PREPARATION, CHARACTERISATION AND PROPERTIES OF MUSCOVITE/ACRYLONITRILE BUTADIENE STYRENE NANOCOMPOSITES

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PREPARATION, CHARACTERISATION AND PROPERTIES OF MUSCOVITE/ACRYLONITRILE BUTADIENE STYRENE NANOCOMPOSITES

by

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
°	Degree
$\AA$	Angstrom
μm	Micrometers
%	Percent
wt.%	Weight percent
h	Hour
nm	Nanometers
g	Gram
g/cm^3	Gram per cubic centimeters
mL	Mililiter
m^2/g	Meter square per gram

LIST OF ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
Al^{3+}	Aluminium ion
$BaCl_2$	Barium Chloride
BET	Brunauer–Emmett–Teller
CAM	Contact Angle Measurement
Ca^{2+}	Calcium ion
$Ca\ (NO_3)_2$	Calcium Nitrate
CTAB	Cetyltrimethylammonium Bromide
$CuNO_3$	Copper Nitrate
DDAC	Dodecylammonium Chloride
DMHDIM	Dimethyl-Hexadecyl-Imidazolium Modified
DTAB	Dodecyltrimethylammonium bromide
EDX	Energy Dispersive X-ray
FDM	Fused Deposition Modeling
Fe^{3+}	Ferum ion
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
HDPE	High Density Polyethylene
HDT	Heat Distortion Temperature
HDTMA	Hexadecyltrimethylammonium Bromide
HMC	Hemimicellar Concentration
K^+	Kalium/Potassium ion
KNO_3	Potassium Nitrate
Li^+	Lithium ion
LiCl	Lithium Chloride
LIF	Laser Induced Fluorescence
$LiNO_3$	Lithium Nitrate
LS	Layered Silicate
MAH	Maleic Anhydride
Mg^{2+}	Magnesium ion
MMT	Montmorillonite
MPa	Mega Pascal
Na^+	Natrium/Sodium ion

NaCl	Sodium Chloride
$NaNO_3$	Sodium Nitrate
NaTPB	Sodium Tetraphenylborate
O	Oxygen
-OH	Hydroxyl group
ODTMA	Octadecyl Trimethylammonium Bromide
OFET	Organic Field Effect Transistors
OM	Organomuscovite
OTAC	Octadecyl Trimethylammonium Chloride
PBD	Polybutadiene
PC	Polycarbonates
PCN	Polymer Clay Nanocomposites
PE	Polyethylene
PET	Polyethylene Terephthalate
PLA	Polylactic Acid
PLSN	Polymer Layered Silicate Nanocomposites
PP	Polypropylene
SAN	Styrene-Acrylonitrile
SBS	Styrene Butylene Styrene
SEBS	Styrene Ethylene Butylene Styrene
SEM	Scanning electron microscopy
Si^{4+}	Silicon ion
SSA	Specific Surface Area
TCRD	Toyota Central Research & Development
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
TMA	Trimethylammonium Chloride
TOT	Tetrahedral Octahedral Tetrahedral
TSS	Tetrasulfane
WAXD	Wide Angel X-ray Diffraction
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

