MECHANICAL, THERMAL AND CHARACTERIZATION OF CHITOSAN, NANO PRECIPITATED CALCIUM CARBONATE SINGLE AND HYBRID FILLER/ POLY(VINYL CHLORIDE) COMPOSITES

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To my beloved husband, parent and all my family members

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ABSTRACT

The aim of this study is to investigate the mechanical, thermal and characterization of chitosan, nano precipitated calcium carbonate single and hybrid filler/ poly (vinyl chloride) (PVC) composites. Graft copolymerization of poly (methyl methacrylate) (PMMA) onto chitosan (CS) was carried out under nitrogen atmosphere by free radical initiation in aqueous medium. Hydrogen peroxide (H_2O_2) and ferrous ions were used as a redox initiator/co-catalyst system. The PMMA homopolymer formed during the reaction was removed from the graft copolymer by extraction using acetone. The presence of PMMA functional groups in Fourier transform infra red (FTIR) spectra of grafted CS at peak 1731 cm^{-1} proved that the grafting process was successfully done. The single fillers (grafted CS, CS and nano-precipitated calcium carbonate (NPCC)) and hybrid fillers ((CS (2 phr)/NPCC (4 phr) and CS (4 phr)/NPCC (2 phr)) were pre-mixed with PVC using a high speed mixer. The dried blend formulations were milled into sheets using a two roll mill at temperature of 170 ^{o}C and then hot pressed at temperature of 175 ^{o}C. The tensile, flexural, impact strength and elongation at break of hybrid composites were increased compared to single fillers. Differences in surface morphology between the single composites and hybrid composites were observed. The hybrid PVC composites had better thermal stability than single composites. The increased 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. PVC/CS (4 phr)/NPCC (2 phr) had reached a balanced properties in mechanical as well as thermal properties.

ABSTRAK

Tujuan kajian ini adalah untuk mengkaji mekanikal, terma dan pencirian kitosan, nano termendak kalsium karbonat berpengisi tunggal dan hibrid komposit poli (vinil klorida) (PVC). Pengkopolimeran cangkuk poli (metil metakrilat) (PMMA) ke atas kitosan telah dijalankan di bawah pemulaan radikal bebas di dalam medium akues. Hidrogen peroksida (H_2O_2) dan ion-ion ferus telah digunakan sebagai sistem redoks pemula/pembantu mangkin. Homopolimer PMMA terbentuk semasa tindakbalas dipisahkan daripada polimer cangkuk melalui kaedah pengekstrakan dengan menggunakan aseton. Kehadiran kumpulan berfungsi PMMA pada spektra infra merah transformasi Fourier (FTIR) kitosan tercangkuk pada puncak 1731 cm^{-1} membuktikan bahawa proses pengcangkukan telah berjaya dilakukan. Kandungan pengisi tunggal (pengcangkukan kitosan, kitosan dan NPCC) dan hibrid pengisi ((CS (2 phr)/NPCC (4 phr) dan (CS (4 phr)/NPCC (2 phr)) telah di pra-campurkan dengan PVC menggunakan sebuah pengisar berkelajuan tinggi. Formulasi adunan kering kemudiannya dijadikan kepingan menggunakan pengguling berkembar pada suhu 170 ^{o}C dan dimampatkan pada suhu 175 ^{o}C. Kekuatan tegangan, lenturan, hentaman dan pemanjangan pada titik putus komposit PVC hibrid lebih tinggi berbanding pengisi tunggal. Perbezaan morfologi permukaan antara komposit tunggal dan komposit hibrid telah diperhatikan. Komposit PVC hibrid mempunyai kestabilan terma yang lebih baik berbanding komposit berpengisi tunggal. Peningkatan rintangan air komposit berpengisi hibrid membuktikan interaksi pengisi-matrik yang baik. Secara keseluruhannya, kajian menunjukkan bahawa komposit PVC berpengisi hibrid menunjukkan sifat-sifat mekanikal dan terma yang lebih baik berbanding komposit PVC berpengisi tunggal. PVC/CS (4 phr)/NPCC (2 phr) telah mencapai keseimbangan pada sifat-sifat mekanikal serta terma.

