PREPARATION AND CHARACTERIZATION OF POLYSTYRENE/POLY (BUTYLACRYLATE-METHACRYLATE ACID) CORE-SHELL NANOSTRUCTURED FILMS

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DEDICATION

This thesis is dedicated to my father, who taught me that the best kind of knowledge to have is that which is learned for its own sake. It is also dedicated to my mother, who taught me that even the largest task can be accomplished if it is done one step at a time. Above all is to Almighty God. Alhamdulillah.

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ABSTRACT

Poly(*n*-butyl acrylate-*co*-methacrylic acid) (PBA-MAA) latex series that contained polystyrene(PS) seed was prepared by seeded emulsion polymerisation. The seed-shell nanoparticles were designed with high (PS seed) and low glass transition temperature (T_g), respectively. Two types of monomer crosslinkers i.e. ethylene glycol and 1,3-butanediol dimethacrylate (1,3-BDDMA) were added into the formulation to prevent the particles from agglomeration, as well as to increase the covalent-crosslinked of polymer chains. In this study, the effects of PS content, surfactant addition mode, the degree of neutralisation, and types of monomer crosslinkers on the physical and mechanical properties of samples were investigated. Analysis using dynamics light scattering showed that the addition of PS seed increased consistency of particle size. The strains of the films were improved when surfactant was added at an initial charge compared to the feeding during polymerisation. The addition of a small percentage of ionic groups zinc oxide (ZnO) and monomeric crosslinkers increased the stress and modulus of the films. By contrast, they decreased the strain and tackiness of the films. Meanwhile, spectra from Fourier transform infrared spectroscopy confirmed that the ZnO had bonded to the carboxylic groups –RCOOH. The stress-strain data showed the neutralisation at 100n was required to increase the stress-at-break up to 0.5 MPa and to decrease strain-at-break by a factor of 2. The addition of 1,3-BDDMA crosslinker had increased the stress-at-break by the factor of 1. Meanwhile, the T_g of the films did not significantly affect by the addition of crosslinkers and ZnO, as shown by differential scanning calorimetry data.

ABSTRAK

Siri lateks poli(n-butil akrilik-ko-asid metakrilik) (PBA-MAA) yang mengandungi benih polistirena (PS) telah disediakan dengan cara pempolimeran emulsi benih. Nanopartikel benih-kulit telah direka dengan suhu peralihan kaca (T_g) masing-masing yang tinggi (benih PS) dan rendah. Dua jenis monomer pautsilang etilena glikol dimetakrilat dan 1,3-butandiol dimetakrilat (1,3-BDDMA) ditambah ke dalam formulasi untuk mengelakkan partikel bergumpal di samping untuk meningkatkan pautsilang kovalen di antara rantaian polimer. Dalam kajian ini, kesan kandungan PS, mod penambahan surfaktan, darjah peneutralan dan jenis monomer pautsilang ke atas sifat-sifat fizikal dan mekanikal sampel telah dikaji. Analisis menggunakan serakan cahaya dinamik menunjukkan penambahan benih PS telah meningkatkan saiz partikel secara konsisten. Peratus terikan filem pula meningkat apabila surfaktan ditambah pada mod awal berbanding dengan penambahan semasa pempolimeran. Penambahan peratusan kecil kumpulan ionik zink oksida (ZnO) dan monomer pautsilang telah meningkatkan kekuatan tegasan dan modulus filem. Sebaliknya, terikan dan kelekitan filem berkurangan. Spektra inframerah jelmaan Fourier mengesahkan bahawa ZnO telah membentuk ikatan dengan kumpulan asid karboksilik -RCOOH. Data dari tegasan-terikan menunjukkan peneutralan sebanyak 100n diperlukan bagi meningkatkan tegasan pada takat putus sehingga 0.5 MPa dan mengurangkan terikan pada takat putus dengan faktor 2. Penambahan 1,3-BDDMA telah meningkatkan tegasan pada takat putus dengan faktor 1. Sementara itu, penambahan monomer pautsilang dan ZnO tidak memberi kesan yang ketara ke atas T_g filem seperti yang ditunjukkan oleh data kalorimeter imbasan kebezaan.

