UNIVERSITI PUTRA MALAYSIA

PREPARATION, CHARACTERIZATION, AND THERMAL DEGRADATION OF POLYIMIDE(4–AMINOPHENYL SULFONE/3, 3', 4, 4'-BENZOPHENONETETRACARBOXYLIC DIANHYDRIDE) NANOCOMPOSITE WITH SiO2, Ag, AND MONTMORILLONITE NANOFILLERS

YADOLLAH GHARAYEBI

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By

YADOLLAH GHARAYEBI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfillment of the Requirement for the Degree of Doctor of Philosophy

June 2014

I'd dedicate each of the 157 pages of this thesis to:

My mother who gave me the courage and support to spread my wings and fly

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

PREPARATION, CHARACTERIZATION, AND THERMAL DEGRADATION OF POLYIMIDE (4–AMINOPHENYL SULFONE/3, 3′, 4, 4′-BENZOPHENONETETRACARBOXYLIC DIANHYDRIDE) NANOCOMPOSITE WITH SiO_2, Ag, AND MONTMORILLONITE NANOFILLERS

By

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June 2014

Chairman: Mansor B. Ahmad, PhD

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Among many engineering polymers, aromatic polyimides (PIs) are recognized by their outstanding thermal stability, excellent mechanical, chemical resistance and electrical properties. In order to further properties enhancement of polyimides, many researchers have made great efforts to preparation of polyimide nanocomposites. The focus in this study is the preparation and characterization of a few binary and ternary of novel polyimide nanocomposite films by names of PI/MMT, PI/SiO_2, PI/Ag, PI/SiO_2-MMT and PI/SiO_2-Ag and also investigation of their thermal properties. The prepared nanocomposites were characterized by XRD, FTIR, TEM, SEM, UV-vis and TGA.

PI/MMT nanocomposite films were successfully prepared using in-situ polymerization and solution-dispersion techniques. The activation energy and estimated lifetime of the solid-state process were calculated using the Flynn-Wall-Ozawa's method and Toop's postulation respectively. The TGA results indicated that thermal stability, activation energy values and estimated lifetime for thermal decomposition of prepared PI/MMT nanocomposite films were increased with increase of MMT loading for both techniques which the mentioned parameters are higher for products prepared by in-situ polymerization techniques.

In this research, PI/SiO_2 hybrid films were successfully prepared via the sol-gel process. The morphological studies indicated that the created SiO_2 particles in presence of coupling agent are much smaller than when no coupling agent is used at the same TEOS loading. The thermal studies showed that the thermal stability, activation energy values, estimated lifetime for thermal decomposition and thermal diffusivity increased with increasing of TEOS loading that the values of these parameters are higher for hybrid films prepared in presence of coupling agent. The studies of optical properties indicated that the absorption of samples were increased with increasing of TEOS loading whiles the band gap values were decreased.
The effect of SiO_2 particles on the dispersion behavior of MMT layers in the PI/SiO_2-MMT nanocomposite film, the changes in molecular structure and

morphology of the polymer matrix were also characterized during the thermal imidization by means of temporal analyses. Moreover, the synergistic effect of MMT layers and SiO_2 particles was investigated. The results showed that in presence of SiO_2 particles, rearrangement of dispersed MMT layers in PI/SiO_2–MMT nanocomposite film is less than in PI/MMT nanocomposite films during the thermal imidization process. The thermal studies showed that thermal stability, activation energy values and estimated lifetime of the thermal degradation for ternary nanocomposite film are higher than PI/MMT and PI/SiO_2 in the same MMT and SiO_2 contents. Ultimately, organo–soluble PI/Ag and PI/SiO_2/Ag as a ternary nanocomposite materials were successfully synthesized and characterized. Synergistic effect of Ag and SiO_2 nanoparticles and kinetic parameters of the degradation processes were also investigated.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENYEDIAAN, PENGKELASAN, DAN DEGRADASI TERMAL BAGI NANOKOMPOSIT POLIMIDA (4–AMINOFENIL SULFON/3, 3′, 4, 4′-BENZOFENONTETRAKARBOKSILIK DIANHIDRIDA) DENGAN PENGISI NANO SiO_2, Ag, DAN MONTMORILONIT

Oleh

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Antara polimer kejuruteraan, polimida aromatik (PIs) terkenal di atas mekanikal berkesan mereka yang sangat stabil, ketahanan kimia dan sifat elektrik. Dalam usaha untuk terus meningkatkan sifat polimida, ramai pengkaji telah berusaha keras menyediakan polimida nanokomposit. Fokus utama dalam kajian ini adalah ke atas penyediaan dan pengelasan beberapa filem nanokomposit polimida binari dan ternari novel seperti PI/MMT, PI/SiO_2, PI/Ag, PI/SiO_2-MMT dan PI/SiO_2-Ag serta menyiasat sifat terma bahan tersebut. Nanokomposit yang telah disediakan telah dicirikan dengan XRD, FTIR, TEM, SEM, UV-vis dan TGA.

