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Effect of PVC-MA Coupling Agent on Tensile, Water Absorption and Morphological Properties of Recycled High Density Polyethylene/Ethylene Vinyl Acetate/Eggshell Powder Composites

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Abstract – *The effects of polyvinylchloride-maleic anhydride (PVC-MA) and filler loading ratio on the mechanical, morphological and water swelling behavior on the recycled high density polyethylene/ethylene vinyl acetate/egg shell powder blends were analyzed. The addition of PVC-MA to the blends has improved the tensile strength, water absorption resistance, and interfacial adhesion between the components of the blends. The results indicated that the polyvinylchloride-maleic anhydride has significant effects on the mechanical, morphological, and water swelling behavior of recycled high density polyethylene/ethylene vinyl acetate/egg shell powder blends.* ***Copyright © 2015 Penerbit Akademia Baru - All rights reserved.***

Keywords: Compatibilization, Ethylene vinyl acetate, Fillers, Eggshell powder, Recycled HDPE

1.0 INTRODUCTION

Polymer blending is capable of providing the required properties than synthesizing new polymers. It has been recognized as an important route to novel and useful polymeric products with properties superior to those of the individual components. With increasing understanding of the science and engineering involved, polymer blend is expected to offer increasing contributions to the plastic industries [1].

High density polyethylene (HDPE) is a thermoplastic material which is a comprehensive resin and having unique properties such as excellent mechanical properties, ozone resistance, good electrical properties, and chemical resistance and has low price [2,3]. Ethylene vinyl acetate (EVA) is a thermoplastic resin made of ethylene monomer and vinyl acetate monomer. It shows high impact strength, stress crack resistance, good ageing resistance, low temperature flexibility, improved clarity, permeability to oxygen and vapours, high moisture absorption, and high electrical resistance [2,3].

Blends of HDPE and EVA are widely used is shrinkable films, multilayer packaging, and wire and cable coating since this blend couples the superior properties of both materials. However, because of difference of chemical structure between HDPE and EVA, HDPE is difficult to compatibilize with EVA. Compared to HDPE, EVA is more polar and less crystalline due to polar vinyl acetate (VA) group and leads to better compatibility with polar polymers and fillers

[4]. The common technique used is to add small amount of compatibilizer due to their ability to improve both physical and chemical interaction between the components [5].

Filler reinforced polymer composites find potentials over traditional engineering materials [6]. Composites based on polyolefins and mineral fillers have been extensively studied, specifically those ones based on polyethylene and inorganic fillers are of great research interest. Inorganic fillers are reported to improve mechanical, thermal and electrical properties of some crystalline polymers, when they are used as reinforcing agents [7]. Besides, the purpose of incorporating fillers into polyolefin is to decrease cost and reduce the consumption of petroleum-based polymer.

The use of natural fillers as reinforcement for thermoplastics is attractive since it is based on abundant and renewable resources and is ecologically sound as it stimulates the recycling of thermoplastics found in domestic waste. This is more interesting since in Malaysia there are abundant chicken eggshell which is a good source of calcium carbonate. Eggshells are generated in thousands or millions of tones every year. These characteristics qualify eggshell as excellent candidate for bulk quantity, inexpensive, low-load bearing composite applications such as the automotive industry, trucks, homes, offices, and factories. Furthermore, using the eggshell from agricultural waste not only reduce waste but also reduce the energy consumed for manufacturing materials with readily available and inexpensive new reinforcement for thermoplastic polymer composites. A concern in polymer/eggshell composites have been started since the last few years as a new inorganic material that can be used as filler in polymer composite [8–16]. A dry eggshell has been reported to contain approximately 95% (by weight) with a typical mass of 5.5 grams in the form of calcite. The effects of calcium carbonate ($CaCO_3$) on thermoplastics are widely reported [17–21].

Attempts have been made to recycle the post-consumer plastics in order to reduce the environmental impact and consumption of virgin plastics. Previous studies show that the properties of the recycled high density polyethylene (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 [22]. 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 recycled plastics offers the prospect of lessening waste disposals and reducing the product costs.

