RHEOLOGICAL BEHAVIOUR OF POLYAMIDE-6/LINEAR LOW DENSITY POLYETHYLENE GRAFTED MALEIC ANHYDRIDE/MONTMORILLONITE NANOCOMPOSITES AND STATISTICAL MODEL

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To my beloved mother, Ooi Sew Tieu, father,Koay Eng Hoe,

my dearest wife, Tan Xiao Ping, and son Koay Ding Yu,

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ABSTRACT

Polyamide 6 (PA6) with different linear low density polyethylene grafted maleic anhydride (LDPE-g-MAH) and montmorillonite (MMT) loadings were produced by melt compounding using single screw extruder. In this study a mixture design of experiment covered three ingredients which contribute to the rheological properties, PA6, LLDPE-g-MAH and MMT multiple level setting were studied on their rheological properties. The rheological test conducted via capillary rheometer to obtain apparent rheological properties which were been converted to real rheological properties through Bagley correction. The additional of LLDPE-g-MAH has increased the viscosity of the system at low shear rate contributed by the interfacial reaction between PA6 with functional group of LLDPE-g-MAH. The bonding between PA6 and LLDPE-g-MAH was sensitive to shear thus no significant different in viscosity observed at high shear rate with different level of LLDPE-g-MAH. However, the incorporation of MMT has shown to lower the overall viscosity due to good dispersion of MMT results in higher interaction induced between polymer chain which was stronger than the adhesion forces between the polymer chain and the die surface wall. The rheological data used to predict the fluid consistency coefficient (m) and flow behavior index (n) within the design space.

$$m = 28.07PA6 + 448.67LLDPE - 840.73MMT$$
$$n = 0.00560PA6 - 0.01099LLDPE + 0.02946MMT$$

where

PA6 is PA6 content in wt % from 85% to 100%
LLDPE is LLDPE-g-MAH content in wt % from 0% to 10%
MMT is MMT content in wt % from 0% to 5%

ABSTRAK

Poliamida 6 (PA6) dengan polietilena lelurus berketumpatan rendah dicantum melaikanhadrida (LDPE-g-MAH) dan montmorillonite (MMT) dihasilkan dengan cara pengadunan menggunakan penyempertitan berskru tunggal. Dalam kajian ini, reka bentuk campuran meliputi tiga bahan yang menyumbang kepada sifat-sifat reologi, PA6, LLDPE-g-MAH dan MMT telah dikaji. Ujian reologi dijalankan menggunakan reometer kapilari untuk mendapatkan sifat-sifat reologi sebenar melalui pembetulan Bagley. Tambahan LLDPE-g-MAH telah meningkatkan kelikatan sistem pada kadar ricih rendah disumbangkan oleh tindak balas di antara PA6 dengan kumpulan fungsi LLDPE-g-MAH. Ikatan antara PA6 dan LLDPE-g-MAH adalah sensitif kepada ricih, menyebabkan tiada perbezaan kelikatan yang ketara diperhatikan pada kadar ricih yang tinggi. Walaubagaimanapun, penambahan MMT telah menunjukkan pengurangkan kelikatan keseluruhan disebabkan oleh penyebaran MMT yang baik dalam polimer menyumbang kepada interaksi yang lebih tinggi antara rantaian polimer lebih kuat daripada kuasa-kuasa melekat antara rantai polimer dan dinding permukaan. Data reologi digunakan untuk meramalkan pekali konsisten leburan (m) dan indeks kelakuan aliran (n) seperti ditunjukkan:

$$n = 0.00560PA6 - 0.01099LLDPE + 0.02946MMT$$

$$m = 28.07PA6 + 448.67LLDPE - 840.73MMT$$

dimana

PA6 adalah kandungan PA6 dalam wt % dari 85% hingga 100%
LLDPE adalah kandungan LLDPE-g-MAH dalam wt % dari 0% hingga 10%
MMT adalah kandungan MMT dalam wt % dari 0% hingga 5%

