MECHANICAL AND THERMAL PROPERTIES OF POLY(METHYL METHACRYLATE)-GRAFTED-OIL PALM EMPTY FRUIT BUNCH /TALC HYBRID FILLED POLY(VINYL CHLORIDE) COMPOSITES

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For my beloved ayah, ibu, kak yong, abg ngah, adik and al hafiz who have been supporting me all this time…..

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ABSTRACT

The aim of this study is to investigate the mechanical and thermal properties of single and hybrid fillers filled poly(vinyl chloride) (PVC) composites. Graft copolymerization of poly(methyl methacrylate) (PMMA) onto oil palm empty fruit bunch (OPEFB) was carried out under nitrogen environment using the free radical initiation technique. Soxhlet extraction was used to remove the PMMA homopolymer from the grafted copolymer. The presence of PMMA functional groups in Fourier transform infra red (FTIR) spectra of grafted OPEFB at peak around 1730 cm^{-1} proved that grafting process was successfully done. The single fillers (grafted OPEFB, ungrafted OPEFB and talc) and hybrid fillers (grafted OPEFB/talc and ungrafted OPEFB/talc) loadings from 0 to 20 phr were pre-mixed with PVC using a high speed mixer. Methyl butadiene styrene (MBS) impact modifier was also added at 10 phr for the impact strength study. The dried blend formulations were milled into sheets using a two roll mill at 170 °C and then hot pressed at 190 °C. The tensile, flexural, impact strength and elongation at break of hybrid composites decreased as the filler content increased. Both, the tensile and flexural modulus of the hybrid composites are increased tremendously compared to the single composites. Adding MBS increased the impact strength of the single and hybrid composites. Differences in surface morphology between the grafted and ungrafted OPEFB were observed. The glass transition temperature (T_g) of the hybrid composites shifted to higher temperature compared to single composites. The storage modulus of talc filled PVC showed the highest storage modulus compared to other composites. Hybrid PVC composites had better thermal stability than single composites. The increase of water resistance of the hybrid composites proved good filler-matrix interaction. Overall, the study showed that the hybrid PVC composites had good mechanical and thermal properties compared to the single filler PVC composites.

ABSTRAK

Tujuan kajian ini adalah untuk mengkaji sifat-sifat mekanikal dan terma komposit poli(vinil klorida) (PVC) berpengisi tunggal dan hibrid. Pempolimeran cangkukan poli(metil metakrilat) (PMMA) ke atas tandan kosong buah kelapa sawit (OPEFB) telah dijalankan dalam keadaan nitrogen dengan menggunakan teknik permulaan radikal bebas. Penyarian Soxhlet digunakan untuk membuang homopolimer PMMA. Kehadiran kumpulan berfungsi PMMA pada spektra infra merah transformasi Fourier (FTIR) OPEFB tercangkuk sekitar 1730 cm^{-1} membuktikan cangkukan telah berjaya dilakukan. Kandungan pengisi tunggal (pengcangkukan OPEFB, tanpa pengcangkukan OPEFB dan talkum) dan hibrid (pengcangkukan OPEFB/talkum dan tanpa pengcangkukan OPEFB/talkum) dari 0 sehingga 20 phr telah dicampurkan dengan PVC menggunakan pengisar berkelajuan tinggi. Pengubahsuai impak metil butadiena stirena (MBS) dicampur sebanyak 10 phr bagi kajian kekuatan hentaman. Campuran formulasi adunan kering kemudiannya dijadikan kepingan menggunakan pengguling berkembar pada suhu 170 °C dan dimampatkan pada 190 °C. Kekuatan tegangan, lenturan dan hentaman komposit PVC berpengisi hibrid menurun dengan pertambahan kandungan pengisi. Kedua-dua, modulus tegangan dan lenturan komposit hibrid meningkat berbanding komposit tunggal. MBS meningkatkan kekuatan hentaman komposit berpengisi tunggal dan hibrid. Perbezaan morfologi permukaan antara OPEFB cangkukan dan tanpa cangkukan OPEFB telah diperhatikan. Suhu peralihan kaca (T_g) komposit hibrid meningkat berbanding komposit tunggal. Modulus simpanan menunjukkan PVC berpengisi talkum mempunyai nilai modulus simpanan yang tertinggi. Hibrid pengisi menunjukkan kestabilan terma yang lebih baik berbanding komposit berpengisi tunggal. Peningkatan rintangan air komposit berpengisi hibrid membuktikan interaksi yang baik antara pengisi-matrik. Secara keseluruhannya, kajian menunjukkan bahawa komposit PVC berpengisi hibrid menunjukan sifat-sifat mekanikal dan terma yang lebih baik berbanding komposit PVC berpengisi tunggal.