PENYEDIAAN, PENCIRIAN DAN SIFAT-SIFAT NANOKOMPOSIT MUSKOVIT/AKRILONITRIL BUTADIENA STIRENA

ABSTRAK

Penghasilan nanokomposit akrilonitril butadiena stirena (ABS) berdasarkan mineral tanah liat tidak boleh dikembangkan menunjukkan pendekatan yang berpotensi yang belum diteroka secara relatif. Muskovit telah dipilih daripada sejumlah mineral tanah liat yang biasa digunakan disebabkan oleh nisbah aspek yang lebih tinggi berbanding montmorilonit (MMT). Oleh itu, kajian ini meneliti kemungkinan muskovit mengembang dan berfungsi sebagai pengisi pengukuhan dalam matriks ABS melalui proses pertukaran ion dua peringkat untuk penyerasian matriks pengisi dan penyebatian lebur bagi pembuatan polimer. Proses pengubahsuaian melibatkan rawatan menggunakan $LiNO_3$ (peringkat pertama) dan pengubahsuaian menggunakan setiltrimetilammonium bromida (CTAB) dengan kepekatan yang berbeza sebagai tindak balas pertukaran kation. Percirian terhadap muskovit terawat dinilai menggunakan pendarflour sinar-X (XRF), belauan sinar-X (XRD), inframerah transformasi Fourier (FTIR), Brunauer–Emmett–Teller (BET), mikroskopi elektron imbasan pancaran medan (FESEM) digandingkan dengan spektroskopi sinar-X tenaga terserak (EDX), dan mikroskopi electron pancaran (TEM). Hasil eksperimen menunjukkan bahawa bukan sahaja jarak dasar tetapi juga luas permukaan tertentu bertambah sementara bilangan lapisan silikat bertindan organo tanah liat semakin berkurang pada kepekatan tinggi CTAB yang menandakan pemisahan dalam lapisan muskovit. Perubahan jarak dasar seterusnya membuktikan bahawa muskovit menunjukkan kemungkinan untuk mengembang. Matlamat seterusnya dalam penyelidikan ini adalah untuk memperluaskan aplikasi matriks ABS berisi organomuskovit (OM). Dalam kes ini, OM dan muskovit yang tidak diubah suai dimasukkan ke dalam matriks ABS dengan muatan pengisi 1, 3, dan 5 wt %. Aspek-aspek kajian yang menjadi tumpuan termasuk kesan pertukaran ion, tahap penyebaran yang dicapai, dan kesan pelbagai muatan pengisi terhadap sifat mekanik nanokomposit ABS. Maka, kajian ini telah menunjukkan bahawa nanokomposit ABS/OM mempunyai kecenderungan untuk menunjukkan sifat mekanikal yang dipertingkatkan berbanding ABS/muskovit. Walau bagaimanapun, penggabungan muskovit pada semua muatan pengisi telah mengakibatkan pengurangan tidak ketara dalam kekuatan tegangan, penurunan yang ketara dalam pemanjangan takat putus, sedikit peningkatan dalam modulus dan kekerasan, serta peningkatan dalam kestabilan terma berbanding dengan sampel ABS tulen. Kekuatan lentur dan modulus masing-masing meningkat sebanyak 10% dan 28% berbanding dengan keputusan yang diperoleh daripada ABS tulen. Belauan sinar-X sudut lebar dan analisis TEM menunjukkan pembentukan campuran struktur terselit dan terkelupas dengan penggabungan OM. Oleh itu, penghasilan muskovit yang tidak boleh dikembangkan yang digabungkan dengan matriks polimer membuka peluang untuk meneroka fungsi-fungsi baharu selain daripada yang terdapat dalam bahan konvensional.

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ABSTRACT

The development of acrylonitrile butadiene styrene **(**ABS) nanocomposite based on non-expandable clay minerals presents a promising approach that has been relatively unexplored. Muscovite was chosen over the most commonly used clay minerals, due to its higher aspect ratio when compared to montmorillonite (MMT). As such, this study investigated the possibilities of muscovite to expand and to function as reinforcement filler in ABS matrix via two-stage ion exchange process for filler-matrix compatibilisation and melt compounding for polymer fabrication. The modification process involved treatment with $LiNO_3$ (first-stage) and modification with cetyltrimethylammonium bromide (CTAB) at various concentrations as a second-stage cation exchange reaction. Characterisation of treated muscovite was assessed by using X-ray fluorescence (XRF), X-ray diffraction (XRD), Fourier transform infrared (FTIR), Brunauer–Emmett–Teller (BET), Field emission scanning electron microscopy (FESEM) coupled with Energy dispersive x-ray spectroscopy (EDX), and Transmission Electron Microscopy (TEM). The experimental outcomes showed that not only basal spacing, but also specific surface area increased while the number of stacked individual silicate layers of organoclay kept decreasing at high CTAB concentrations, which signified separation within the muscovite layers. The changes in basal spacing further evidenced that muscovite displayed a possibility for expansion. A further goal of this research is to extend the application of organomuscovite (OM) filled ABS matrix. In this case, OM and unmodified muscovite were embedded in ABS matrix at various filler loading of 1, 3, and 5 wt.%. The aspects addressed included the effect of ion-exchange process, the degree of dispersion that was achieved, and the effect of various filler loading on the mechanical properties of ABS nanocomposites. Along this line, this study reveals that the ABS/OM nanocomposites possessed a tendency to exemplify enhanced mechanical properties, in comparison to those of ABS/muscovite. Nevertheless, incorporation of muscovite at all filler loadings led to a slight reduction in tensile strength, a significant decrease in elongation at break, a slight improvement in modulus and hardness, and increment in thermal stability over those of the neat ABS. Flexural strength and modulus were improved by 10% and 28%, respectively, when compared to those retrieved from neat ABS. Both wide angle x-ray diffraction (WAXD) and TEM analyses indicated the formation of mixed intercalated and exfoliated structures with incorporation of OM. Therefore, the development of non-expandable muscovite incorporated with polymer matrices provide the opportunities to explore new functionalities beyond those found in conventional materials.