Therefore this paper presents the results of the effect of polyvinylchloride-maleic anhydride (PVC-MA) coupling agent to mechanical, water absorption, and morphological properties of the composites formed by mixing polymer blend of rHDPE and EVA with chicken eggshell powder (ESP).

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 939.9kg/m3 and EVA contains 6.5 wt.% VA, with melt index of 2.5g/10 min (80°C; 2.16kg) and density of 0.93g/cm3 was supplied from A.R. Alatan Sdn. Bhd., Kedah Darul Aman, Malaysia. The chicken egg shells were obtained from local food industry in Negeri Sembilan, Malaysia. Poly(vinylchloride) (PVC) and maleic anhydride (MA) powder was purchased from MERCK company while 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.

2.2 Preparation of Eggshell Powder

The eggshells were washed and crushed into small pieces. Then they were dried in an oven at 80°C until the weight is constant to evaporate all moisture. The dried eggshells were grinded to powder using kitchen blender, which is designated ESP. Sieve was used to obtain an average filler sizes of 63**μ**m. ESP was dried in vacuum oven at 80°C till the constant weight to make it free from moisture as reported in Shuhadah et. al. [8].

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, PVC, MA, DCP, and ESP 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 PVC and MA was added as compatibilizer together with 1% DCP as radical initiator to the compatibilized blends. The proposed interaction between the PVC and MA in the internal mixer is displayed in Figure 1.

Table 1: Formulation of rHDPE/EVA/ESP samples.

Composite code	rHDPE (phr)	EVA (phr)	ESP (phr)	PVC-MA (phr)	DCP (phr)
rHDPE/EVA	50	50	-	-	-
rHDPE/EVA/ESP5	50	50	5	-	-
rHDPE/EVA/ESP10	50	50	10	-	-
rHDPE/EVA/ESP15	50	50	15	-	-
rHDPE/EVA/ESP20	50	50	20	-	-
rHDPE/EVA/ESP25	50	50	25	-	-
rHDPE/EVA/ESP5$_{PVC-MA}$	50	50	5	6	1
rHDPE/EVA/ESP10$_{PVC-MA}$	50	50	10	6	1
rHDPE/EVA/ESP15$_{PVC-MA}$	50	50	15	6	1
rHDPE/EVA/ESP20$_{PVC-MA}$	50	50	20	6	1
rHDPE/EVA/ESP25$_{PVC-MA}$	50	50	25	6	1

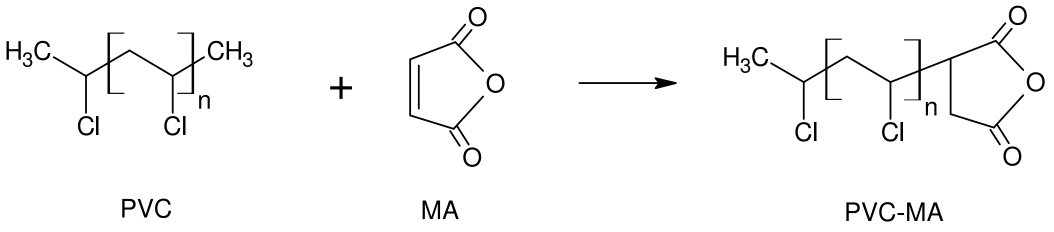


Figure 1: Proposed interaction between the polyvinyl-chloride and maleic anhydride

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 Wd and WN 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/ESP composites with and without maleic anhydride 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 2 shows the effect of filler loading on tensile strength of rHDPE/EVA/ESP and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites. The tensile strength for both composites gradually decreased from 5 phr to 25 phr filler loading. The decreased of tensile strength was probably attributed to the weak interfacial adhesion and low compatibility between the hydrophilic ESP and hydrophobic rHDPE/EVA. Supri et al (2010) reported that as the amount of filler loading increased, the tendency for filler-filler interaction increased rather than filler-matrix interaction to form agglomeration due to the difficulties to achieve homogenous dispersion of filler at higher filler loading [15]. As can be seen in Figure 2, rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites exhibited higher tensile strength than rHDPE/EVA/ESP composites at similar filler loading. This was due to the presence of PVC-MA acts as coupling agent which enhanced the interfacial adhesion between the rHDPE and EVA matrix, thus significantly increased the tensile strength of rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites. The PVC-MA has improved the mechanical capacity of the material by means of a chemical mechanism. This mechanism is based on the establishment of vinyl bonds of the PVC and the C-C aliphatic chains of the rHDPE besides the interaction between PVC and the acetate group of EVA [23]. The proposed interaction between the rHDPE/EVA/ESP with PVC-MA coupling agent is displayed in Figure 3.