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LIST OF ABBREVIATIONS

$CaCO_3$	-	Calcium carbonate
Fe^{2+}	-	Ferrous ion
FTIR	-	Fourier transformed infrared
g	-	Grafted
GE	-	Grafting efficiency
H_2O_2	-	Hydrogen peroxide
Mg	-	Magnesium
MgO	-	Magnesium oxide
MMA	-	Methyl methacrylate
NH_4	-	Ammonium
OPEFB	-	Oil palm empty fruit bunch
PG	-	Percentage of grafting
phr	-	Part per hundred resins
PMMA	-	Poly(methyl methacrylate)
SiO_2	-	Silica
Tg	-	Glass transition temperature
ZnO	-	Zinc oxide

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

PVC resin has become one of the major components for polymer composites manufacturing especially for construction parts, pipes, hoses, electric cables, and packaging material. PVC offers several unique properties and advantages which include excellent chemical and weathering properties, nonflammable, and also cheaper compared to other plastics (Abu Bakar *et al.*, 2008). PVC resin can be made into products with a wide range of properties from soft and flexible to light and rigid by the addition of additives. Other ingredients must typically be added to convert PVC into a finished product. Another ways to improve the PVC properties is by introducing the organic and inorganic fillers.

Natural fiber as organic filler or reinforcement into thermoplastic has attracted many researchers since natural fiber showed an excellent alternative of filler into plastic industry. According to Stokke (2002), the demand of natural fillers for plastic composite applications will grow at least six-fold in the next 5 to 7 years. There are many types of natural fiber that have been introduced as filler in PVC such as wood flour (Mengeloglu *et al.*, 2000, Sombatsompop *et al.*, 2003, Jiang *et al.*, 2004 and Zhoa *et al.*, 2006), rice straw (Kamel, 2004), sugarcane bagasse (Zheng *et al.*, 2007), rice husk (Sivaneswaran, 2002) and pineapple leaf (Mohanty *et al.*, 2000).

Oil Palm Empty Fruit Bunch (OPEFB) fiber is one of the applied natural fibers to be used as reinforcing filler in polymer composite. OPEFB consists of three main parts; hemicelluloses, cellulose and lignin which known as lignocellulosic (Hassan *et al.*, 2010). The seed oil from the oil palm is being extracted and the waste materials after the extraction are known as OPEFB. OPEFB is generally used as mulch for oil palms, converted to bunch ashes or discarded as waste.

The by-product from the palm oil, OPEFB has now become commercially used in Malaysia and also other countries in Asia since OPEFB has been planted in large amount. In order to minimize the abundance of this industrial waste, new applications are required for OPEFB to be more useful. Therefore, due to its low cost and availability factors, OPEFB has been utilized as fillers in many polymer composite technologies. Hence, OPEFB is selected as filler into the polymer composites due to the several benefits offered by this organic material such as less abrasiveness to equipment, low density, low cost, environmentally friendly and biodegradable (Raju *et al.*, 2008).

OPEFB has been used extensively as filler in the polymer composites. Many studies have been conducted on OPEFB filled thermoplastics polymer such as polypropylene (Rozman *et al.*, 2000 & 2001 and Khalid *et al.*, 2008), polyurethane (Rozman *et al.*, 2001 & 2002 and Badri *et al.*, 2002 & 2007), polyesters (Hill and Khalil, 2000 and Khalil *et al.*, 2007 & 2008) and others. However, there were limited studies that have been done on OPEFB filled PVC composites (Abu Bakar *et al.*, 2005a, 2005b & 2010). Most of these researchers focused on the effect of fiber loading on the mechanical behavior.

Abu Bakar *et al.* (2005a and 2005b) showed that there are new trends in PVC composite technology by adding OPEFB as filler. In these researches it has been reported that upon increasing of OPEFB fillers loading, the impact strength of composites decreased linearly. The reasons of the low strength properties were due to the poor adhesion and/or dispersion of OPEFB due to the incompatibility between hydrophobic of the polymer and hydrophilic OPEFB during mixing.

Thus, modification has to be done onto the surface of the natural fiber to increase the compatibility of phases between the thermoplastics and natural fiber. Previous studies have reported that a grafting technique can be used to overcome this problem. OPEFB may be grafted with various types of polymers which includes poly (butyl acrylate) (PBA), poly (methyl methacrylate) (PMMA) and poly (acrylamide) (PAM) (Das *et al.*, 1999). This hydrophobic property exhibits solubility similarities with most thermoplastic matrix and expects to allow the grafted copolymer to improve the interaction between thermoplastic matrix and OPEFB.

In accordance, the copolymer grafting technique has been widely used and becoming more popular currently (Prasanth *et al.*, 2005). PMMA which consists of carbonyl compound has good compatibility with PVC (CHCl) due to the hydrogen bonding (Chen *et al.*, 2006). Abu Bakar *et al.* (2008) found and reported that PMMA has successfully been grafted onto OPEFB by using the optimum conditions. The percentage of grafting that has been achieved by using these optimum conditions was 173%.

