alatan Sdn. Bhd., Kedah Darul Aman, Malaysia. Benzyl urea ($C_8H_{10}N_2O$) and calcium carbonate ($CaCO_3$) were purchased from AR Alatan Sdn. Bhd., Alor Setar, Kedah, Malaysia. Dicumyl peroxide (DCP, purity 98%) used as an initiator was purchased from Aldrich, and its half-lifetime at the melt grafting temperature (175 °C) was about 1.45 min.

2.3 Composite Preparation

For the composites preparation, the compounding of the blends was carried out by melt blending in an internal mixer (Plasticoder, Brabender). The rHDPE was first mixed in the internal mixer at 190 °C, 50 rpm for 4 min and then pre-weighed amounts of EVA, benzyl urea, DCP, and $CaCO_3$ were added to the mixer and the mixing process continued for a further 10 minutes. Each of the molten samples was compression molded into sheets with a thickness of about 2 mm using a hydraulic press at 190 °C for 2 minutes and cooled under pressure for 4 minutes. Table 1 presents the formulation and designation of the samples. It should be pointed out that all the formulations included a matrix of 50 phr rHDPE and 50 phr EVA. 6 wt.% of

benzyl urea (BU) was added as compatibilizer together with 1% DCP as radical initiator to the compatibilized blends.

Table 1: Formulation of rHDPE/EVA/CaCO$_3$ samples.

Composite code	rHDPE	EVA	CaCO$_3$	BU	DCP
	(phr)	(phr)	(phr)	(phr)	(phr)
rHDPE/EVA	50	50	-	-	-
rHDPE/EVA/CaCO$_{3}$-5	50	50	5	-	-
rHDPE/EVA/CaCO$_{3}$-10	50	50	10	-	-
rHDPE/EVA/CaCO$_{3}$-15	50	50	15	-	-
rHDPE/EVA/CaCO$_{3}$-20	50	50	20	-	-
rHDPE/EVA/CaCO$_{3}$-25	50	50	25	-	-
rHDPE/EVA/CaCO$_{3-BU}$-5	50	50	5	6	1
rHDPE/EVA/CaCO$_{3-BU}$-10	50	50	10	6	1
rHDPE/EVA/CaCO$_{3-BU}$-15	50	50	15	6	1
rHDPE/EVA/CaCO$_{3-BU}$-20	50	50	20	6	1
rHDPE/EVA/CaCO$_{3-BU}$-25	50	50	25	6	1

2.4 Tensile Test

Tensile properties were determined according to ASTM D638 by using the Instron 5569 with a cross-head speed of 50 mm/min. Five dumb-bell shaped samples were used for each blend composition. Tensile strength, elongation at break, and Young's modulus of each composite were obtained from the test.

2.5 Water Absorption Analysis

Water absorption test was carried out according to ASTM D750-95 standard. It involved total immersion of five samples in distilled water at room temperature. All the specimens were previously dried in an oven at 50 °C for 24 h and stored in desiccators. The water absorption was determined by weighing the samples at regular interval. A Mettler balance type AJ150 was used with precision of ±1 mg. The percentage of water absorption (Mt) was calculated using Equation 1, where W_d and W_N are original dry and weight after exposure, respectively.

$$Mt = \frac{W_N - W_d}{W_d} \times 100\% \tag{1}$$

2.8 Scanning Electron Microscopy

Morphology of the tensile fracture surface of rHDPE/EVA/CaCO$_3$ composites with and without benzyl urea were carried out using a SEM, model JEOL JSM 6460LA. Surfaces of the samples were coated with a thin palladium layer of about 12 µm thickness using Auto Fine Coater, model JEOL JFC 1600.

3.0 RESULTS AND DISCUSSION

3.1 Tensile Properties

Figure 1 shows the effect of filler loading and the presence of benzyl urea as coupling agent on tensile strength of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-}BU}$ composites. It can be seen that the tensile strength of the rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-}BU}$ composites decrease with the increasing content of filler. This is due to the incompatibility of the filler and rHDPE/EVA phases. Besides, the filler was unable to support the stress transfer from rHDPE/EVA matrix phase. A similar observation was reported by Fatimah et al., where the tensile strength of r-HDPE/EVA/waste tire dust composites decreased as the loading of the waste tire dust increased [10]. This incompatibility resulting in reduced tensile properties because fractures would be initiated from the weak interface of the composites due to their poor interfacial adhesion.