Figure 4 illustrates the effect of filler loading on elongation at break of rHDPE/EVA/ESP and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites. The elongation at break of both composites decreased with the increasing of filler loading. This showed that the mobility of the polymer chains has reduced by the rigid fillers. On the other hand, a lower value of elongation at break can be observed for rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites compared to rHDPE/EVA/ESP composites at any filler loading. This was due to the addition of PVC-MA which had improved the adhesion of rHDPE/EVA, thus increased the stiffness of the composites. Ismail et al. (2004) reported that the addition of maleic anhydride to the waste PVC/NBR blends showed lower elongation at break, E_B compared to the untreated blends [24].

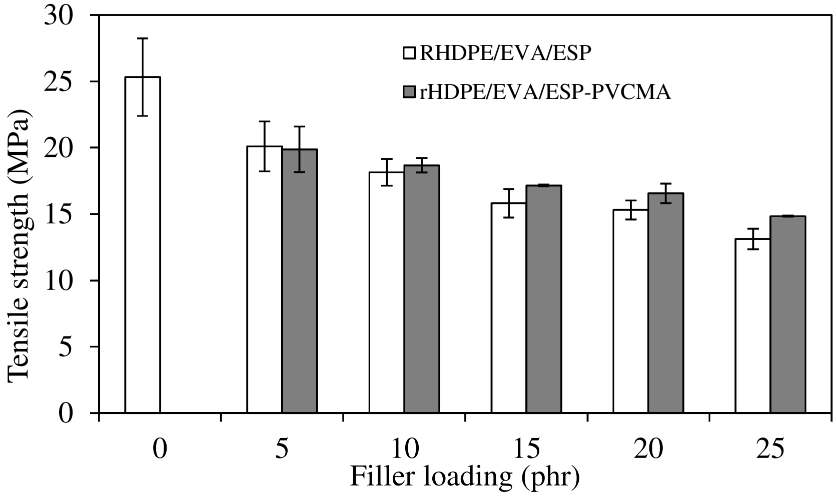


Figure 2: Effect of filler loading on tensile strength of rHDPE/EVA/ESP composites and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites

The effect of filler loading and compatibilizer on Young's modulus of rHDPE/EVA/ESP and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites is shown in Figure 5. The Young's modulus of both composites increased as the filler loading increased. This might due to the ability of ESP to impart greater stiffness to the rHDPE/EVA matrix. Moreover, ESP possessed higher modulus compared to rHDPE/EVA phases, as a result, the composites provided higher modulus than polymer blends. It can be noted that rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites exhibited higher Young's modulus compared to rHDPE/EVA/ESP composites at similar filler loading. As mentioned earlier, the function of PVC-MA as a compatibilizer which enhanced the interaction between the rHDPE and EVA, thus produced higher stiffness to the composites.