CHAPTER 1

INTRODUCTION

1.1 Overview

Polymer nanocomposites based on layered silicate (LS) have garnered much interest in the present materials field due to their possibility in achieving impressive enhancements in the properties, in comparison to virgin polymers (Ray et al., 2005). Such improvements include high moduli, enhanced strength and heat resistance, as well as decreased gas permeability and flammability (Liu, 2007; Pavlidou & Papaspyrides, 2008). Interestingly, these improvements can be attained without significantly increasing the density of polymer or changing its opaque properties after incorporating minimal loading of fillers. These unique characteristics enable its use in broad applications, such as automotive, aerospace, filling industries, electronics, and food packaging (Alexandre & Dubois, 2000; Fu et al., 2008). As a result, this scenario has attracted interest from researchers at the global scale.

Among all the LS, those based on clays have been more widely investigated probably because the starting clay materials are easily available, naturally abundant, economical, and more importantly, possess higher aspect ratio, hence making them a favourable material to be applied in polymer layered silicate nanocomposites (PLSN). Aside from these properties, there are two essential characteristics that make it a good candidate in preparing PLSN. First, their layered structures enable them to be separated into individual sheets, thus generating an aspect ratio of as high as 1000 (Lin et al., 2010). Second, ion-exchange within the interlayers provides clay with rich intercalation chemistry. This surface chemistry can be fine-tuned with various organic or inorganic cations to make them compatible with a wide range of polymer. In fact, the intercalation chemistry has been assessed since a long time and has gained attention since the pioneering work of Toyota researchers in the late 1980s, whom have demonstrated an outstanding application of clay-polyimide 6 nanocomposites within the automotive industry (Kojima et al., 1993; Okada & Usuki, 1995). Ever since then, a vast range of scientific publications have emphasised on the incorporation of LS with several polymers, such as polyethylene terephthalate (PET) (Ammala et al., 2008; Parvinzadeh et al., 2010), polypropylene (PP) (Ataeefard & Moradian, 2011; Hasegawa et al., 2000), polycarbonates (PC) (Xiao et al., 2013), polylactic acid (PLA) (Chang et al., 2003), polyethylene (PE) (Yang et al., 2003) , polyester (Sreekanth et al., 2009), and epoxy (Lin et al., 2010).

The commonly used clays for preparing PLSNs belong to the same general family of 2:1 layered or phyllosilicates. MMT, hectorite, saponite, and koalinite, are among the most widely used fillers in PLSN since decades ago (Mittal, 2009). Be that as it may, despite the numerous studies that have focused on these types of clay minerals, none has looked into muscovite, a subdivision of the Mica group. Muscovite is a kind of clay mineral that has been employed for various applications, including electrical installations and equipment, wastewater absorbent, and as fillers in polymer, paint, and cosmetics industries. In truth, very rarely has the literature reported regarding the application of muscovite in thermoplastic composites, especially in its micron size. Hence, a need emerges for the development of a new filler material, in which this present work has undertaken to address the suitability of muscovite to be incorporated in polymer matrix. Exploring these abilities has been reckoned as a good starting point in preparing PLSN with extensive delaminated clay stacks.

In this aspect, a substantial number of PLSN preparation methods have embedded LS materials into polymer matrix materials in a fine dispersion manner (Lebaron et al., 1999; Pavlidou & Papaspyrides, 2008; Ray et al., 2003; Usuki et al., 1993). Surface modification by organic surfactant on silicate layers is a vital process to generate conditions for PLSN. A proper surface modification technique can be performed by using a variety of mechanisms, such as silanization (Di Gianni et al., 2008; Romanzini et al., 2015), grafting (Solhi et al., 2012), and ion exchange (Metz et al., 2015). In relation to this, the ion-exchange reaction method has been widely implemented because it is an easy and rapid technique (Lagaly et al., 2006). Additionally, a study was reported for muscovite, wherein modification via ion exchange seemed to be a better choice than using silylating agents that failed to reach the few hydroxyl groups buried within aluminosilicate crystals (Proust et al., 1988). This method helps to modify the surface properties of inert minerals through the ionically-bound organic monolayers (Osman et al., 2003). The diverse applications of the ion exchange process has been extensively used to prepare various organoclays, such as sepiolite (Pratap Singh et al., 2016), bentonite (Kwolek et al., 2003; Shen, 2001), MMT (Gallego et al., 2010; Jian et al., 2016; Merijs Meri et al., 2015; Pourabas & Raeesi, 2005), and hectorite (Voulgaris & Petridis, 2002).

Therefore, this study investigated the potential of non-expandable muscovite to serve as reinforcement filler in polymer matrix. Although muscovite particles used are in micron size, it is believed that they could be delaminated into nanometre platelets with approximately one nm thickness. Likewise, muscovite is believed to be non-exchangeable with inherent expansion and incompatible with most of the polymer systems. Due to such issues, studies on muscovite of clay mineral-polymer