At similar filler loading, the composites with BU coupling agent exhibited higher tensile strength compared with composites without BU coupling agent. Figure 2 shows the proposed possible interactions scheme between rHDPE/EVA matrix and BU coupling agent. It involved the reaction of methyl (-CH$_3$) groups on EVA with the amino (-NH$_2$) groups of BU, forming an intermediate. By referring to the study of Balakrishna et al., they suggested similar possible interactions of silane coupling agent with rattan powder [11]. The amino group of the intermediate tended to be attracted to rHDPE/EVA matrix by forming van der Waals forces between them due to similar hydrophobicity. This explained the improvement in interfacial adhesion between HDPE/EVA matrix and CaCO3 with the addition of BU coupling agent.
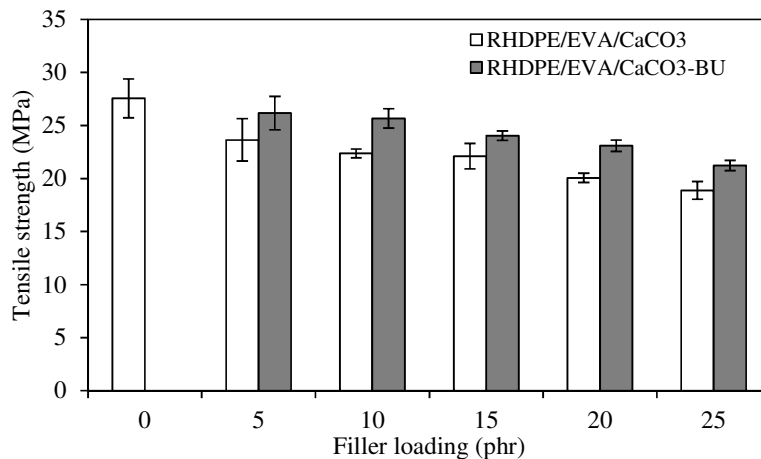

Figure 1: Effect of filler loading on tensile strength of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-}BU}$ composites.

Figure 3 shows the effect of filler loadings and BU coupling agent on the elongation at break of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-}BU}$ composites. It can be observed that the elongation at break of the composites decreased with the increasing filler loading for all composites with and without BU coupling agent. Similar observations had been reported by Supri et al and Yazid et al. [12,13]. The increase in stiffness and brittleness as the filler loading increased was responsible for the decrement in the elongation at break of the composites. As

the filler loading increased, the restriction of the chain mobility of the rHDPE/EVA matrix increased, leading to higher breaking tendency (lower deformation) of the composites. However, at similar filler loading, the elongation at break for composites in the presence of BU coupling agent was lower than the composites without BU coupling agent. As explained earlier, the decrease in the elongation at break in the presence of BU coupling agent was due to the enhancement in the interfacial adhesion of the rHDPE/EVA matrix along with the filler.
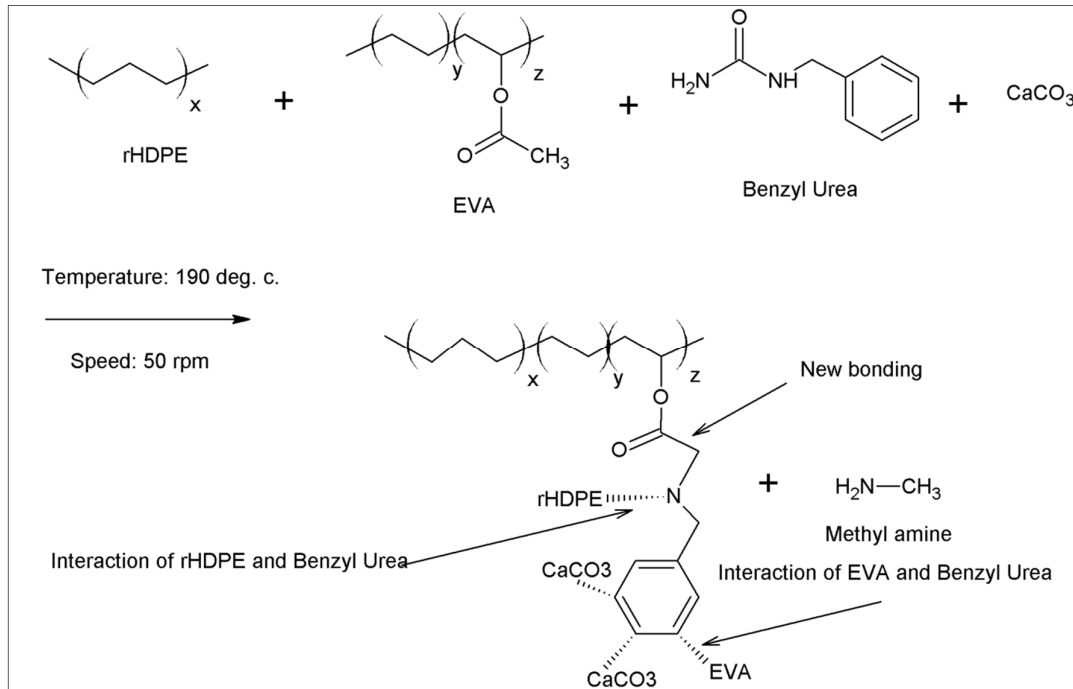
Figure 2: Proposed possible interactions scheme between rHDPE/EVA matrix and benzyl urea coupling agent.