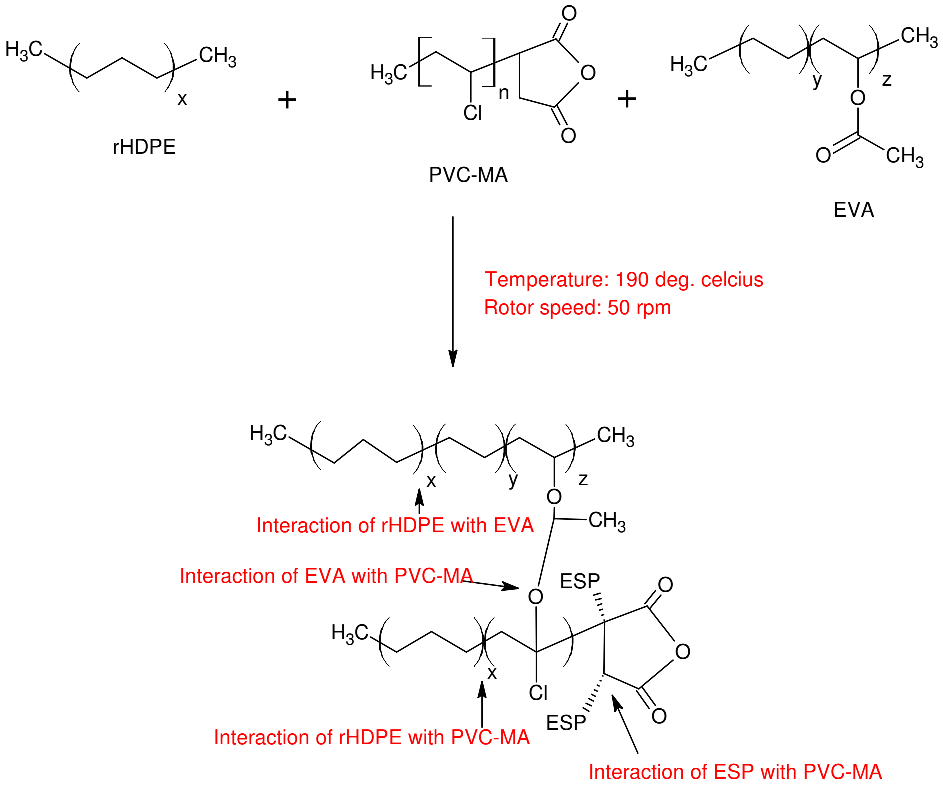


Figure 3: Proposed interaction between the rHDPE/EVA/ESP composites with the PVC-MA coupling agent

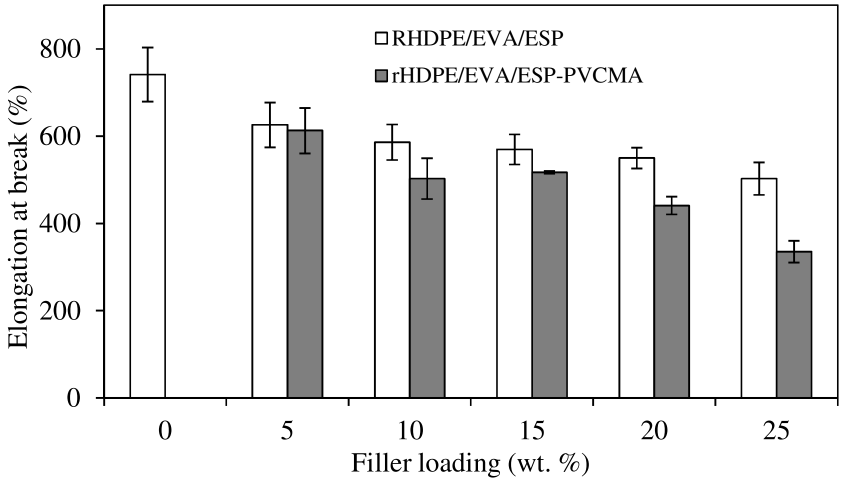


Figure 4: Effect of filler loading on elongation at break of rHDPE/EVA/ESP composites and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites

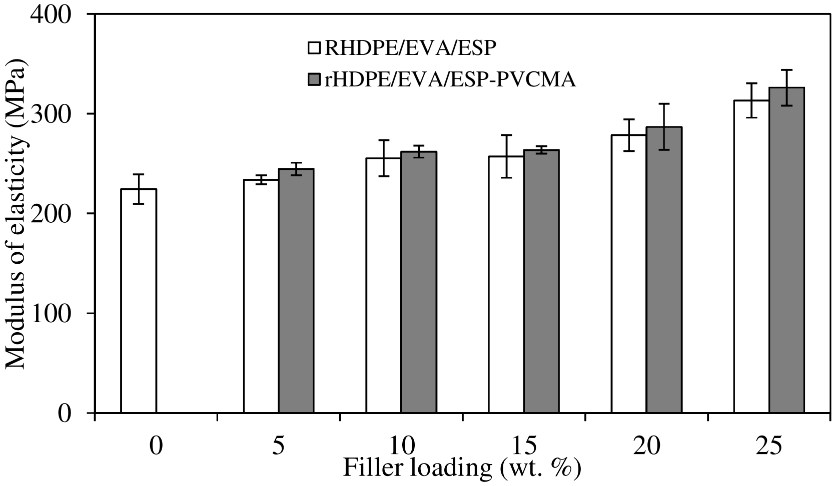


Figure 5: Effect of filler loading on Young's modulus of rHDPE/EVA/ESP composites and rHDPE/EVA/ESP$_{PVC-MA}$ composites

