EFFECT OF DIFFERENT FILLER PREPARATION METHOD ON PROPERTIES OF NATURAL RUBBER / PALYGORSKITE NANOCOMPOSITES

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by

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile butadiene styrene
ASTM	American Society of Testing and Materials
ATP	Attapulgite
BA	Butyl acrylate
BKF	2,2'-Methylenebis(6-tert-butyl-4-methylphenol)
BPR	Ball to Powder Ratio
BR	Polybutadiene rubber
CaCl	Calcium chloride
CEC	Cation exchange capacity
CTAB	Cetyltrimethylammonium chloride
CNT	Carbon nanotube
CR	Polychloroprene rubber
DDA	(1-Dodecyl)trimethylammonium
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
EDX	Energy dispersive x-ray
ENR	Epoxidized natural rubber
EPA	Environmental Protection Agency

EVA	Ethylene vinyl acetate
EPDM	Ethylene-propylene-diene rubber
FESEM	Field emission scanning electron microscopy
FTIR	Fourier transform infrared spectoscopy
GPTMS	3-glycidoxypropyltrimethoxysilane
HA	High ammonia
HCl	Hydrochloric acid
HDA	Hexadecylammonium
HNT	Halloysite nanotube
KBr	Potassium bromide
KOH	Potassium hydroxide
LGM	Lembaga Getah Malaysia
LS	Layered silicates
MMT	Montmorillonite
MQT	2-methacryloyoxy)ethyl trimethyl ammonium chloride
NBR	Acrylonitrile-butadiene rubber
NR	Natural rubber
OMMT	Octadecylammonium montmorillonite
ODA	Octadecylamine

PAL	Palygorskite
PE	Polyethylene
PEEK	polyether ether ketone
PET	Polyethylene terephthalate
PLLA	Poly L-lactic acid
PMMA	Polymethylmethacrylate
PVC	Polyvinylchloride
PVP	Polyvinylpyrrolidone
SBR	Styrene butadiene rubber
SEM	Scanning electron microscopy
SMR	Standard Malaysian Rubber
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMTD	Tetramethyl thiuram disulfide
XNBR	Carboxylated acrylonitrile-butidiene rubber
XRD	X-ray diffraction
ZDEC	Zinc diethyldithiocarbamate
ZnO	Zinc oxide

LIST OF SYMBOLS

ρ	Rho/density
φ	Phi
θ	Theta
$\tan \delta$	Tan delta
$\pm$	Plus minus
˚C	Degree celcius
T_g	Glass transition temperature
Na^+	Sodium ion
K^+	Potassium ion
h	Hour
wt %	Weight percent
t_{90}	Cure time
ts_2	Scorch time
M_L	Minimum torque
M_H	Maximum torque
ΔM	Torque difference
Q_f/Q_g	Rubber-filler interaction
E'	Storage modulus

E"	Loss modulus
mm	Milimeter
ml	Mililiter
g	Gram
MPa	Megapascal
phr	Part per hundred rubber
dNm	Desinewtonmeter
N	Newton
cm^{-1}	Per centimeter
kV	Kilo volt
mA	Miliampere