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LIST OF ABBREVIATIONS

1,4 BDDMA	-	1,4 Butanediol dimethacrylate
AA	-	Acrylic acid
AIBN	-	Azobisisobutyronitrile
AN	-	Acrylonitrile
BA	-	Butyl acrylate
Bd	-	Butadiene
CMC	-	Critical micelle concentration
CTA	-	Chain transfer agent
EGDMA	-	Ethyl glycol dimethacrylate
KPS	-	Potassium persulfate,
MAA	-	Methacylic acid
Mw	-	Molecular weight
N-MA	-	N-methylol acrylamide
pphm	-	Part per hundred monomer
PS	-	Polystyrene
rpm	-	Rotation per minute
SEM	-	Scanning electron microscopy
TEM	-	Transmission electron microscopy
TSC	-	Total solid content
VOC	-	Volatile organic compound
ZnO	-	Zinc oxide

LIST OF SYMBOLS

% - Percentage
°C - Celsius
cP - Centipoise
g - Gram
mPa.s - Milipascal.second
nm - Nanometer
T_g - Glass transition temperature
µm - Micrometer

CHAPTER 1

INTRODUCTION

1.1 Research Background

Polymer latex is defined as a dispersion of polymeric materials that are stabilized within an aqueous medium with a size ranging from tens to hundreds of nanometres.[1–4] Polymer latexes or emulsions are one of the most important types of products in the polymer industry. With several different physicochemical properties, latex polymers be used in different applications. Mostly they are used in the coatings and paint industry and also used for adhesives, textiles, paper industry and various other markets.[5]

Polymer latexes with core-shell nanostructured have attracted considerable fundamental interest due to their controllable and well-defined structures[6–9]. Generally, the core-shell particles can be built up of a rigid core and a soft shell or vice versa. In the case of an emulsion based adhesive or coating, the rigid core–soft shell type is preferable, as the crosslinked core offers sufficient cohesive strength while the flexible shell provides enhanced wetting and adhesion to a substrate[10]. Pérez-Carrillo et al[11] had synthesized the core-shell polystyrene/poly(butyl acrylate) copolymer via emulsion and microemulsion polymerization. They found that the mechanical properties of the core/shell polymers are strongly influenced by the particle size through the shell thickness and by the nature (T_g) and location of the composing polymers.

Another researcher had added N-methylol acrylamide (N-MA) crosslinker in the nanostructured PS/PBA system through a two-step emulsion polymerization. Results showed that the system had improved tensile strength and higher resistance against organic solvent.[12]

Meanwhile, Borthakur et al.[13] had investigated on core-shell PS/PBA emulsion based adhesives by changing the core-shell ratio and crosslinked the core with ethylene glycol dimethacrylate (EGDMA). The films simultaneously exhibited high cohesive and adhesive strength via structured core-shell particle design. The high cohesive strength of the adhesive was provided by the crosslinked core part, while the relatively soft shell facilitates adhesion by enabling the proper wetting of the substrate. The crosslinked EGDMA-core was able to avoid any probability of gel formation and to bind both the core and the shell phase together. Musa et al.[14] had incorporated 1,4-butanediol diacrylate (BDDA) crosslinker in the shell poly(BA-BDDA) copolymer. It was found that the presence of BDDA prevented from latex swelling at high pH of latex and enabling the formation of nanoparticle films. Meanwhile Riosl et al.[15] had investigated core-shell PS/poly(BA-co-MAA) latex at different BA/MAA ratios. Results revealed that the amount of MAA in the copolymer shell could control the particle shape and morphology. The shape of the structured particles was non-spherical, and the shape irregularities are the function of reaction time.

Emulsion polymerization is an important polymerization process on an industrial scale and widely used method for the production of polymer latex products.[16] Since the continuous phase is aqueous, it used less solvent and emits less VOC; therefore from an environmental perspective it is a preferred method of polymerization compared to other methods. However, to produce nanostuctured polymer particles, a simple batch emulsion polymerisation cannot be used; other approaches such as heteroaggregation, copolymer micelles and sequential seeded emulsion polymerisation are among commonly adopted methods to produce such nanostructured particles. The later i.e. sequential or semi-batch seeded emulsion polymerisation method is appealing for fundamental studies and manipulation of end-use properties due to easy control over the structure and cost-effectively scaled up[17]. This method also produces a narrower particle size distribution, more uniform copolymer composition.

Many polyacrylate-based emulsions that consist of carboxyl group ($RCOO^-$) need to neutralized with alkali such as sodium hydroxide (NaOH) or potassium hydroxide (KOH)in order to maintain the stability of particles in water. Apart from alkali, metal oxide such as zinc oxide (ZnO) can be used as a neutralising agent. In return, the polymeric materials will have a small number of ionic side groups in their hydrophobic backbone chains, called as ionomers.[18] The presence of a small ionic group concentration (<10 mol %),[19] can greatly improve the mechanical properties of the ionomers. The interaction between the ionic groups in the polymer matrix leads to the formation of ionic aggregations. The aggregations form physical crosslinking between the chains which influence the viscoelastic behavior of ionomers[20].