3.2 Water Absorption Analysis

Figure 6 shows the water absorption of rHDPE/EVA/ESP composites. As can be seen, the equilibrium water absorption of both composites increased as filler loading increased. As more filler were added into the polymer matrix, they caused absorption of more water due to the increasing content of the ESP. This is because ESP is a natural material and its main constituents have hydroxyl groups. These groups are hydrophilic in nature. Meanwhile, the percentages of the equilibrium water absorption for rHDPE/EVA/ESP$_{PVC-MA}$ composites are lower than uncompatibilized rHDPE/EVA/ESP composites.

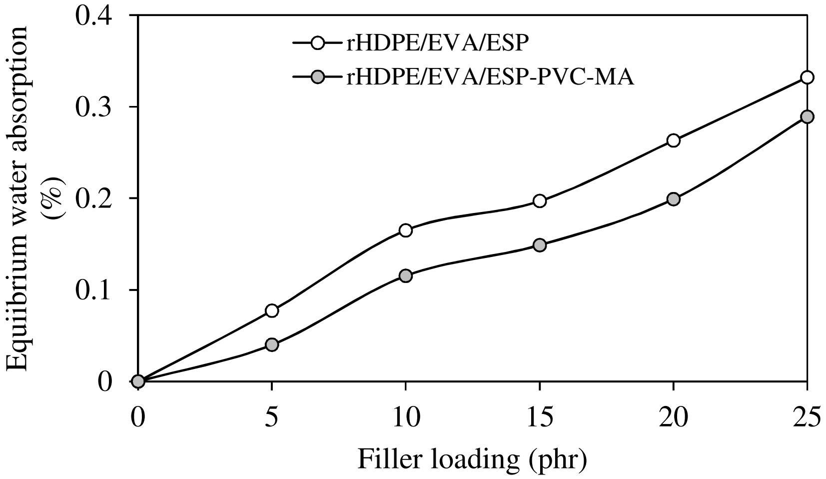
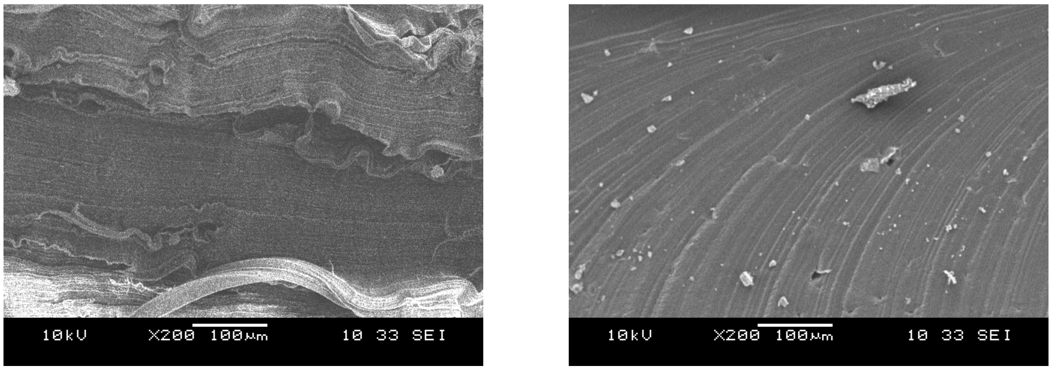


Figure 6: Percentage of equilibrium water absorption versus filler loading for rHDPE/EVA/ESP composites

After compatibilization, some hydroxyl groups of ESP reacted with maleic anhydride and increased compatibility with rHDPE/EVA matrix which can be referred in the proposed interaction as in Figure 3. Therefore, fewer hydroxyl groups were present in the resulting composites, which resulted in less water absorption. This difference was due to good interfacial adhesion between rHDPE/EVA and ESP with the presence of PVC-MA. Consequently, composites with PVC-MA compatibilizer exhibit better tensile strength compared to uncompatibilized rHDPE/EVA/ESP composites. Marais et al (2004) found that the interaction between PVC and EVA will reduce water and gas permeability due to the low segmental mobility of PVC which enables it to create hydrogen bonds between the hydrogen atoms and the Cl-substituted carbon of PVC with VA carbonyls, which decreases the diffusivity [25].

