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Poly(ethylene-co-vinylacetate) Copolymer Based Nanocomposites: A Review

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Abstract. Nowadays, there is huge demand for novel materials which are desired for new functions and new technological advancements. All technological demands for new applications cannot be implemented by many of the well-established materials, such as single plastics, metals or ceramics. Hence, engineers and scientists realized that, in comparison with pristine counterparts of material, the mixtures of materials can produce much better properties. Polymer nanocomposites is a new form of materials that resulted by the combination of polymers and nanofillers which contributed to various benefits over the neat polymer such as improvement in biocompatibility, biostability, thermal stability, flame retardancy, mechanical and barrier properties. Due to these factors, nanocomposites have received an extraordinary consideration for use in broad range of applications. However, the polymer nanocomposites which comprised of copolymer as matrix material are not widely studied, especially those involved poly(ethylene-co-vinyl acetate) (PEVA). The production of PEVA copolymer-based nanocomposites for various applications has been reported by few research papers. In this communication, a review on the properties of PEVA-based nanocomposites with different types of nanofiller was summarized, revealing the high potential of this class of nanocomposite for advanced applications.

1. Introduction

Polymer nanocomposites are polymer matrices which contain homogeneous nanoscopic structure of an organic or inorganic filler, having normally 10-100 nm in at least one of its dimension, prepared by chemical polymerizing technologies or physical blending technique in order to enhance and achieve high performance properties [1,2]. As compared to conventional polymer composites, polymer nanocomposites have several advantages. The nano-size filler provides greater surface area, mobility and dispersion ability to allow more significant improvement in tensile strength, modulus, thermal stability, heat distortion temperature, barrier properties, biodegradability and flame resistant of polymers. Polymer matrix nanocomposites are widely applied in several industries due to their ease of processing, lightweight and good specific strength and toughness [1-3].

The properties of the polymer nanocomposites can be tailored to meet the requirements of certain applications by manipulating several aspects such as the types of polymer matrix, nano-scale filler (nanofiller) and processing conditions [2, 3]. Generally, polyethylene (PE), polypropylene (PP), poly (vinyl chloride) (PVC), polystyrene (PS), epoxy, nylon6, nylon 11 and polyacrylonitrile (PAN) are among the most common examples of homopolymers that widely used as matrix material in the formation of polymer nanocomposites [1-3]. As opposed to the homopolymer matrix, the use of copolymer type matrix to form nanocomposite is rare, due to the complexity of the resultant 'copolymer nanocomposite' structure that require further study and understanding on structure-processing-properties aspect [4]. In the following section, we have summarized the findings from previous studies specifically devoted to copolymer based nanocomposites.

2. Copolymer Based Nanocomposites

Copolymer is defined as polymer that produced from two or more different monomers combined together through copolymerization process. The combination of copolymer and nanofiller materials will produce the copolymer based nanocomposites. The copolymer generally has combination properties of the two monomers used to form it. These properties are useful to meet certain targeted properties requirement, therefore the use of copolymer other than homopolymer can provide greater prospect for broader applications. Furthermore, the copolymer based nanocomposites are more promising for biomedical applications such as biomedical implant and tissue engineering. The addition of low nanofiller loading can give the positive impact to the host copolymer behaviour due to the larger surface area of nanofiller which allows a good matrix-filler interaction. Research by Helal et al. proved that the dielectric breakdown strength of two different copolymers (SEBS grafted with maleic anhydride and polystyrene-b-poly(ethylene-co-butylene)-b-polystyrene (SEBS)) can be improved through incorporation of nanoclay due to the good nanoclay/polymer interfacial bonding. Both copolymer nanocomposites achieved the maximum state of dispersion at a clay loading of 5wt%, where optimum matrix-filler interactions led to the highest achievement in interfacial polarization but lowest value in dynamic mechanical damping factor [5]. Verma et al. reported that multiwall carbon nanotube (MWCNT) content affects the crystallization process of the polypropylene random copolymer (PPCP) under isothermal conditions. Crystallization temperature was found to be increased under dynamic conditions which confirmed the nucleating effect of MWCNT on crystallization of the PPCP. The finding was also corroborated by crystallization studies under isothermal conditions [6].