Filem nanokomposit PI/MMT telah berjaya disediakan menggunakan teknik pempolimeran *in-situ* dan penyebaran-larutan. Pengaktifan tenaga dan jangkaan tempoh hayat bagi proses keadaan pepejal telah dikira menggunakan kaedah Flynn-Wall-Ozawa dan postulasi Toop. Dapatan TGA menunjukkan yang kestabilan terma, nilai pengaktifan tenaga dan jangkaan tempoh hayat bagi penguraian terma bagi filem nanokomposit PI/MMT yang disediakan dengan peningkatan muatan MMT bagi kedua-dua teknik yang telah menunjukkan parameter yang dinyatakan adalah lebih tinggi bagi produk yang disediakan dengan teknik pempolimeran *in-situ*.

Dalam kajian ini, filem hibrid PI/SiO_2 telah berjaya disediakan menerusi proses sol-gel. Kajian morfologi mendapati bahawa zarah SiO_2 yang disediakan dalam kehadiran agen yang jauh lebih kecil apabila tiada agen gandingan digunakan pada muatan sama TEOS dilaksanakan. Kajian terma menunjukan bahawa kestabilan terma, nilai pengaktifan tenaga, jangkaan tempoh hayat bagi penguraian terma dan peningkatan resapan terma dengan meningkatnya muatan TEOS dan nilai bagi parameter tersebut adalah tinggi bagi filem hibrid yang disediakan dalam kehadiran agen gandingan. Kajian bagi sifat optik menunjukkan bahawa penyerapan sampel bertambah dengan muatan TEOS manakala nilai ruang kosong bagi gabungan telah berkurangan.

Kesan zarah SiO_2 ke atas kelakuan penyebaran lapisan MMT dalam filem nanokomposit PI/SiO_2-MMT, perubahan dalam struktur molekular dan morfologi bagi matrik polimer juga telah dicirikan semasa imidizasi terma dengan cara analisis temporal. Tambahan pula, kesan sinergi bagi lapisan MMT dan partikel SiO_2 telah dikaji. Hasil menunjukkan bahawa dalam kehadiran zarah SiO_2, susun atur bagi lapisan MMT yang terurai dalam filem nanokomposit PI/SiO_2–MMT adalah kurang daripada filem nanokomposit PI/MMT semasa proses imidizasi terma. Kajian terma menunjukkan kestabilan termal, nilai pengaktifan tenaga dan jangkaan tempoh hayat bagi penguraian terma bagi filem nanokomposit ternari adalah lebih tinggi daripada PI/MMT dan PI/SiO_2 dengan kandungan MMT dan SiO_2 yang sama. Akhirnya, PI/Ag terlarut-organik dan PI/SiO_2/Ag sebagai bahan nanokomposit ternari telah berjaya disintesis dan dicirikan. Kesan sinergi bagi nanozarah Ag dan SiO_2 dan juga parameter kinetik bagi proses penurunan turut dikaji.

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APPROVAL

I certify that a Thesis Examination Committee has met on (date of viva voce) to conduct the final examination of Yadollah Gharayebi on his thesis entitled"PREPARATION, CHARACTERIZATION AND THERMAL DEGRADATION OF POLYIMIDE(4–APS/BTDA) NANOCOMPOSITE WITH SiO2, Ag AND MONTMORILLONITE NANOFILLERS" in accordance with the niversities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the (insert the name of relevant degree).