Recently, there was a study conducted in comparing between the loading of 20 phr of ungrafted and grafted OPEFB fiber filled PVC composite. The elongation at break and tensile strength increased while the stiffness (Young's modulus) of the composites was decreased (Abu Bakar *et al.*, 2010). Kee (2010), showed that the incorporation of the same loading amount (20 phr) of grafted and ungrafted OPEFB has reduced the impact strength of the composites. For the flexural testing, ungrafted OPEFB filled PVC reduced the flexural strength while grafted OPEFB composites showed otherwise results. The Young's modulus showed the same trend from the previous study done by Abu Bakar *et al.* (2010) where the stiffness of the composites of grafted OPEFB decreased compared to the ungrafted OPEFB.

Inorganic fillers are being used extensively in thermoplastics such as polyethylene, polypropylene, nylon and also poly(vinyl chloride) To improve the applicability of the PVC composites, the composite should achieve good combination properties, therefore many types of inorganic filler are being introduced into PVC such as glass fibers, calcium carbonate and talc (Wiebking, 1986 and Xie

et al., 2001). Inorganic fillers play an important role to improve and enhance the Young's modulus of the PVC composites.

Talc is a natural product that is widely used in industry. It is a phyllosilicate mineral, $Mg_3Si_4O_{10}(OH)_2$ with a tri-octahedral layered structure. Because of its plate-like structure with a high aspect ratio material, the composite filled with talc give certain good properties, such as good strength and stiffness (Bee *et al.*, 2012b). Talc is being used as reinforcing filler in various PVC formulations to achieve higher strength, stiffness, and dimensional stability (Radosta and Trivedi, 1987). The use of talc filler into PVC as flow aid/dusting agent to impart a slick surface to the calendered flexible film and to reduce plate out in the extrusion process (Wilkes *et al.*, 2005). Talc filler is commonly employed in PVC compounds in order to reduce cost.

Several studies have been done on hybrid filler between organic filler and inorganic fillers into PVC composite. From the previous study by Maldas and Kokta (1991) showed that the outstanding and superior results on the strength and also modulus of treated wood fiber/mica compared to the untreated composites. Study on the mechanical properties of PVC/wood flour/glass fiber hybrid composites showed that the impact strength of hybrid composites increased without losing flexural properties (Jiang *et al.*, 2003).

The use of OPEFB fiber as filler in PVC composites has been studied extensively. There is no single study focusing on hybrid OPEFB/inorganic filler into PVC. There were only few studies of hybrid filler between the OPEFB and inorganic filler onto other thermoplastics. Natural rubber hybrid composites using OPEFB and glass fiber in PP matrix was done by Rozman *et al.* (2001a and 2001b) and Anuar *et al.* (2006).

The addition of natural fiber as filler into PVC increased the stiffness of the PVC composite but decreased the toughness of the composites. To achieve good mechanical properties, the composites need to strike balance of the strength, toughness and also stiffness (Mohd Ishak *et al.*, 2000). Therefore, by adding impact modifier into the PVC blend improved the toughness and ductility of the composites. The enhancement of the impact strength is due to the phase of rubbery particle of the impact modifier. Some of the common impact modifiers used in PVC are acrylic, chlorinated polyethylene (CPE), ethylene-vinyl acetate (EVA) and methyl butadiene styrene (MBS).

Based on the previous studies by Abu Bakar *et al.* (2005a, 2005b and 2005c), untreated OPEFB with any chemical surface reagents into PVC matrix was impact modified with acrylic impact modifier in order to improve the mechanical properties of OPEFB filled PVC composites. From these studies, the ability of acrylic impact modified PVC to shear yield before fracture has improved the impact and flexural strength. A recent study by Abu Bakar *et al.* (2012) showed that the addition of impact modifier into the treated OPEFB with PMMA filled PVC enhanced in the impact strength properties.

Core-shell acrylic impact modifier was selected as an impact modifier in the previous studies to improve the impact strength of the PVC composites (Abu Bakar *et al.*, 2005a, 2005b, 2005c and 2012). In this study, core shell MBS impact modifier was selected. This is because, MBS provides a step-change in PVC impact modification, as MBS allowed compounder to efficiently handled and incorporate into the blending system. Besides that, MBS dispersibility in the melt showed less process dependence than other type of modifiers (Wilkes *et al.*, 2005).

1.2 Problem Statement of Study

Poly (vinyl chloride) has been used for a long time ago because of its low cost, chemical inertness, and also good in heat resistivity. But, PVC also has many other imperfections like brittleness, limited strength and stiffness. Adding various types of fillers such as organic, inorganic, impact modifier and others (e.g. heat stabilizer, lubricant, processing aid and pigment) into the PVC can improve the mechanical properties.