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LIST OF ABBREVIATIONS

ANN	-	Artificial neural networks
CNT	-	Carbon nanotubes
CP/MAS	-	Cross polarization magic angle spinning
DCP	-	Dicumyl peroxide
DOE	-	Design of experiment
DSC	-	Differential scanning calorimeter
GRNN	-	Generalized regression neural networks
HDPE	-	High Density Polyethylene
LD	-	Length over diameter
LDPE	-	Low Density Polyethylene
LLDPE	-	Linear Low Density Polyethylene
LLDPE-g-MAH	-	LLDPE grafted Maleic Anhydride
m	-	Fluid consistency coefficient
MFI	-	Melt flow index
MMT	-	Montmorillonite
MWNT	-	Multi-walled carbon nanotube
n	-	Flow behavior index
N-NMR	-	N cross polarization magic angle spinning spectroscopy
OFAT	-	One-Factor-at-a-Time
PA	-	Polyamide
PA1010	-	Polyamide 1010

PA6	-	Polyamide 6
PE	-	Polyethylene
R-Sq	-	Coefficient of determination
R-Sq(adj)	-	Adjusted coefficient of determination
Tg	-	Glasss transition temperature
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 Background

Polymers are important parts of everyday life. Polymers are not only important in industry which commonly known in electric, electronic, automotive and packaging, they are also common in sophisticated biological product such as prosthetic hip and knee joints to disposable food utensils. Polymers are complex to understand as they consist of both viscous and elastic properties which is the key behavior making polymers one of the most interesting and challenging material. Polymers properties are influence by many factors such as molecular structure, molecular weight and molecular weight distribution of repeating units, side chain branching, length and polarities, degree of crystallinity, copolymerization, modification through enormous range of additives and polymer blends. Nevertheless another important part is polymer rheology.

Rheology is a fundamental prerequisite for processing polymers in a controlled manner (Chiu and Pong, 1999). In order to bring out polymers value in certain application, appropriate knowledge of rheological behavior of polymer is crucial to predict and control the properties of relevance to the various stages of processing. Rheology is the science of deformation and flow of fluids in which they respond with plastic flow rather than deforming elastically in response to an applied force. In other words, rheology generally accounts for the behavior of non-Newtonian fluids, by characterizing the minimum number of functions that are needed to relate stresses with rate of change of strains or strain rates. The rheological properties of molten polymers influence many aspect of processing for example throughput rate, screw speed, generation of mechanical heat and die pressure. While in molten state, polymers are viscous fluids which continue to deform as long as a stress is applied. Depends on the screw design and processing parameter rapid shear stress applied is dissipated as heat. In a situation when the amount of heat produced is greater than the heat transfer or removed, the melt temperature raises and consequently reduces its viscosity (Hay *et al*, 2000). The raises of polymer melt temperature might be helpful to processor but overheating will be detrimental to polymer properties.

Generally, some equations will be used to develop the rheological model with the help of technology from relevant computer software. There are several types of polymer rheological model that have been developed before. Kinetic theory and statistical mechanics give important fundamental principles governing the systems at the molecular scale. The principles include: the concepts of statistical ensembles, Liouville's equation and Boltzmann's equation. Combined with the computing resources that have today, these statistical principles can be used to yield excellent predictions of the properties of polymeric liquids. This research will be very useful for the next researchers to easier their works in conducting the test with thermoplastic polymers. However there is very limited study reported on the use of statistical principle in predicting rheological behavior.

Nowadays enormous Polyamides (PA) have been developed and are widely used in many fields in the group of aliphatic polyamide, semi aromatic polyamide etc. As far as environmental issue is concern, polyamides from renewable resources are another hot topic. PA are semi-crystalline polymer which often form crystal up to 50% degrees of crystallinity and form excellent fibers (Vroom, 1997). There are many advantages with polyamide for example tough, strong, low coefficient of friction, abrasion resistance, high temperature resistance, good solvent and bases resistance. Although PA is a material with a number of desirable properties, it also consists of certain disadvantages such as high moisture adsorption with dimensional instability, electrical and mechanical properties influenced by moisture content. The idea to incorporate linear low density polyethylene grafted maleic anhydride (LLDPE-g-MAH) into polyamide 6 (PA6) matrix in order to reduce the compound moisture adsorption. Maleic anhydride grafted in order to improve the interfacial interaction between PA6 and linear low density polyethylene (LLDPE). LLDPE are grouped based on their differences of their molecular weight, branching and their melt flow index (MFI).