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LIST OF ABBREVIATIONS

$CaCO_3$	-	Calcium carbonate
CaSt	-	Calcium strearate
g	-	Grafted
Fe^{2+}	-	Ferrous ion
FTIR	-	Fourier transform infrared
HSt	-	Stearic acid
H_2O_2	-	Hydrogen Peroxide
KBr	-	Potassium Bromide
MMA	-	Methyl methacrylate
PA-Acr	-	Acrylic polymer
PMMA	-	Poly(methyl methacrylate)
PVC	-	Poly(vinyl chloride)
rpm	-	Revolution per minute
FE-SEM	-	Field emission scanning electron spectroscopy
Sn	-	Tin stabilizer
Phr	-	Part per hundred resins
TGA	-	Thermogravimetry analysis
TiO_2	-	Titanium dioxide
CS	-	Chitosan
NPCC	-	Nano-precipitated calcium carbonate
DD	-	Degree of deacetylation

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

More than half of all poly (vinyl chloride) (PVC) polymer produced annually in the United States is used in the manufacturing of products consumed by the building industry because of PVC versatility, performance, easy installation and cost effectiveness (Mengeloglu and Matuana, 2001). The rigidity of PVC can be modified by adding plasticizer. The cost reduction and /or property improvement can also be achieved by incorporating fillers into the PVC matrix (Mengeloglu and Matuana, 2001). PVC is versatile due its ability to incorporate additives to suit many different applications. Compounding PVC with organic and nano fillers is a convenient and efficient method to develop new polymeric material.

The addition of fillers can improve the properties of PVC. The nano-sizes of fillers were able to enhance the strength, modulus and toughness of polymer (Chabert *et al.*, 2004). A variety of nano fillers such as montmorillonite (MMT), silica and calcium carbonate filled-polymer composites possess greatly superior polymer composites properties.

Chitosan(CS) is naturally occurring and environmental friendly. CS differs from chitin by the presence of a higher proportion of amino groups. CS also widely used in different applications due to properties such as non-toxicity, good bio-compatibility, biodegradability and antibacterial properties (Rinaudo, 2006). CS is a linear polysaccharide composed of glucosamine and *N*-acetyl-glucosamine (Husseinsyah *et al*., 2011).

CS can be copolymerized with poly (methyl methacrylate) (PMMA) and the properties of the graft copolymer can be tailored by adjusting the concentration of the reactants. Basically, CS is grafted with polymers to improve its adsorption and mechanical properties (Konaganti *et al.*, 2010). Graft copolymerisation is considered to be a promising approach for designing a wide variety of molecular matrices (Radhakumary *et al*., 2005).

Lagos and Reyes (1988) studied grafting of methyl methacrylate onto CS with Fenton's reagent as a redox initiator. Prashanth *et al*. (2003) studied graft copolymerization of CS with synthetic monomers. Prashanth *et al*. (2005) also studied biodegradation of CS-graft-PMMA films. Abu Bakar *et al*. (2008) studied the optimized conditions for the grafting reaction of PMMA onto oil-palm empty fruit bunch fibres. The graft technique for CS was applied in this study in order to enhance the interaction of CS and PVC and alters the physical or chemical characteristic of polymers. The properties of the grafted copolymer depend not only on the type of polymer but also on the grafting level and distribution of monomer units.

Lagos and Reyes (1988) have come out with a conclusion that the optimum conditions for reaction period, reaction temperature, monomer, initiator and co-catalyst concentration (Fe^{2+}: H_2O_2) and CS weight were 2 hr, 70 ^{o}C, 0.216 g/mL (3.0 mL), 0.01, 0.3 g respectively. However, they never introduced the grafted CS into the polymer matrix and hybrid filler. Therefore, an effort was made to study the CS-grafted-PMMA/nano precipitated calcium carbonate hybrid fillers in composite materials. This research focused on CS-grafted-PMMA fillers. Graft copolymerization is considered to be one of the most promising approaches to a wide variety of molecular designs leading to a novel type of tailored hybrid materials (Radhakumary *et al.*, 2005).

Unfortunately, in this study the ungrafted filler composites show better mechanical properties such as flexural properties and impact strength compared to the grafted composites. Nevertheless, natural CS is still in the initial stage when used as filler to PVC composites. There are still many necessary properties that need to be investigated deeply before the CS filler can be utilized in more reliably in the practical production. In this study, the CS was used to compound with nano-precipitated calcium carbonate (NPCC) to produce the hybrid PVC composites.

1.2 Problem Statement

Poly (vinyl chloride) (PVC) is an important commercial thermoplastic, which is widely used in industrial fields due to its good properties and low-cost. However, its brittleness, low thermal stability and poor processability limit its application. Incorporation of fillers into PVC to form composites is an effective method for improving the mechanical and thermal properties.