According to Rahman *et al.* (2006) more than 55 million tons of oil palm biomass was generated annually in Malaysia, with all of this waste was not used and discarded. To avoid this problem, polymeric technology has offered some new technique to produce new material using the natural fiber. This can reduce the waste banishment to landfill. OPEFB as filler in PVC has become a new attraction in polymer composite technology, especially when PVC is widely used in plastic and building industry, strengthening the mechanical properties of the composite will bring more benefits into those industries (Zaini *et al.*, 1996).

From the previous study by Abu Bakar *et al.* (2008), the OPEFB fiber was grafted with methyl methacrylate (MMA) for the purpose of improving the compatibility of hydrophilic OPEFB with hydrophobic polymer matrix by using the optimum condition (Abu Bakar *et al.*, 2008). Recently a study on ungrafted and grafted OPEFB filled PVC by Abu Bakar *et al.* (2010 and 2012) showed that the stiffness and impact strength of the composites decreased while the tensile strength and elongation at break increased with the incorporation of 20 phr PMMA-*g*-OPEFB fiber into the PVC matrix. The grafted OPEFB filled acrylic-impact modified composites showed better properties compared to the ungrafted composites. The size of the fiber used in these previous studies was less than 75μm.

For the polymeric materials development, the most important things are to achieve a good combination of mechanical properties at a relatively low cost. With this in mind, the talc filler was used as reinforcement to enhance the stiffness of PMMA-*grafted*-OPEFB filled PVC composites. Many research works have been done on the flexural, tensile and impact properties of ungrafted and grafted OPEFB filled PVC composite but not much on the use of hybrid filler system in PVC composites. In this study, the combination of ungrafted OPEFB/talc and grafted OPEFB/talc fiber was used as hybrid fillers on PVC composites.

In order to achieve good properties of the PVC composites, PVC needs to be toughened. Since from the previous study showed that the addition of ungrafted and grafted OPEFB into PVC produced more brittle than PVC, therefore, the conventional approach by incorporating impact modifier into the composites is introduced (Wilkes *et al.*, 2005). In this study, the main reason for the addition of impact modifier is to achieve good toughness properties of the single and hybrid composite without losing the good stiffness properties of the composites.

In this study, OPEFB with the size less than 50μm was grafted with MMA by using the optimum conditions from the previous study by Abu Bakar *et al.* (2008). This research was conducted to investigate the effect of single filler (ungrafted OPEFB,grafted OPEFB or talc) and hybrid filler (ungrafted OPEFB/talc and grafted OPEFB/talc) filled PVC composites on the mechanical and thermal properties.

1.3 Objectives of Study

The overall aim of this research is to discover how the single filler (ungrafted OPEFB, grafted OPEFB, talc) and hybrid filler (ungrafted OPEFB/talc, grafted OPEFB/talc) can enhance the mechanical and thermal properties of PVC composites.

The overall objectives can be sub-divided into the followings:

1) To prepare the grafted oil palm empty fruit bunch fibers (PMMA-*g*-OPEFB) using optimum conditions grafting reaction .

2) To determine the ability of the ungrafted OPEFB, grafted OPEFB, talc, ungrafted OPEFB/talc and grafted OPEFB/talc content in affecting the PVC composites such as tensile, flexural and impact properties.

3) To study the effect on the thermal properties of ungrafted OPEFB, grafted OPEFB, talc, ungrafted OPEFB/talc and grafted OPEFB/talc content filled PVC composites.

4) To determine the effect of MBS impact modifier on the ungrafted OPEFB, grafted OPEFB, talc, ungrafted OPEFB/talc and grafted OPEFB/talc in affecting impact properties of the PVC composites.

1.4 Scope of the Study

1) Preparation of PMMA-*g*-OPEFB fiber in bulk. The reaction conditions gained from the study by Abu Bakar *et al.* (2008) were used to prepare the grafted OPEFB.

2) Preparation of single filler (ungrafted OPEFB, grafted OPEFB, talc) and hybrid filler (ungrafted OPEFB/talc, grafted OPEFB /talc) and MBS impact modified filled PVC composites.

3) The blended samples were roll-milled and molded into testing specimens using a compression molding.

4) The ungrafted OPEFB, grafted OPEFB and talc filler content were varied in order to formulate the best formulation. While the MBS impact modifier were fixed at optimum content.

5) Characterization of the OPEFB fiber with the OPEFB-g-PMMA and hybrid OPEFB-g-PMMA/talc-filled PVC composites using FTIR analysis.

6) Mechanical properties were determined based on tensile, flexural and impact properties.

7) Thermal properties determination based on DMA and TGA.

8) Surface morphology was examined using SEM.

9) Physical properties determination based on water absorption.

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