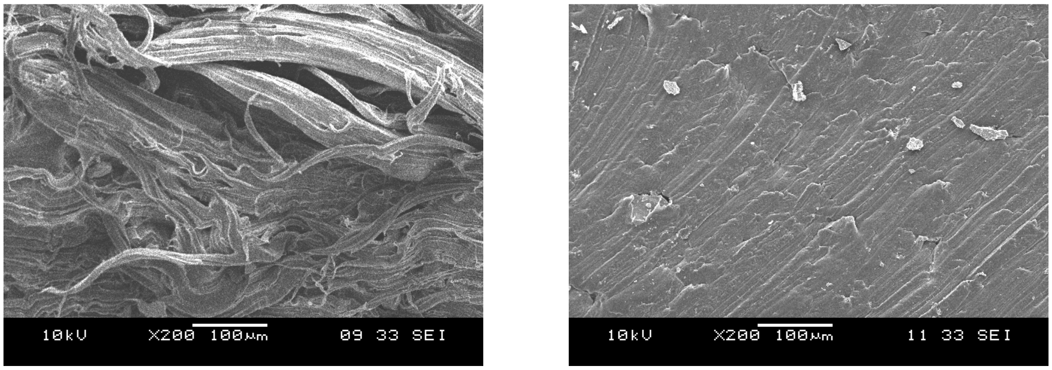
3.5 Scanning Electron Microscopy

Scanning electron microscopic analysis reveals the surface morphology of the uncompatibilized and compatibilized composites. Figure 7 shows the tensile fracture surface of rHDPE/EVA/ESP and rHDPE/EVA/ESP$_{\text{PVC-MA}}$ composites at different filler loading. The uncompatibilized composites present broad interfaces between both components of the composite, characterized by the holes around the fillers and the holes left by them by pull out when the specimens were assayed. Filler pull-out could act as initial flaws leading to localized stress concentration during deformation, finally premature failure of composites occurs and decreases the tensile strength. This result is consistent with a low adhesion of the polymer matrix on the surface of the fillers due to the low compatibility [26]. Figures 7(b), 7(d) and 7(f) show homogenous materials characterized by a well dispersed reinforcement inside the polymer matrix and by the absence of holes between the matrix and the fillers. This result clearly demonstrated that the compatibilization of the composites provided strong interfacial adhesion and good wetting. The improved interfacial adhesion attributed to the strong chemical interaction between the rHDPE/EVA matrix and PVC-MA and to the strong physical interaction between the PVC and the acetate group of EVA, and the vinyl group of PVC with the long chain of rHDPE. When the coupling agent was situated at the interface between the matrices and interacted with both, the interfacial tension was reduced and compatibility was increased.