Figure 4 shows the effect of filler loading and the presence of BU coupling agent on the Young's modulus of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3-BU}$ composites. The Young's modulus of the composites was found to increase with an increasing filler loading for all composites with and without BU coupling agent. This was because the incorporation of CaCO$_3$ filler had resulted in high stiffness in the composites. The addition of CaCO$_3$ filler had lowered the chain mobility of rHDPE/EVA matrix and hence produced composites with higher rigidity. At similar filler loading, it can be seen that the composites with BU coupling agent had shown higher Young's modulus than the composites without BU. Again, the higher Young's modulus was due to the better interactions between the rHDPE/EVA matrix and the filler in the presence of BU coupling agent. Similar observation was reported by Ali Dadfar et al [14].

Water Absorption Properties

The effect of filler loading and the presence of BU coupling agent on the water absorption properties of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3-BU}$ composites are shown in Figure 5. The results show that the water absorption of the composites increased when the filler loading increased. As the filler loading increases, the hydrophilic content increases, which in

turn result in the absorption of more water. The composites with benzyl urea show lower water absorption than rHDPE/EVA/CaCO$_3$ composites. This indicates that the resistance to water absorption in rHDPE/EVA/CaCO$_3$ composites with benzyl urea was better than rHDPE/EVA/CaCO$_3$ composites. As discussed earlier, the reaction of methyl (-CH$_3$) groups on EVA with the amino (-NH$_2$) groups of BU has restricted the water absorption of the composites. The BU has builds up chemical bonds, which reduce the moisture-caused rHDPE/EVA debonding. This in turn reduces the extent of water absorption. Similar observation was reported by Atul Rajan et al [15].
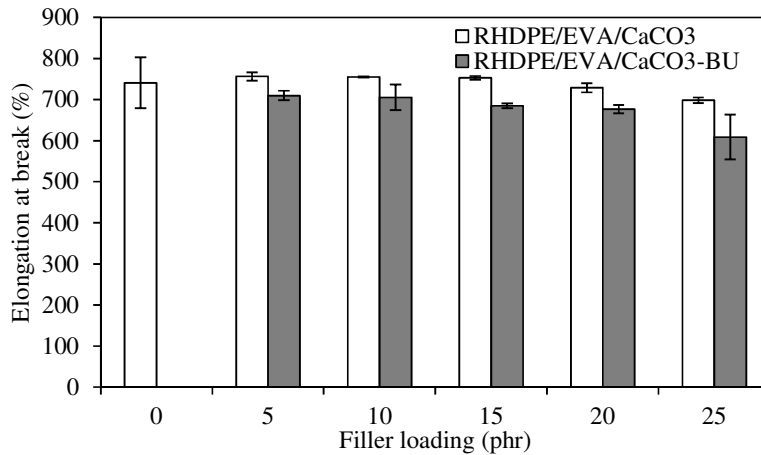

Figure 3: Effect of filler loading on elongation at break of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-BU}}$ composites.
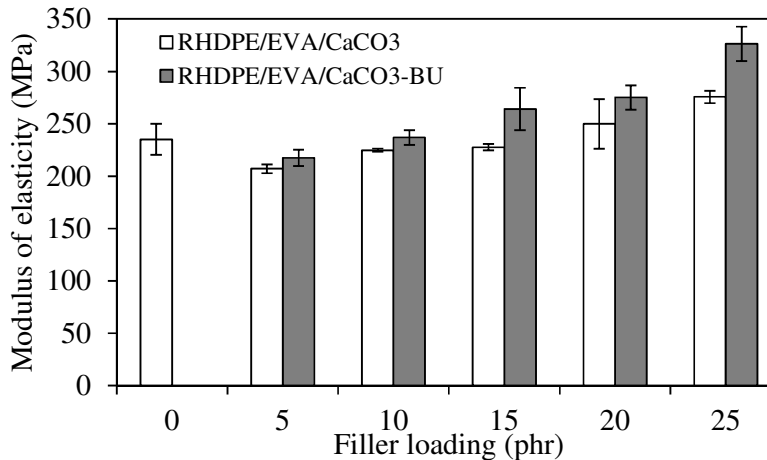