For this project, the PS/poly(BA-co-MAA) core-shell nanoparticles was prepared via semi-batch emulsion polymerization. The PS/PBA ratios were varied at three PS levels while PMAA was fixed at 5 pphm. The shell i.e. poly(BA-co-MAA) was crosslinked with EDGMA and BDDA to reduce the swelling of nanoparticles at high pH. Furthermore, the PS/poly(BA-co-MAA) latex was neutralized with KOH and ZnO; with the latter formed ionomer. It was expected that the latex would have hard/soft nanoparticles due to higher T_g of core (PS seed) and low T_g shell poly(BA-co-MAA).

1.2 Problem Statement

The ability to tune properties through independent control of the materials comprising the core and shell structures continues to attract considerable interest.[21–23] In previous work, polybutadiene/poly (acrylonitrile-co-methacrylic acid) PBd/poly(AN-co-MAA) latex with core-shell nanoparticles was synthesised.[18,19] The latex was partially neutralized with KOH before further neutralized with ZnO. This had introduced ionic crosslinking to the system. The modulus values were shown to be affected by the proportions of AN and MAA and extents of neutralisation. However, despite having good ductility, those nanostructured ionomer films also had low modulus values. Furthermore, since the use of Bd, which has a boiling point of -5 °C, had restricted the versatility for nanoparticle preparation because a high pressure reactor was required.[24] Therefore, to overcome both the versatility and modulus deficiencies, core–shell nanoparticles were prepared using n-butyl acrylate (n-BA) to replace Bd[20]. n-BA has a much higher boiling point (145 °C) which enabled the use of conventional (non-pressurised) reactor. The PBA/poly(AN-co-MAA) core-shell nanoparticles was synthesised by introducing 1,4-butanediol diacrylate (BDDA) crosslinker into the shell. The latex was neutralized with KOH dan ZnO. It was found that the use of PBA as core had increased the T_g values close to room temperature. The elastomer film showed high modulus and strongly depended on the AN content and extent of neutralization of the –COOH groups. Although PBA/poly(AN-co-MAA/BDDA) showed excellent properties to be used in glove industry, acrylonitrile is a toxic material.

Therefore, this study was conducted to prepare PS/poly(BA-co-MAA) nanoparticles by replacing PBA core with PS (to provide high T_g) and polyacrylonitrile with BA in shell (to provide low T_g). Furthermore two types of crosslinkers i.e. BDDMA and ethylene glycol dimethacrylate (EGDMA) were introduced in the poly(BA-co-MAA) shell to provide continuous and a percolating film phase. Effects of monomer composition, the core-shell volume fraction and the extent of neutralization (KOH and ZnO) on the physical and the mechanical properties of the nanoparticles were investigated.

1.3 Objective

The objectives of this work based on PS/poly(BA-co-MAA) core-shell nanoparticle systems were:

1. To study a different volume ratio core-shell on physical and thermal and tensile properties of the nanostructured film.
2. To investigate the effect of monomer crosslink on physical, thermal and tensile properties of the nanostructured film.
3. To study the effect of neutralization (KOH and ZnO) on the physical, thermal and tensile properties of the nanostructured film.

1.4 Scope of Study

The scopes of study are as follows:

1. Synthesis of PS/Poly(BA-co-MAA) core-shell nanoparticle via semi-batch emulsion polymerisation.
   1. i) Core:shell volume fraction

      Polystrene seed was used as a core and Poly (BA-co-MAA) as a shell with different volume fraction of core-shell (PS seed 1, 2 and 3.5wt %).
   2. ii) Two type of monomer-crosslinker

      EGDMA and BDDMA were added to improve the properties of nanoparticle.
   3. iii) Neutralization with KOH and ZnO.

      KOH and ZnO were used to neutralize the pH of the latex and introducing ionic crosslinking to the shell.

2. Testing and characterizations
   1. i) Fourier-transform infrared spectroscopy (FTIR)

      FTIR measurement was conducted using a Nicolet 5700 FTIR equipped with an attenuated total reflectance (ATR) unit.
   2. ii) Tensile test

      Stress-strain measurements were conducted using a Lloyd LR10k instrument. Tensile testing was conducted according to ISO 37 standard.
   3. iii) Dynamic light scattering (DLS)

      Z-average diameter was measured by using dynamic light scattering (DLS) model Malvern ZetaSizer NanoZS90.

iv) Viscometer

The viscosity of latex was measured using a Brookfield LVT viscometer using spindle 3 at speed of 60 rpm. A unit of measurement was calculated in units of centipoise (cP).

v) Differential scanning calorimetry (DSC)

The glass transition temperature of latex was measured by a TA Instrument Differential Scanning Calorimetry (DSC) Q200.

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