PREPARATION OF STYRENE ACRYLIC COPOLYMERS AS TONER RESIN BY SUSPENSION POLYMERIZATION

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ABSTRACT

Toner resins are polymeric materials used in the manufacturing of toners to be used in the photocopy machines and LaserJet printers. The popular commercial resins are the styrene acrylic copolymers. A typical toner resin has a bimodal molecular weight distribution, having one fraction of lower molecular weight and another of higher molecular weight, so that it can impart good fixing and offset properties to provide the performance of a good toner.

This research project describes the synthesis of toner resins by suspension polymerization, using poly(vinyl alcohol) and benzoyl peroxide as a colloid stabilizer and initiator respectively, in an aqueous medium to produce the copolymers in the form of tiny beads. Three series of experiments were carried in the study: (i) synthesis of low molecular weight styrene acrylic copolymers, (ii) synthesis of high molecular weight styrene acrylic copolymers and (iii) blending the both high and low molecular weight copolymers at different ratios to obtain the desired properties.

Gel permeation chromatography (GPC) was used to study molecular weight distribution (MWD); melt flow index (MFI) reflected the flow ability of resin; Differential Scanning Calorimetry (DSC) was used to study the thermal properties; and acid number (AN) to quantify the amount of acidic groups in the resin.

The effects of monomer ratio, concentration of initiator and concentration of crosslinking agent on the properties of high and low molecular weight resins had been investigated. The desired glass transition temperature of toner resin was obtained by

varying the monomer ratio. By increasing the concentration of initiator, the number average of molecular weight of resin tends to shift to lower molecular weight presumably due to the excess free radicals that could lead to more chain termination and chain transfer reactions. The addition of cross-linking agent leads to gel formation. The percentage of tetrahydrofuran (THF) insoluble fraction has increased as the concentration of cross-linking agent was increased. The properties of synthesized toner resins were compared to those of selected commercial resins.

The synthesized resins after blend at different ratios have glass transition temperature in the range of 56-69^{o}C; MFI in the range of 13 – 55 g/10 min; AN in the range of 2.5 - 3.4 mg KOH/g; M_w in the range of $7.00 \times 10^3 - 3.20 \times 10^3$ Daltons (1 Daltons = 1.66×10^{-27} kg) with 9 - 14% of tetrahydrofuran (THF) insoluble fraction. Three of the synthesized resins with desired properties had been tested in a lab scale production of toner. Print test had been carried out to evaluate the print quality. Image density of the test images are in the range of 1.33 - 1.58 which is comparable to commercial toner, while background density is around 0.12-0.13 which is slightly higher than commercial toner.

ABSTRAK

Resin toner adalah polymer yang digunakan untuk membuat toner bagi mesin fotokopi dan alat pencetak laserjet. Resin komersial yang paling popular adalah kopolimer stirena akrilik. Resin toner biasanya mempunyai taburan berat molekul bimodal tinggi dengan bahagian berat molekul rendah. Ini dapat memberi sifat penetapan dan pengimbangan agar menjadi toner yang baik.

Projek ini melibatkan sintesis resin toner dengan kaedah pempolimeran ampaian. Penstabil koloid yang digunakan dalam pempolimeran adalah poli(vinil alkohol), manakala pemula adalah benzoil peroksida. Pelarut dalam proses pempolimeran ampaian adalah air suling. Tiga siri eksperimen telah dijalankan sepanjang kajian: (i) sintesis kopolimer stirena akrilik berberat molekul rendah, (ii) sintesis kopolimer stirena akrilik berberat molekul tinggi, (iii) Pencampuran kedua-dua kopolimer stirena akrilik dengan berat molekul rendah dan berat molekul tinggi. Nisbah antara kopolimer dengan berat molekul rendah dan tinggi telah dicampur untuk mendapat sifat-sifat yang dikehendaki.

Kromatograf Penelapan Gel (GPC) telah digunakan untuk mengkaji taburan berat molekul; Alat Indeks Aliran Leburan (MFI) menunjukkan keupayaan aliran resin; Kalorimetri Pengimbasan Pembeza (DSC) telah digunakan untuk mengkaji sifat-sifat terma resin; Nombor asid (AN) untuk jumlah kumpulan berasid dalam resin toner. Kesan-kesan bagi nisbah monomer, kepekatan pemula dan kepekatan penyilangan ejen pada sifat-sifat resin dengsan berat molekul rendah dan tinggi telah dikaji. Sifat-sifat resin toner yang disintesis dan resin toner komersial telah dibandingkan.

Resin yang disintesis yang telah dicampur pada nisbah berbeza mempunyai suhu peralihan kaca, T_g dalam lingkungan 56 - 69^oC; MFI dalam lingkungan 13 – 55 g/10 min; AN dalam lingkungan 2.5 - 3.4 mg KOH/g; M_w dalam lingkungan 7.00×10^3 – 3.20×10^3 Daltons (1 Daltons = 1.66×10^{-27} kg) dengan mengandungi 9 - 14 % yang tidak larut dalam THF. Tiga resin yang disintesis yang mempunyai sifat-sifat yang dikehendaki telah diuji untuk menghasilkan toner dalam skala makmal. Tiga siri ujian cetakan telah dijalankan untuk menilai mutu cetakan dengan kaedah membandingkan mutu cetakan toner komersial. Kepadatan imej yang diperolehi daripada imej yang diuji adalah dalam lingkungan 1.33 – 1.58, nilai ini adalah sebanding dengan toner komersial. Kepadatan latar belakang adalah dalam lingkungan 0.12 – 0.13, nilai ini adalah lebih tinggi daripada toner komersial.

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CONTENTS

CHAPTER THREE: RESULTS AND DISCUSSION

APPENDIX

LIST OF FIGURES

CHAPTER ONE: INTRODUCTION

CHAPTER TWO: EXPERIMENTAL

CHAPTER THREE: RESULTS AND DISCUSSION

APPENDIX A: Machines used to produce raw toner

APPENDIX B: Instruments used for sample characterization

APPENDIX C: DSC profiles of toner resins and toners

APPENDIX D: TGA profiles of toners

APPENDIX E: GPC profiles of toner resins and toners

LIST OF TABLES

CHAPTER THREE: RESULTS AND DISCUSSION

APPENDIX G: Calculation of Acid Number of High Molecular Weight Styrene Acrylic Copolymers and Blended Resins

APPENDIX H: Calculation of Percentage of THF Insoluble Fraction of High Molecular Weight Styrene Acrylic Copolymers and Blended Resins

APPENDIX I: Estimation of Tg by using Fox equation and Gordon-Taylor equation

LIST OF ABBREVIATIONS

AA	Acrylic Acid
AN	Acid Number
BA	Butyl Acrylate
BD	Background density
BPO	Benzoyl Peroxide
CCA	Charge Control Agent
CLA	Cross-linking Agent
CPT	Chemically Produced Toner
DSC	Differential Scanning Calorimetry
GPC	Gel Permeation Chromatography
ID	Image Density
MFI	Melt Flow Index
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
M_p	Peak Value for Molecular Weight Distribution
M_z	Z-average Molecular Weight
Q	Polydispersity Index
MWD	Molecular Weight Distribution
T_g	Glass Transition Temperature