Hellati et al. investigated the effects of a styrene–ethylene/butylene–styrene block copolymer grafted with maleic anhydride (SEBS–MAH) compatibilizer on the micromechanical properties and structure of PET/isotactic PP and PET/HDPE blends implanted with organoclay [7]. They found that the hardness of the nanocomposite increased in the presence of the compatibilizer. Cui, Ma and Paul reported that strong connections of the polymer chains with the inorganic substrate occur when random ethylene–propylene copolymer (EPM) functionalized with embed diethyl succinate groups was melt blended with up to 20 wt% amount of organophilic montmorillonite (OMMT) to form the EPM nanocomposite [8]. Yonekura and Wakayama investigated the self-assembled block copolymer-based nanocomposites structures induced by magnetic field. They have introduced an impact route to manufacture the nanocomposites materials in highly efficient and also precise manner, which can improve the material properties of the nanocomposites [9].

Research by Sciancalepore, et al. highlighted the possibility to obtain the 'true' nanocomposites by direct insertion of pre-synthesized oleic acid capped TiO2 nanorods into the functionalized poly(methyl methacrylate) copolymers. The copolymer nanocomposite showed high optical transparency in the visible region, even at high TiO2 nanorod content [10]. Yilmaz et al. prepared the MMT/poly(BA-co-MMA) by dispersing organo-MMT straight into monomers using usual emulsion polymerization [11]. The results were convincing however final polymer nanocomposites had a solid content lower than 25 wt%. This causes higher increments of barrier, thermal, mechanical and glossiness properties for coating applications [11]. Pradhan et al. produced SBR copolymer nanocomposite incorporating hybrid multiwalled carbon nanotube (MWCNT) and MMT fillers in different weight ratios of MMT to MWCNT (10 : 1, 6 : 1, 3 : 1, 1 : 1, and 1 : 3). The effectiveness of carbon nanotubes and clay platelets in reinforcing the SBR nanocomposites was examined. The tensile strength of the SBR containing 1% w/ w of the MMT/MWCNT (1 : 1) hybrid was enhanced by 215%, where the SBR filled with MMT or MWCNT single-handedly showed an enhancement of 46% and 25%, respectively [12].

3. Poly(ethylene-co-vinyl acetate) Nanocomposites

Poly(ethylene-co-vinyl acetate (PEVA) is a copolymer from vinyl acetate and ethene monomers. PEVA is synthesized via ethylene and vinyl acetate copolymerization through bulk polymerization technique and also by high temperature and pressure. Figure 1 shows the monomer used for copolymerization of PEVA and the structure of the PEVA copolymer, where m and n is repeating unit [13].

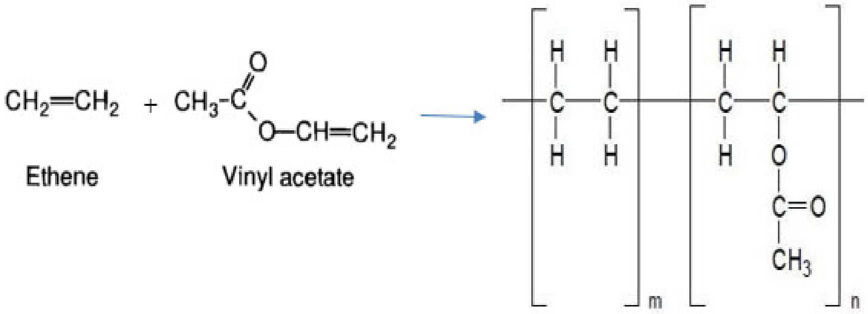

Figure 1: Monomer and structure of Poly(ethylene-co-vinyl acetate (PEVA) copolymer

The PEVA is catogerized as random copolymer. It has excellent mechanical properties, ozone resistance and weather resistance. Furthermore, it is versatile and low cost material [13, 14]. EVA possess thermoplastic characteristics, which means it can be easily moulded and processed by conventional industrial method such as calendaring, injection, extrusion, blow moulding and rotational moulding. The properties of PEVA are close to elastomeric materials in flexibility and softness. Thus, its properties are intermediate between vinyl and rubber products. In electrical applications, PEVA copolymers are among the vital engineering polymers for use as cable insulation, wire, packaging, carpet and hot melt adhesives. PEVA is a widely used material, specifically as zero-halogen stuff in the cable industry. It is often added with greater quantities of inorganic filler material, such as aluminium trihydroxide (ATH). PEVA shows a good resistance to UV radiation. Further, it has a good clarity [14]