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LIST OF ABBREVIATIONS

°C	Celsius degree
4-APS	4-Aminophenyl sulfone
6FDA	4,4’-(hexafluoroisopropylidene) diphthalic arhydride
6FHP	2,2-Bis (3-amino-4-hydroxyphenyl) hexafluoropropane
A°	Angestrom (10^{-8} meter)
AFM	Atomic force microscopy
APCSNPs	Ag/poly(m-phenylenediamine) core−shell nanoparticles
APTES	γ-aminopropyltriethoxysilane
BPDA	3,3′,4,4′-biphenyltetracarboxylic dianhydride
BTDA	3,3', 4,4'-benzophenonetetracarboxylic dianhydride
DDBBDA	1,4-bis(3,4-dicarboxyphenoxy)-2,5-di-tert-butylbenzene dianhydride
DDE	4,4′-diaminodiphenyl ether
DMONT	Dodecyl-montmorillonite
DNA	Deoxyribonucleic acid
FTIR	Fourier transform infrared
GOTMS	γ-glycidyloxypropyltrimethxysilane
Hz	Hertz
ITER	International Thermonuclear Experimental Reactor
K	Absolute temperature
KH 550	γ-aminopropyltriethoxy silane
MMT	Montmorillonite
MV/cm	Milivolt per centimeter
NCs	Nanocomposits
NLO	Nonlinear optical
NMP	N-methyl-2-pyrrolidone
O	Octahedral
ODA	Oxydianiline
ODA	Octadecylamine
OMMT	Organo–Montmorillonite
PAA	Polyamic acid
PAN	Polyacrylonitrile
PCNs	Polymer clay nanocomposites
PDA	*p*-Phenylenediamine
PET	
PIs	Polyimides
PLS	Polymer layered silicate
PMAA	Polymethacrylic acid
PMDA	Pyromellitic dianhydride
PNC	Polymer nanocomposites
POSS	Polyhedral oligomeric silsesquioxane
R	Gas constant
SEM	Scanning electron microscope
SPI	Soluble polyimide
T	Tetrahedral
TBT	Tetrabutyl titanate
T_d	Decomposition temperature

TEM	Transmission electron microscopy
TEOS	Tetraethoxysilane
t_f	Estimated time to failure
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
TMOS	Tetramethoxysilane
T-silica	Silica tube
UV-Vis	Ultraviolet-visible spectroscopy
V.cm	Volt centimeter
WPNC	Wood polymer nanocomposite
Wt	Weight
WXRD	Wide angle X-ray diffraction
XRD	X-ray diffraction
β	Heating rate

CHAPTER 1

INTROUCTION

1.1 Background of the Study

Nanotechnology is now recognized as one of the most promising areas for technological development in the 21st century and the most popular areas for current research and development in basically all technical disciplines (Gacitua et al., 2005).

In the area of nanotechnology, polymer nanocomposites have generated a significant amount of attention in the recent literature and is rapidly emerging as a multidisciplinary research activity both in industry and in academia. This is because they often exhibit remarkable improvement in materials properties when compared with virgin polymer or conventional micro and macro-composites.

Of the many polymers used in industry, aromatic polyimides (PIs) are recognized by their outstanding thermal stability, excellent mechanical, chemical resistance, and electrical properties, thus leading to their popular use in different industries.(Z.-d. Wang, Lu, et al., 2006; Y.-H. Zhang, Dang, et al., 2005; Y.-H. Zhang, Fu, et al., 2005). In order to further enhance the properties of polyimides, many researchers have made great efforts in the preparation of polyimide nanocomposites. In other words, in those applications that demand more enhanced properties, inorganic micro– and nano-fillers like silica are incorporated to obtain the desired enhancement(Duo et al., 2006; Y.-Q. Li et al., 2007; F.-X. Qiu et al., 2004b), montmorillonite (MMT) (Z.-M. Liang et al., 2003; Y.-H. Zhang, Dang, et al., 2005), mica (Y.-H. Zhang, Fu, et al., 2005), bariumtitanate (Devaraju et al., 2005), titanium dioxaide (Kong et al., 2002), manganese dioxaide (J.-c. Huang et al., 2000), Ag nanoparticles (Faghihi et al., 2010; Quaranta et al., 2006) and carbon nano–tubes (L. Gao et al., 2007) into polyimide matrix.