KESAN KAEDAH PENYEDIAAN PENGISI YANG BERBEZA KE ATAS SIFAT - SIFAT NANOKOMPOSIT GETAH ASLI / PALYGORSKITE

ABSTRAK

Tanah liat telah digunakan secara meluas sebagai pengisi untuk meningkatkan sifat-sifat dalam nanokomposit polimer pada pembebanan pengisi yang rendah. Bagaimanapun, penambahbaikan sifat-sifat bergantung sepenuhnya kepada keupayaan tanah liat untuk tersebar dalam matriks polimer. Dalam kajian ini, sifat-sifat mekanikal, morfologikal dan fizikal nanokomposit yang mengandungi getah asli (GA) dan palygorskite (PAL) telah disediakan dengan menggabungkan kaedah pembekuan lateks dan pencampuran leburan telah dikaji. Dalam usaha untuk menyediakan pengisi nano dengan keserasian yang baik dengan matriks polimer, kaedah penyediaan pengisi yang berbeza telah digunakan (bebola pengisar, kaedah perrtukaran kation). Kesan parameter bebola pengisar yang berbeza pada nanokomposit GA/PAL dikaji untuk menghasilkan penyebaran PAL yang homogen. PAL juga dirawat dengan menggunakan kaedah pertukaran kation. Komposit telah dijalankan ujian ciri-ciri pematangan, sifat tegangan, kekuatan carikan, kekerasan, pembengkakan, spektroskopi fourier inframerah (FTIR), analisis pembelauan x-ray (XRD), mikroskop imbasan elektron (SEM), spektroskopi penghantaran elektron (TEM) dan analisis mekanikal dinamik (DMA). Didapati, nanokomposit GA/PAL dengan parameter bebola pengisar bernisbah 5:1 mengunakan bebola pengisar bersaiz besar (35 mm) dan dirawat dengan octadecylamine (ODA) mempunyai sifat-sifat mekanikal, morfologikal dan fizikal yang lebih baik berbanding komposit yang tidak dirawat. Nanokomposit ini mempunyai sifat-sifat tegangan yang lebih tinggi, ketumpatan sambung silang yang tinggi dan interaksi getah-pengisi yang rendah.

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ABSTRACT

Recently, clay has been widely used as fillers to enhance properties in polymer nanocomposites at lower filler loading. However, the improvement of the properties depends on the ability of the clay to disperse in the polymer matrix. In this study, the mechanical, morphological and physical properties of nanocomposites containing natural rubber (NR) and palygorskite (PAL) prepared by combining latex coagulation and melt mixing method were investigated. In attempts to prepare nanofillers with enhance compatibility with polymer matrix, different types of filler preparation method were applied (ball milling and cation exchange). The effect of different ball milling parameters on NR/PAL nanocomposites was investigated to prepare homogenous PAL dispersion. PAL also was prepared by treated using cation exchange method. The composites were subjected to curing characteristics, tensile properties, tear strength, hardness, swelling, fourier transform infrared spectroscopy (FTIR), x-ray diffraction analysis (XRD), scanning electron microscopy (SEM), transmission electron spectroscopy (TEM) and dynamic mechanical analysis (DMA) test. It was found that NR/PAL nanocomposites with ball milling parameters of 5:1 ratio using large size ball mills (35 mm) and treated with octadecylamine (ODA) have improved mechanical, morphological and physical properties compared to untreated composites. These nanocomposites have higher tensile properties, high crosslink density and lower rubber-filler interaction.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Polymer-clay nanocomposites have attracted intense industrial and academic interests due to their remarkable and enhanced properties at low filler loading (Munusamy et al. 2009) compared to unfilled polymer or conventional composite materials. Major development in this field including applications to engineering polymers and investigation of the properties has been carried out over the last two decades. There are three classes of polymer which are thermoplastic, thermoset and elastomer.

Natural rubber (NR) is a kind of unique material, it is an elastomer. In uncure state, it is behaved as thermoplastic. Nevertheless, once it is vulcanised, it will become thermoset. Natural rubber is an essential elastomer with a wide range of applications (Zhang et al. 2010; Gu et al. 2010) as a result of reinforcement by fillers. It is found in the sap of a tree named *Hevea brasiliensis*. It is a natural biosynthesis polymer possessing excellent characteristics, such as high tensile strength, due to its ability to crystallise upon stretching (Wang & Chen 2013). The purpose of choosing NR as rubber matrix is to develop renewable rubber composites. NR latex is a natural polymer of isoprene, mostly *cis*-1,4-isoprene and its stereoregularity contributes to the strain-induced crystallization as well as good green and tensile strength. NR is reinforced with various types of fillers with different surface energy and particle size for practical applications in order to enhance its properties especially mechanical properties.