The main advantage of this copolymer is the prospect to attain a broad range of properties by altering the vinyl acetate (VA) content in its composition. Therefore, it is probable to broaden their applications from rigid plastic to the rubber like/elastic products [13, 14]. Vinyl acetate ratio governs the crystallinity of the PEVA, which controls the properties of the resultant PEVA. The properties of PEVA depend on the molecular weight and VA content. When VA content is greater, PEVA copolymer with higher polarity, lower crystallinity, better flexibility, better adhesion strength and clarity is obtained [13]. PEVA copolymers with superior properties were employed in various applications such as adhesive, photovoltaic encapsulants, cable, flexible packaging wire, tube, hose and biomedical / drug delivery devices [14, 15]. The copolymers are also used for sport applications such as ski boots, waterski boots and mixed martial parts [15].

While a large body of research concerning polymer nanocomposites exists, the number of studies specifically devoted to ethylene vinyl acetate (EVA) nanocomposite is relatively small [4, 13]. The use of PEVA copolymer as the nanocomposite matrix presents some interesting challenges to understand the complex morphology of the PEVA, due to existence of semicrystalline, non-polar polyethylene (PE) and amorphous, polar poly(vinyl acetate) (PVA) structure [13, 14]. Ugel et al. investigated the consequence of nanoclay addition on the properties of PEVA nanocomposites as new material for film packaging applications. They studied the effect of compatibilising agents and clay nature on mechanical, thermal and morphological properties of this material and found the benefits of using nanoclay and compatibilizer to improve both mechanical and thermal properties of the nanocomposite [16].

Our research group has published several papers regarding the PEVA nancomposites [17-21]. Our findings indicate that PEVA-based nanocomposites have potential to be further developed for biomedical applications as their flexibility, thermal properties, biostability and biocompatibility can be further enhanced by the incorporation of organically modified montmorillonite (OMMT) [18, 20]. The study on the exfoliation strategy of the OMMT through pre-dispersing technique shows that high level of OMMT exfoliation improved the matrix-nanofiller interface bonding through polar-polar interactions and non-polar-non-polar interactions (see figure 2). Improved matrix-nanofiller interactions resulted in reduced cytotoxicity level and also enhanced tensile strength, toughness, thermal stability and biostability of the PEVA nanocomposite upon the in vitro exposure [19, 20]. The softness and flexibility of the copolymer is good for intimate contact with human soft tissues, while enhancement in biostability and toughness is vital to prolong its life period for implantable device's insulation material [20]. Our researches also suggest the potential of using the hybrid O-MMT/Bentonite nanofillers for "biostability enhancement" of the PEVA and reducing the cost of the nanocomposite production by adding cheaper natural bentonite as co-nanofiller with the OMMT [17, 21]. Results show that the addition of OMMT2.75/Bent0.25 hybrid nanofillers can lower the degradation of the EVA copolymer under physiological fluid environment. The obtained nanocomposite material have achieved the best retention in thermal and tensile properties upon 4 weeks exposure in the in-vitro physiological fluid [17]. Our most recent publication reported that the 'destabilized' bentonite prepared by the combination of pH control and salt addition is most efficient in reinforcing the PEVA matrix when combined with the OMMT by allowing most significant improvement in toughness, tensile strength and elongation at break values. This could be related to the improved dispersion of bentonite upon the destabilization process that allows greater matrix-filler interactions in the nanocomposite system [21].