Polyimide films reinforced by clay such as montmorillonite (MMT) have received much attention in both scientific and industrial areas (Yudin et al., 2005). Due to its attractive low price, high aspect ratio and good, suitable nanostructure as well as interfacial interactions, clays have the ability to give dramatic improvement in its adjustable properties with much lowered loadings, thus enhancing the usefulness of the original properties in the remaining polymer but for the preparation of these nanocomposites, there is an initial challenge for all researchers. The MMT is a hydrophilic compound which cannot be mixed with organic polyimide and therefore, its surface should be modified. Of the many ways to modify clay, ion exchange with alkylammonium ions is the common and preferred method in preparing organoclays.
There can be variation in the performance of polyimide nanocomposite utilizing modified MMT, which is dependent on the dispersion level, the type of alkyl ammonium ions used as modifier and also the type and structure of Polyimide (Agag et al., 2001; Delozier et al., 2002). The dispersion of modified layered silicates in polymer matrices is one of the most important factors effecting in the performance of prepared nanocomposites (J. H. Chang et al., 2002). However, three methods have commonly been employed in the dispersion of modified layered silicates into a

polymer matrix. Among them, the methods of in situ polymerization (Okamoto et al., 2000) and solution dispersion (Aranda et al., 1992) are used to prepare PI/clay nanocomposite films.

The Toyota Research Group in 1990s was the first to succeed in preparing a kind of PI/clay hybrids using two–step polymerization of polyimide. Since then, many researchers have attempted to prepare different kinds of PI/clay nanocomposite films with different materials and routes in order to improve the polyimide properties. Of the various clays, MMT has been most accepted in polymers and many researchers have attempted to prepare differnt polyimide nanocomposites based on MMT nanofiller (Agag et al., 2001; Magaraphan et al., 2001; Y. H. Yu et al., 2004). Their results showed the remarkable improvement in properties such as thermal stability, glass transition temperature, mechanical properties, anticorrosive properties and electrical properties when compared with their origin polyimide.

Besides clay, silica is another important and widely–used nanofiller. There are many researches that have proven the performance of polyimides can be also increased with incorporation of SiO_2 particles. Therefore in recent years, PI/SiO_2 hybrid materials have attracted much attention in efforts to improve the optical (Tommalieh et al., 2010), electerical (Babanzadeh et al., 2012; Ho et al., 2006), thermal stability (J. Liu et al., 2002) and mechanical properties of polyimides (B. K. Chen et al., 2004; Musto et al., 2004). Recent studies have also shown the applicability of PI/SiO_2 hybrid materials in many applications, such as electronic devices, optical waveguide materials, materials with high transparency, nonlinear optical materials, photovoltaic devices and fuel cells (Y.-Y. Yu et al., 2010).

Today, among the different methods, the sol–gel process is widely used to prepare PI/SiO_2 hybrid materials because it is a unique and versatile approach to produce homogeneous hybrid materials films (Musto et al., 2004; C. Zhang et al., 2007b). In order to further improve the properties of the PI/SiO_2 hybrid materials, many researchers have largely attempted to use different types of coupling agents to enhance compatibility between SiO_2 and the polyimide matrix and reduce SiO_2 size (C.-C. Chang et al., 2002; Kioul et al., 1994; F.-X. Qiu et al., 2004b).

To date, one nano material has been reported to reinforce nanocomposites but recently, many researches have studied the possibility of incorporating two kinds of nano materials with varying forms, layers and particles, into the polymer matrix in order to successfully prepare comprehensive high–performance polymer nanocomposites. The use of two combined nano materials with varying shapes could produce better performance because of the expected synergistic effect and new reinforcement mechanism. Using two kinds of nano materials of varrying forms can also change other properties in nanocomposites (T. Yu et al., 2007).

Many researchers have attempted to produce and improve various ternary polymer nanocomposites such as PI/SiO_2–TiO_2 (W. Qiu et al., 2003), Polyacrylonitrile/Na-MMT/SiO_2 (T. Yu et al., 2007), epoxy/O-MMT/nano-SiO_2 (X. Li et al., 2012), Polymethacrylic acid/Na-MMT/SiO_2 (Bao et al., 2011) and PI/SiO_2 hybrid–clay (Park et al., 2005) and studies have shown the expected synergistic effect and new performance as a result of the existence of different nanofillers in nanocomposite.

The chemical composition, shape, size, and size distribution of composite materials play an important role on their unique physical and chemical properties. The composite materials with different compositions and specific morphologies can be used in different applications (Gau et al., 1999). In recent years, core/shell nanocomposites have been intensively investigated because of their unique functionalities (Guo et al., 2008). Moreover, the core/shell process can create new properties in nanoparticles, can be used such as carbon (X. Sun et al., 2004) polymer (Aizawa et al., 2006; Xiong et al., 2006) and different inorganic compounds (Sakai et al., 2006; H.-F. Zhang et al., 2002).