Figure 4: Effect of filler loading on Young's modulus of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-BU}}$ composites.
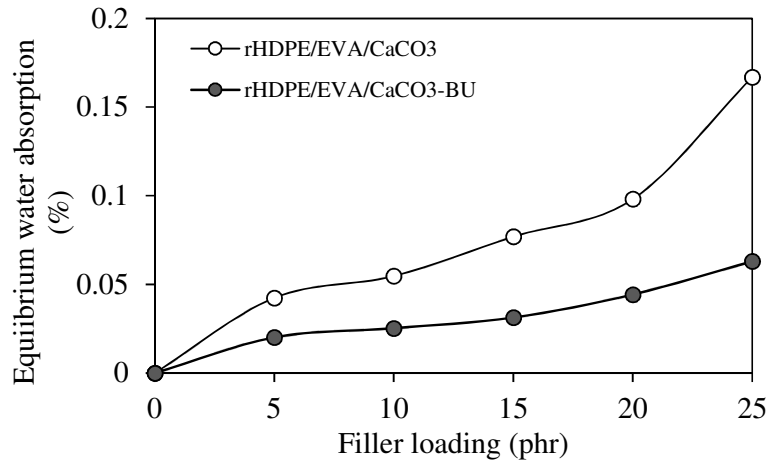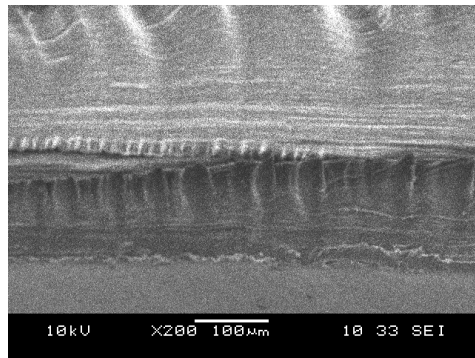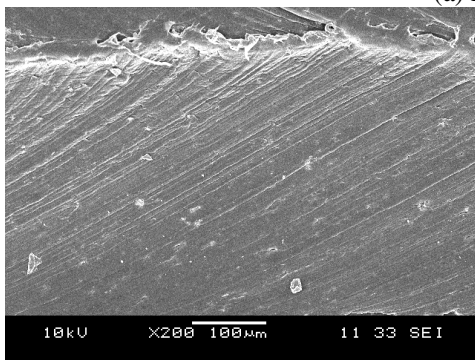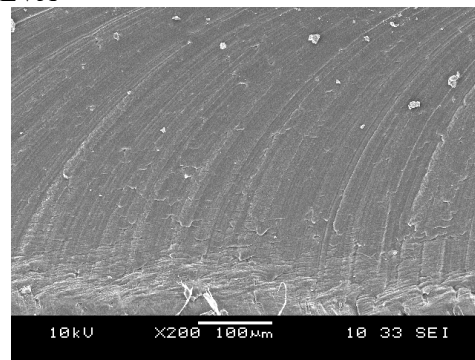
Figure 5: Effect of filler loading on water absorption properties of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-BU}}$ composites.