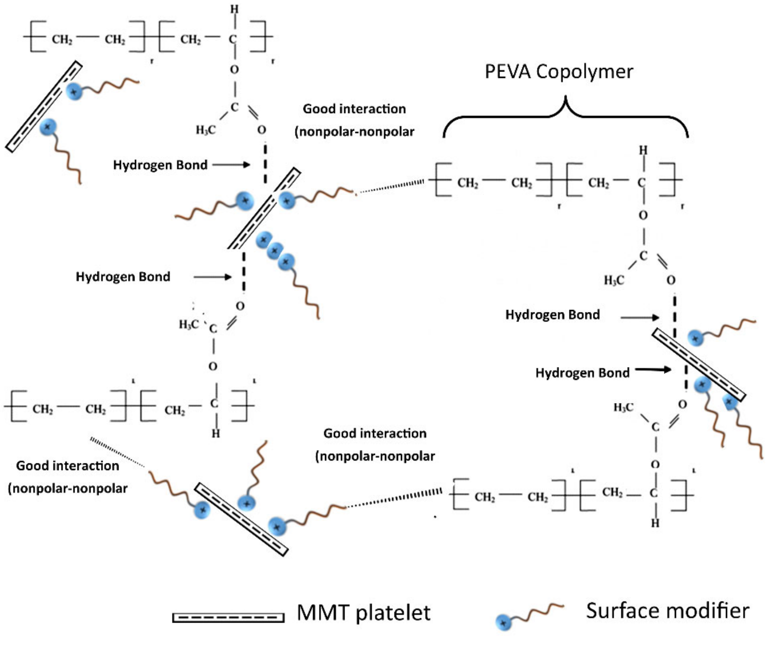

Figure 2. Good matrix-nanofiller interactions in the PEVA nanocomposite system with well-dispersed organically surface modified montmorillonite (OMMT)

Research on PEVA nancomposite was also performed by several other research groups. Shi et al. studied the ways to enhance flame retardancy of the PEVA copolymers. Masterbatch process was done to produce exfoliated EVA/silicate nanocomposites. The cationic surface modifier was used to modify the silicate surface to improve the nanofiller compatibility with the PEVA copolymer containing 39 wt% vinyl acetate (VA). Strong electrostatic interactions between the copolymer with the anionic silicate surface makes the nanocomposite completely exfoliated and eventually exhibits improvement in its flame retardancy [22]. Lee et al. prepared the PEVA copolymer with 40 wt.% vinyl acetate content (EVA40)/ organoclay nanocomposites using melt intercalation method with different clay concentrations (2.5, 5.0, 7.5, and 10.0 wt%). Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis proved the production of the exfoliated nanocomposite [23]. Peeterbroeck et al. used melt blending technique to prepare nanocomposites based on various (organo-modified) clays and an PEVA copolymer matrix (27 wt% vinyl acetate). The obtained result showed that tensile and nanostructure properties are majorly depends on the character of the organic modifier while the setback in thermal volatilisation of the PEVA during thermo-oxidation is majorly caused by the character of the clay (mainly its aspect ratio), with no considerable influence of the nanostructure of the nature of the organic modifier [24]. Wilson et al., (2012) have performed the research on the gas-transport properties of EVA/clay nanocomposite membranes. According to the authors, well dispersed nanoparticles was obtained when 3wt% of nanoclay was incorporated into the PEVA matrix, where nanocomposite with good barrier properties was obtained. However, agglomeration of nanoparticles happened at higher clay loadings [25]. Gupta et al. investigated the effects of organobentonite morphology/structure and loading on the rheological properties of PEVA nanocomposites when the PEVA copolymer containing 28% of vinyl acetate (PEVA28) was used as matrix. PEVA28 nanocomposites shear viscocity was found to significantly increase as well as the storage and loss moduli although complete exfoliation was not achieved [26]. Çağlayan and Güven have investigated the effect of radiation assisted modified clay on the morphology, tensile and thermal properties of PEVA nanocomposites produced by melt blending process. The PEVA copolymer with 18% VAc was used as matrix while Na-MMT (commercial organomodified clay) and Na-MMT (modified with charged monomer (METMAC) by in-situ radiation polymerization) were used as nanofiller. After modification, maximum opening between silicate layers was 2.29 nm obtained for 30 kGy irradiated sample. Based on TEM and XRD analyses, nanocomposites prepared by using commercially available organomodified clays exhibit intercalated structures, while the nanocomposites based on radiation modified clays exhibit both intercalated and exfoliated structures. The improvement in mechanical as well as thermal properties was greater in the PEVA nancomposite sample containing the radiation assisted modified Na-MMT.

4. Conclusion

The above short review highlights the promising properties of the PEVA copolymer-based nanocomposites for use in various applications. The clever introduction of nanofillers into this multiphase copolymer morphology can ensure the success of obtaining the desired PEVA nanocomposite property profile. In conjunction with this, the level of interaction between the nanofiller-PEVA copolymer has to be characterized and understood, so that the correct nanofiller type, loading, processing parameters and etc. can be chosen to produce an optimized nanocomposite system. The degree of nanofiller dispersion affects the mechanical and thermal performance of the resulting PEVA nanocomposite. The well dispersed nanofiller such as nanoclays can result in greater tensile strength, toughness, thermal stability biostability and flame retardancy of the PEVA nanocomposite. These improvements are beneficial for PEVA nanocomposite intended for use in advanced applications such as biomedical implant, drug delivery and electronic packaging.