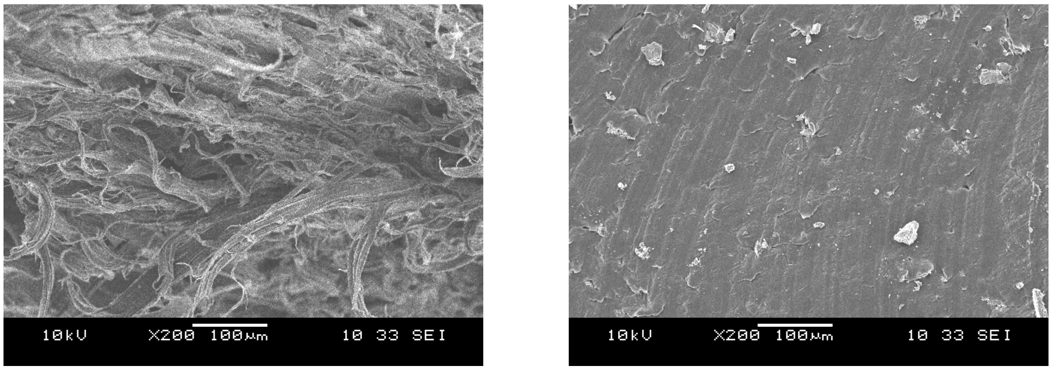


(a) rHDPE/EVA/ESP5

(b) rHDPE/EVA/ESP5$_{\text{PVC-MA}}$



(c) rHDPE/EVA/ESP15 (d) rHDPE/EVA/ESP15$_{PVC-MA}$



(e) rHDPE/EVA/ESP25 (f) rHDPE/EVA/ESP25$_{PVC-MA}$

Figure 7: SEM micrograph of tensile fracture surface of (a) rHDPE/EVA/ESP5, (b) rHDPE/EVA/ESP5$_{PVC-MA}$, (c) rHDPE/EVA/ESP15, (d) rHDPE/EVA/ESP15$_{PVC-MA}$, (e) rHDPE/EVA/ESP25, and (f) rHDPE/EVA/ESP25$_{PVC-MA}$ composites

4.0 CONCLUSSION

The investigation on the effect compatibilizer PVC-MA on the properties of rHDPE/EVA/ESP composites was done in this study. PVC-MA was used as the compatibilizer for rHDPE and EVA matrix filled with ESP filler. The addition of PVC-MA 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/ESP$_{PVC-MA}$ composites as compared to rHDPE/EVA/ESP composites. The rHDPE/EVA/ESP$_{PVC-MA}$ composites exhibited better interfacial adhesion between the filler and matrices than the rHDPE/EVA/ESP composites as observed from the morphological studies.

REFERENCES

[1] Azman Hassan, A. Akbari, N.K. Hing, C.T. Ratnam, Mechanical and Thermal Properties of ABS/PVC Composites: Effect of Particles Size and Surface Treatment of Ground Calcium Carbonate, Polymer-Plastics Technology and Engineering 51 (5) (2012) 473-479.

[2] J.Z. Liang, F. Wang, Flexural and Impact Properties of POM/EVA/HDPE Blends and POM/EVA/HDPE/nano-$CaCO_3$ Composites, Polymer Bulletin 72 (4) (2015) 915-929.

[3] Y. Chen, H. Zou, M. Liang, Y. Cao, Melting and crystallization behavior of partially miscible high density polyethylene/ethylene vinyl acetate copolymer (HDPE/EVA) blends, Thermochimica Acta 586 (2014) 1-8.

[4] C. Lia, Q. Kong, J. Zhao, D. Zhao, Q. Fan, Y. Xia, Crystallization of partially miscible linear low-density polyethylene/poly(ethylene-co-vinylacetate) blends, Materials Letters 58 (27-28) (2004) 3613-3617.

[5] M.A. Paula, M. Alexandrea, P. Degéea, C. Henrist, André Rulmont, Philippe Dubois, New Nanocomposites Materials Based on Plasticized Poly (L-lactide) and Organo-modified Montmorillonites: Thermal and Morphological Study, Polymer 44 (2) (2003) 443-450.

[6] J. Jancar, E. Fekete, P.R. Hornsby, B. Pukánszky, R.N. Rothon, Mineral fillers in thermoplastics I: Raw Materials and Processing, Advances in Polymer Science, first ed., Springer-Verlag Berlin Heidelberg, 1999, pp. XI-233.

[7] G.C. Psarras, E. Manolakaki, G.M. Tsangaris, Electrical relaxations in polymeric particulate composites of epoxy resin and metal particles, Composites - Part A: Applied Science and Manufacturing, 33 (3) (2002) 375–384.

[8] Siti Shuhadah, A.G. Supri, LDPE-Isophthalic Acid Modified Egg Shell Powder Composites (LDPE/ESP_I), Journal of Physical Science 20 (1) (2009) 87–98.

[9] A.A. Hussein, R.D. Salim, A.A. Sultan, Water absorption and mechanical properties of high-density polyethylene/egg shell composite, Journal of Basrah Researches ((Sciences)) 37 (3A) (2011) 36–42.