Recently, the use of organic or natural fibers as reinforcing fillers to replace of synthetic fibers or inorganic materials has received much attention. Due to the environmental concerns, the biocomposite materials were prepared by using natural fillers. Natural fillers are inexpensive and also minimize the environmental pollution due to their characteristic biodegradability.

In this research, CS is being used as filler and grafted with PMMA. PMMA is a commodity plastic with excellent optical clarity, good weathering resistance, high tensile strength and tensile modulus. However, due to its brittle nature, its application is quite limited. Meanwhile, CS has very good properties such as biomaterial, biodegradable, non-toxic, easy availability, low cost and density and high specific surface area properties. However, CS has poor wettability, high level of moisture absorption and insufficient adhesion between untreated fibers CS and the polymer leads to debonding with age (Gassan and Bledzki, 1997). CS can be modified chemically to make composites with enhanced properties (Liu *et al.*, 2003).

The properties of CS obtained by blending synthetic polymers do not last long due to the separation of blended synthetic polymers, whereas CS obtained by grafting of monomer gives rise to everlasting properties (Gupta *et al.*, 2002). However, CS has some undesirables ones such as low tensile strength and high moisture regain. Thus, grafting of synthetic polymers on CS eliminates these drawbacks and allows the acquisition of additional properties of grafted polymers without destroying its own properties.

Based on our knowledge, there are very few researches (Liu *et al.*, 2003; Mohd. Nordin, 2007; Donate-Robles and Martín-Martínez, 2011) reporting on the combination of nano and natural fillers. CS is used as natural filler. CS has good tensile and thermal properties for further processing (Agboh and Qin, 1998). Moreover, the grafting of methyl acrylate (MA) onto CS could augment the thermal stability of pure CS. This is due to the presence of poly(methyl acrylate) (PMA), the copolymer exhibits enhanced hydrophobic character compared to pure CS (Liu *et al.*, 2003).

As reported by Nurjehan (2007), tensile strength for PVC/NPCC decreased with increasing amount of NPCC, while Young's modulus of PVC/NPCC increased with increasing NPCC content. A study about mechanical properties of PVC / NPCC by Xie *et al*. (2004) showed that when the NPCC added to PVC matrix, the nanocomposites showed ductile behavior such as stress whitening and necking compared to the pure PVC. Xie *et al*. (2004) also reported that PVC/NPCC composites have a good thermal stability.

Further research on calcium carbonate filler has been done by Donate-Robles and Martin-Martinez (2011). They proved that the addition of precipitated calcium carbonate reduced the cost, improved the processing of rigid PVC by extrusion and injection, improved PVC plastisol performance, enhanced color and among other benefits.

In development of commodity thermoplastics it is important to achieve a good balanced of mechanical properties and processability. Previous studies have shown that the addition of NPCC improved the stiffness of PVC and finer particles size of calcium carbonate is more effective in impact strength. CS increases the flexural modulus or stiffness of a rigid PVC formulation, but this increase in stiffness is usually accompanied by severe decrease in impact strength. NPCC is effective in improving impact strength of PVC without decreasing the flexural modulus of PVC. However, no studies have yet been reported on the effect of hybrid CS/NPCC on the mechanical and thermal properties of PVC. Due to this matter, this research was carried out to investigate the effects of CS/NPCC hybrid fillers contents on the PVC properties. It is expected that the use of hybrid CS/NPCC will result in PVC composites with balance in both impact strength and stiffness.

1.3 Objectives of Study

This research was carried out with the following aims:

1) To prepare and characterize the ungrafted CS and CS-*g*-PMMA fillers.

2) To investigate the mechanical and thermal properties of ungrafted CS, CS-*g*-PMMA and NPCC filled PVC composites.

3) To characterize and investigate the mechanical and thermal properties of CS and NPCC hybrid fillers PVC composites.

1.4 Scopes of Study

In order to achieve the objectives of the research, the following works were carried out:

a) Literature research on the latest development and related study on:
   i. Grafting copolymerization

   ii. Flexural and impact properties of PVC blend, ungrafted and grafted composite

   iii. Capability of PMMA in bringing CS, NPCC and PVC together

b) Characterization of the CS, grafted CS, PVC/CS, PVC/CS-*g*-PMMA and hybrid filler filled PVC using field emission scanning electron spectroscopy (FESEM) morphology and fourier transform infrared (FTIR) analysis.

c) Mechanical and thermal studies using the tensile machine, Izod impact machine and thermogravimetry analysis (TGA) for PVC blend, ungrafted, grafted and hybrid composite.

d) Particle size analysis and water absorption studies.

e) Data analysis

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