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References

[1] Bhattacharya M 2016 *Materials* **9** 262
[2] Zaferani S H 2018 *Polymer-based Nanocomposites for Energy and Environmental Applications* p. 1-25
[3] Kotal M and Bhowmick A K 2015 *Prog. Polym. Sci.* **51** 127–187
[4] Feldman D 2016 *J. Macromol. Sci. A* **53** 651–658
[5] Helal E, Demarquette N R, Amurin L G, David E, Carastan D J and Fréchette M 2015 *Polymer* **64** 139-152
[6] Verma P and Choudhary V 2015 *J. Appl. Polym. Sci.* 132
[7] Hellati A, Benachour D, Cagiao M E, Boufassa S and Baltá Calleja F J 2010 *J. Appl. Polym. Sci.***118** 1278-1287
[8] Cui L, Ma X and Paul D R 2007 *Polymer* **48** 6325-6339
[9] Yonekura H and Wakayama H 2017 *Intermetallics* **85** 125-129
[10] Sciancalepore C, Cassano T, Curri M L, Mecerreyes D, Valentini A, Agostiano A, Tommasi R and Striccoli M 2008 *Nanotechnology* **19** 205705
[11] Yilmaz O, Cheaburu C N, Durraccio D, Gulumser G and Vasile C 2010 *App. Clay Sci.* **49** 288-297
[12] Pradhan B, Roy S, Srivastava S K and Saxena A 2015 *J. Appl. Polym. Sci.* **132** 41818–41829
[13] Osman A F, Fitri T F M, Abdul Hamid A R, Hashim F, Rakibuddin M and Alakrach A M 2019 *Processing and Characterization of Multicomponent Polymer Systems: New Insights, , editor: Jose James, Sabu Thomas, Nandakumar Kalarikkal, Yang Weimin, Kaushik Pal, Apple Academic Press, Florida, USA* p. 3-41
[14] Fink J K 2010 *Handbook of engineering and specialty thermoplastics: polyolefins and styrenics, Wiley, Hoboken* 101
[15] Fink J K 2010 *John Wiley & Sons*
[16] Ugel E, Giuliano G and Modesti M 2011 *Soft Nanoscience Letters* **1** 105-119
[17] Osman A F, Hamid A R A, Rakibuddin M, Weng G K, Ananthakrishnan R, Ghani S A 2017 *J. App. Polym. Sci.* 134 44640
[18] Osman A F, Alakrach A M, Kalo H, Azmi W N W and Hashim F 2015 *RSC Adv.* **5** 31485–31495
[19] Osman A F, Kalo H, Hassan M S, Hong T W, Azmi F 2016 *J. App. Polym. Sci.* **133** 43204-43220
[20] Osman A F, Fitri T F M, Rakibuddin M, Hashim F, Johari S A T T and Ananthakrishnan R 2017 *Mater. Sci. Eng. C.* **74** 194–206
[21] Fauzi A A A, Osman A F, Abdullah M A A, Mandal S Ananthakrishan R 2019 *J. Vinyl Addit. Techn.* **25** 396–411
[22] Shi Y, Kashiwagi T, Walters R N, Gilman J W, Lyon R E and Sogah D Y 2009 *Polymer* **50** 3478-3487
[23] Lee H M, Park B J, Choi H J, Gupta R K and Bhattachary S N 2007 *J. Macromolecular Sci. Part B: Physics* **46** 261-273
[24] Peeterbroeck S, Alexandre M, Jérôme R and Dubois P 2005 *Polymer Degradation and Stability* **90** 288-294
[25] Wilson R, Plivelic T S, Aprem A S, Ranganathaiagh C, Kumar S A and Thomas S 2012 *J. App. Polym. Sci.* **123** 3806-3818
[26] Gupta R K, Pasanovic-Zujo V and Bhattacharya S N 2005 *J. Non-Newtonian Fluid Mechanics* **128** 116-125