The most important fillers in rubber composites are carbon black and silica because of their features that improve the performance of rubber product (Peng et al. 2007). Recently, researchers have introduced and used nanoscale filler such as clay particles (Rezende et al. 2010) as an initiative to replace the use of carbon black. The improvement of properties depends heavily on the ability of clay to disperse in the polymer matrix, the interfacial interaction between the rubber matrix and nanoclay, the clay loading, and the modification of clay (Lopattananon et al. 2015; Naderi et al. 2014). Examples of clay particles include kaolin (Murray 2000), montmorillonite (Wang & Chen 2013), attapulgite (Galan 1996) and mica (Güven et al. 1992). Significant improvement in the physical properties of thermoplastics and thermosets achieved through the use of clay minerals as fillers in polymer matrix has been frequently reported. This is due to the characteristics of the polymer filled with clay exhibit better properties, such as, improved barrier and chemical resistance, better mechanical properties, improved heat resistance, improved thermal stability (Galimberti et al. 2015; Ramôa et al. 2015; Paul & Robeson 2008) and decreased flammability (Tan et al. 2012; Varghese et al. 2003).

Attapulgite often known as palygorskite, is a term for hydrated magnesium aluminium silicate mineral. The International Nomenclature Committee has specified palygorskite as the preferred name, but in trade circles the name attapulgite is well known and is also used by producers and consumers (Murray 2000). The structure of palygorskite contains ribbons, where the inversion of SiO_4 tetrahedra links each ribbon along a set of Si-O-Si bonds (Galan 1996). Based on the model of Bradley (1940), the ideal structural formula for palygorskite is $Si_8O_{20}(Mg_2Al_2)(OH)_2(OH_2)_4(H_2O)_4$. Palygorskite is widely used in different industrial fields due to its sorptive and rheological properties. It is mostly used as an animal waste adsorbent, pesticide carrier, decolorizing agent, in the oil refining and pharmaceutical industries, and as a catalyst and catalyst support (Barrios et al. 1995). The term fuller's earth is used to describe clays which have sorptive and bleaching qualities. Since palygorskite has these values, it is also known as fuller's earth.

The use of clay masterbatch has been introduced as a recent method to achieve intercalation or exfoliation of this filler in polymer composites. The masterbatch is usually prepared with a specific surfactant or low molar mass polymer, with structures compatible to that of polymeric material (Kaneko et al. 2010; Hasegawa et al. 2003). The basic idea is to increase the clay interlayer spacing by polymerization of monomers or suspension of clay in water/solvents or low molar mass polymers. Melt intercalation of high polymers is a powerful approach to produce layered silicate polymer nanocomposites. This method is quite general and is broadly applicable to a range of commodity polymers. It is harmless to the environment due to the absence of organic solvents and compatible with current industrial process. However, the dispersion of the clay in the polymer prepared by melt mixing is not good compared to the latex compounding (Kaneko et al. 2010). Rubber–clay nanocomposites prepared from latex by a coagulation method was reported to show an improvement in mechanical properties (Wang & Chen 2013). Tan (2012) has reported that clay layers can be dispersed homogenously and produce exfoliation by using a latex compounding method. Therefore, the advantages of melt mixing and latex compounding have led to the preparation of rubber composites by the combination of both methods through a masterbatch process in order to achieve the intercalation or exfoliation structure (Tan et al. 2012).

Palygorskite is naturally hydrophilic which makes it poorly suited to mixing and interacting to rubber matrix which is hydrophobic. Therefore, the clay must be treated to be able to give a better interaction with rubber matrix as composite made out of untreated clay could not give a good result due to poor interaction between the clay and the matrix. One way to modify or treat the PAL is by using ion exchange method. Cation exchange method is the process of ion exchange between PAL and alkyl-ammonium ions. Alkyl ammonium surfactants are generally used as organic surfactants. The reason for choosing cations exchange method instead of anion is because of the cations feature that is not strongly bound to the clay surface, so, small molecules cations can replace the cations present in the clay (Singla 2012). By exchanging ions present in between layers with organic cations, PAL clay can be compatibilized with NR matrix. In the meantime, this process enables the clay platelets to be separated so that they can be more easily intercalated and exfoliated.

Hence, in this study, the investigation was focused on analysing the properties of NR-PAL nanocomposites prepared by using the combination of latex compounding and melt mixing with the addition of ball milling method to improve the dispersion of PAL. Furthermore, the PAL was undergoing surface treatment using cation exchange method and the properties of treated PAL was compared to untreated PAL using similar method of compounding.