(a) rHDPE/EVA

(c) rHDPE/EVA/CaCO$_3$-5

(d) rHDPE/EVA/CaCO$_{3\text{-BU}}$-5

(e) rHDPE/EVA/CaCO$_3$-15

(f) rHDPE/EVA/CaCO$_{3\text{-BU}}$-15

(g) rHDPE/EVA/CaCO$_3$-25

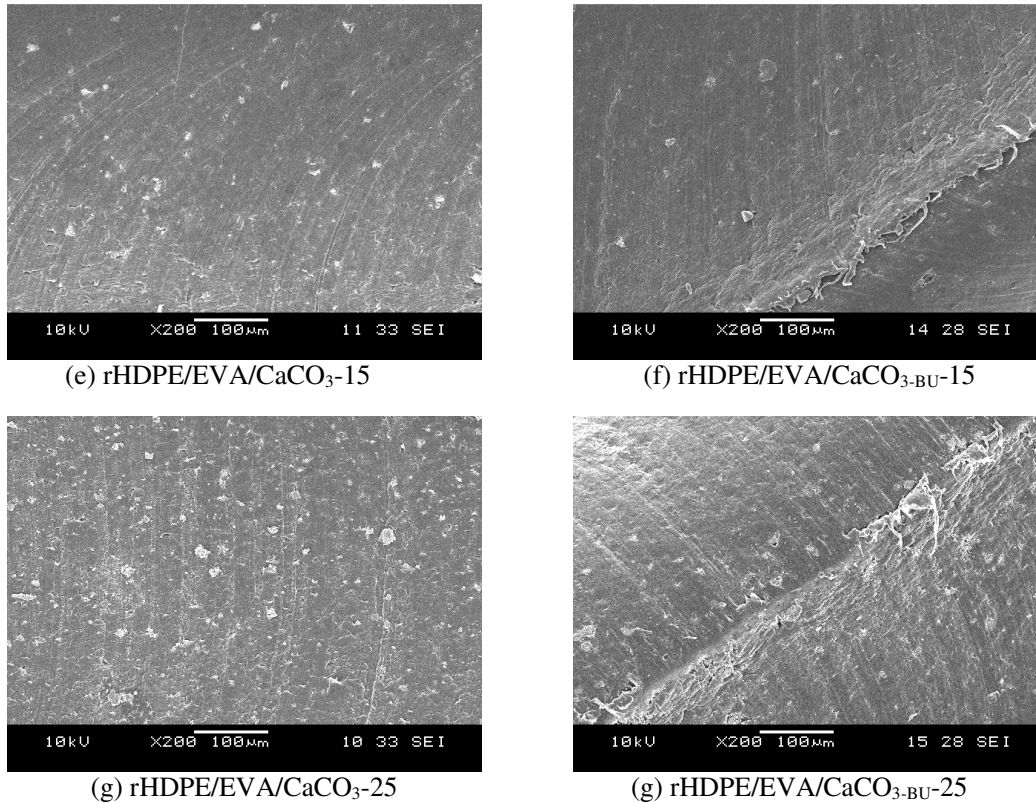(g) rHDPE/EVA/CaCO$_{3\text{-BU}}$-25

Figure 6: The SEM morphologies of tensile fracture surfaces of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-BU}}$ composites, (a) rHDPE/EVA, (b) rHDPE/EVA/CaCO$_3$-5, (c) rHDPE/EVA/CaCO$_{3\text{-BU}}$-5, (d) rHDPE/EVA/CaCO$_3$-15, (e) rHDPE/EVA/CaCO$_{3\text{-BU}}$-15, (f) rHDPE/EVA/CaCO$_3$-25, (g) rHDPE/EVA/CaCO$_{3\text{-BU}}$-25

Morphology Analysis

Figure 6 shows the SEM morphology of tensile fracture surface of rHDPE/EVA/CaCO$_3$ and rHDPE/EVA/CaCO$_{3\text{-BU}}$ composites at different filler loading. From the micrographs, it can be seen that as the filler loading increases, the micrographs show the detachment of filler from the matrix. This was due to poor interfacial adhesion between the rHDPE/EVA matrix and filler and more pull-out of the filler from matrix, which resulted in lower tensile strength of the composites as shown in previous section. As a filler loading increased, the fillers tended to agglomerate because of the increased tendency for filler-filler interaction rather than filler-matrix interaction [16]. The lower filler loading shows better dispersion and less pull out of filler from matrix compared to the higher filler loading. From the micrographs below, we can see that the composites with BU coupling agent indicated rough surfaces and good dispersion of filler in the rHDPE/EVA/CaCO$_3$ composites with benzyl urea. This results show that BU has improves the interfacial adhesion between the rHDPE/EVA matrix and filler. Accordingly, the interfacial strength is improved.

4.0 CONCLUSSION

The investigation on the effect compatibilizer benzyl urea (BU) on the properties of rHDPE/EVA/CaCO$_3$ composites was done in this study. Benzyl urea was used as the

compatibilizer for rHDPE and EVA matrix filled with $CaCO_3$ filler. The addition of benzyl urea as a compatibilizer with the presence of DCP as an initiator increased the tensile strength, and Young's modulus but reduced the elongation at break and equilibrium water absorption of rHDPE/EVA/$CaCO_{3-BU}$ composites as compared to rHDPE/EVA/$CaCO_3$ composites. The rHDPE/EVA/$CaCO_{3-BU}$ composites exhibited better interfacial adhesion between the filler and matrices than the rHDPE/EVA/$CaCO_3$ composites as observed from the morphological studies.

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