However, PA6 and LLDPE both are semi-crystalline polymers where they exhibit higher shrinkage during cooling compared to amorphous polymer. Addition of filler will helps in their dimensional stability. Thus this study will focus in the use of low aspect ratio filler to produce nanocomposite. Nanocomposites are known as a new era of composites, whereby the use of nano scales filler instead of micro scales filler. It has been proven that nanofillers were better in enhancing the tensile modulus and strength of a material compare to microfiller. Certain loading of nanofiller into the polymer matrix will increase significantly the tensile modulus and strength of the material without sacrificed its impact strength (Zhang *et al*., 2003; Liu *et al*., 1999). Although the increasing of nanofiller content can enhance the mechanical properties of the material, however over loading of nanofiller will in turn results the material to loss its properties (Ou *et al*., 1998). As a result, the optimum content of nanofiller is the limitation of the particular types of nanofiller.

This research will focus on the study of the rheological behavior of PA6/LLDPE-g-MAH nanocomposites. Based on the data obtain, a predictive model will be proposed to predict the rheological properties of PA6/LLDPE-g-MAH nanocomposites.

1.2 Problems Statement

Excess processing condition will deteriorate the polymer properties by polymer chain scissoring. Although there is a possibility to optimize the processing condition with trial runs but this will incur some cost such as material wastage, machine time and man power. Understanding a material rheological behavior enable to reduce these wastage by utilizing rheological measurements, process condition can easily be determined. Thus the final product properties and performance can be predicted. The need to accurately set and control processing condition in order to optimize product performance and ensure product acceptance, accurate rheological measurements have become essential in the characterization of pseudoplastic material.

PA6 are selected as one of the famous engineering plastic with incorporation of LLDPE-g-MAH to reduce its sensitivity to moisture. Moreover, there are very limited studies with regards to rheological behavior of PA6/LLDPE-g-MAH nanocomposites. There is no study reported on the use of statistical approach to simulate a predictive model for rheological behavior of PA6/LLDPE-g-MAH nanocomposites. This study will bring value in solving the following rheological problems:

i. What is the rheological effect of MMT in PA6/LLDPE-g-MAH nanocomposites?
ii. What is the rheological effect of LLDPE-g-MAH into PA6 nanocomposites?
iii. What is the predictive model for PA6/LLDPE-g-MAH nanocomposites?

1.3 Objective

Based on the problem statement, the present work aims to study the effect of MMT and LLDPE-g-MAH content on rheological behavior of PA6/LLDPE-g-MAH/MMT system and to propose a predictive rheological behavior models for PA6/LLDPE-g-MAH/MMT system in term of MMT loading, shear rate and processing temperature as a function of shear viscosity.

1.4 Scope

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

1. Literature search on the overview of the definition of rheology, current development of models involved in rheological study and the latest development related to thermoplastic nanocomposites.

2. Involve preparing various samples of polymer and additives to develop the specimen formulation. This involves compounding process to produce thermoplastic nanocomposites (PA6/LLDPE-g-MAH/MMT) from raw material feeding, extrusion, strand handling and pelletizing.

3. Study the effects of nanofiller concentration on PA6, LLDPE-g-MAH and PA6/LLDPE-g-MAH blends on

i. Rheological properties

Conduct rheological test using capillary rheometer to discover the rheological properties PA6/LLDPE-g-MAH/MMT.

ii. Modeling

Based on data obtained, several theoretical rheological equations used to develop a suitable model for PA6/LLDPE-g-MAH/MMT. Minitab is software which provided two modules suitable to be used in this study, surface response and mixture design as part of design of experiment. Surface response is widely used for 3 factors system and mixture design is developed for formulation purpose.

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