1.2 Problem Statement

Today, many polymers are widely utilized to improve our lives, but their use has been limited because their thermal stability is negatively affected by high temperatures (L.-H. Lee et al., 2001). Polyimides are a kind of polymers that are characterized by their outstanding thermal stability. They also possess excellent mechanical, chemical resistance and electrical properties and have been widely applied in different industries such as aerospace and microelectronic at elevated temperatures (Z.-d. Wang, Lu, et al., 2006; Y.-H. Zhang, Fu, et al., 2005). However, with the rapid development in some special applications such as superconductive cable and spacecraft, the mechanical, electrical and thermal properties of polyimide films especially, at cryogenic temperature are not good enough to meet the extremely severe requirements (Y.-H. Zhang, Dang, et al., 2005). In other words, in some uses, their properties need to be significantly enhanced and this can be achieved by incorporating inorganic nano–fillers including silica, clay and metallic nanoparticles. Hence, despite the existence of many reports on the preparation of polyimide nanocomposites, there are so far no reports providing this type of polyimide nanocomposites based on aromatic dianhydride (3,3',4,4'–benzophenonetetracarboxylic dianhydride) (BTDA) and aromatic diamine (4–Aminophenyl sulfone) (4–APS) monomers and also investigation about of kinetic parameters of their thermal degradation process. Considering the importance and application of nanocomposites in various industries and the need to develop these materials, there is an urgent need to prepare the new polyimide nanocomposites. Furthermore, there are few reports on the preparation of ternary polyimide nanocomposites based on MMT, SiO_2 and Ag nano–fillers and also very few reports on their thermal properties. As such, there should be further investigation on the properties of these products.

According to the application of polyimide nanocomposite films at high temperature conditions, and also considering the absence of research about determination of kinetic parameters of thermal degradation in the literature, investigation of thermal degradation of polyimide nanocomposites is needed.

1.3 Scope of Research

This research includes several different sections with the overall goal being the development of polyimide nanocomposite films using new combinations and also investigation of their physical properties such as thermal and optical properties and synergistic effects of different nanofillers.

In detail, the scope of this research is to prepare several new polyimide nanocomposites based on aromatic dianhydride (3,3',4,4'–benzophenonetetracarboxylic dianhydride) (BTDA), aromatic diamine (4–Aminophenyl sulfone) (4–APS) and different nano–fillers such as MMT, SiO_2 and Ag. The products are characterized by Fourier transform infrared (FTIR) spectroscopy, Ultraviolet–visible spectroscopy (UV–Vis), X-ray diffraction (XRD), Scanning electron microscope (SEM), Transmission electron microscopy (TEM) and Thermogravimetric analysis (TGA). To expand or delaminate clay layers such as MMT is the key to the preparation of polymer/clay nanocomposites that is dependent on the type and size of organic intercalating agents and also the preparation techniques of polymer/clay nanocomposites. Hence, the polyimide nanocomposite films based on MMT layers as nano–fillers are prepared and compared via solution dispersion and in situ polymerization techniques. The thermal and optical properties of prepared nanocomposite films and the synergistic effect of SiO_2 particles and MMT layers and also SiO_2 particles and Ag nanoparticles on prepared ternary nanocomposite films are investigated. Kinetic parameters of thermal degradation process, such as activation energy and estimated lifetime for the all products are also investigated through Flynn–Wall–Ozawa's method and Toop's postulation respectively.

Objectives

The objectives of this study are:

1 To prepare and characterize PI(BTDA/4–APS)/MMT and PI(BTDA/4-APS)/SiO_2 as binary nanocomposite films and PI(BTDA/4-APS)/SiO_2–MMT as a ternary nanocomposite film and investigate the their thermal properties
2 To study of effect of SiO_2 particles on dispersion of MMT layers in PI/SiO_2–MMT as a ternary nanocomposite film during thermal imidization.
3 To prepare and characterize organo–soluble PI(BTDA/4–APS)/Ag and PI(BTDA/4–APS)/SiO_2/Ag nanocomposite films and investigate the thermal properties of the prepared nanocomposite films.
4 To study of synergistic effects of different nanofillers such as SiO_2, MMT and Ag in ternary nanocomposite films of PI(BTDA/4–APS)/SiO_2–MMT and PI(BTDA/4–APS)/SiO_2/Ag.

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