[10] R.A. Ghani, M.H. Abidin, A.Z. Romli, The tensile and impact testing on low loading chicken eggshell filled epoxy composite, in: Malaysia Poly International Conference, 2009, pp. 117–124.

[11] G. Ji, H. Zhu, A. Chenze Qi, M. Zeng, Mechanism of interactions of eggshell microparticles with epoxy resins, Polymer Engineering & Science 49 (7) (2009) 1383–1388.

[12] P. Toro, R.Quijada, M. Yazdani-Pedram, J.L. Arias, Eggshell, a new bio-filler for polypropylene composites, Materials Letters 61 (22) (2007) 4347–4350.

[13] P. Toro, R. Quijada, J.L. Arias, M. Yazdani-Pedram, Mechanical and Morphological studies of poly(propylene)-filled eggshell composites, Macromolecular Materials and Engineering, 292 (9) (2007) 1027–1034.

[14] Z. Lin, Z. Zhang, K. Mai, Preparation and properties of eggshell/β-polypropylene bio-composites, Journal of Applied Polymer Science 125 (1) (2012) 61–66.

[15] A.G. Supri, H. Ismail, S. Shuhadah, Effect of Polyethylene-Grafted Maleic Anhydride (PE-g-MAH) on Properties of Low Density Polyethylene/Eggshell Powder (LDPE/ESP) Composites, Polymer-Plastics Technology and Engineering 49 (4) (2010) 347–353.

[16] A.G. Supri, C.Y. Heah, Conductive polymer based on polyaniline-eggshell powder (PANI-ESP) composites, Journal of Physical Science 21 (2) (2010) 81–97.

[17] S. Mishraa, G.B. Perumal, J.B. Naika, Studies on mechanical properties of polyvinyl chloride composites, Polymer-Plastics Technology and Engineering 36 (4) (1997) 489–500.

[18] K. Prempheta, P. Horanont, Improving performance of polypropylene through combined used of calcium carbonate and metallocene-produced impact modifier, Polymer-Plastics Technology and Engineering 40 (3) (2001) 235–247.

[19] H.Q. Honga, H. He, D.M. Jia, C. Ding, Y.P. Huang, F. Xuea, Influences of ternary graft copolymers on the morphology and properties of polypropylene/calcium carbonate composites, Polymer-Plastics Technology and Engineering 45 (3) (2006) 379–387.

[20] N. Chen, C. Wan, Y. Zhang, Y. Zhang, Effect of nano-CaCO3 on mechanical properties of PVC and PVC/Blendex blend, Polymer Testing 23 (2) (2004) 169–174.

[21] Y.L. Yang, S.L. Bai, C. G'Sell, J.M. Hiver, Mechanical properties and volume dilatation of HDPE/$CaCO_3$ blends with and without impact modifier, Polymer Engineering & Science 46 (11) (2006) 1512–1522.

[22] C. Pattanakul, S. Selke, C.L. And, J. Miltz, Properties of recycled high density polyethylene from milk bottles, Journal of Applied Polymer Science 43 (11) (1991) 2147–2150.

[23] D. Hammiche, A. Boukerrou, H. Djidjelli, A. Djerrada, Effects of some PVC-grafted maleic anhydrides (PVC-g-MAs) on the morphology, and the mechanical and thermal properties of (alfa fiber)-reinforced PVC composites, Journal of Vinyl and Additive Technology 19 (4) (2013) 225–232.

[24] H. Ismail, Supri, A.M.M. Yusof, Blend of waste poly(vinylchloride) (PVCw)/acrylonitrile butadiene-rubber (NBR): the effect of maleic anhydride (MAH), Polymer Testing, 23 (6) (2004) 675–683.

[25] S. Marais, E. Bureau, F. Gouanvé, E. Ben Salem, Y. Hirata, A. Andrio, C. Cabot, H. Atmani, Transport of water and gases through EVA/PVC blend films—permeation and DSC investigations, Polymer Testing 23 (4) (2004) 475–486.

[26] A.I. Vicente, J. Campos, J.M. Bordado, M. Rosario Ribeiro, Maleic anhydride modified ethylene-diene copolymers: Synthesis and properties, Reactive and Functional Polymers, 68 (2) (2008) 519–526.