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Name of Degree: Ph.D

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

"Studies on chitosan based films obtained by blending with agar and poly vinyl alcohol"

Field of Study: Physical Chemistry

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ABSTRACT

This work deals with blends of chitosan (CS) with agar (AG) and/or polyvinyl alcohol (PVA) at different proportions in solution and solid film forms with the aim to develop biopolymer blends with established rheological, mechanical, thermal, swelling and surface properties. In the first part of this work, a number of blended solutions of (CS/AG), (CS/PVA) and (CS/AG/PVA) at different proportions (considering chitosan as the major component) were prepared. The effects of temperature, shear rate, shearing time and storage time on the rheological properties of the three blended solutions with respect to the apparent viscosity and the shear stress were investigated in correlation with the shear rate. Rheological results showed that Newtonian-like behavior was observed at temperatures from 40 to 55^{o}C for the CS/AG blended solutions at low concentrations of AG, whereas a shear thinning behavior (pseudoplastic non-Newtonian behavior) was remarkably observed at high concentrations of AG. A Newtonian behavior was observed at the same range of temperature for all CS/PVA blended solutions with various ratios. In addition, the ternary blended solutions of CS/AG/PVA were found to display a shear thinning behavior only at high concentrations of AG and PVA. The increase in the viscosity and the appearance of shear thinning behavior with the increase in the concentration of AG in CS/AG blended solutions and both of AG and PVA in CS/AG/PVA ternary blended solutions could be due to the existence of good interaction among the components. The viscosity of the three blended solutions was found to be a function of temperature and follow Arrhenius equation. Studying the effect of shearing time on the apparent viscosity of all blended solutions did not show any significant differences at all shearing times applied in this study except the proportion 50/50 for CS/AG blended solution and the ratios containing higher concentrations than 15% of each of AG and PVA for the CS/AG/PVA ternary blended

solutions. In addition, different behaviors were observed for the blended solutions when the period of storage was extended to three weeks. In the second part of this work, CS/AG, CS/PVA and CS/AG/PVA blended films were prepared by blending different proportions similar to those in blended solution. The chemical structure and the morphology of the obtained blended films were investigated using Fourier transform infrared (FTIR) and field emission scanning electron microscope (FESEM). The thermal stability of the blended films was also studied using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Generally, it was found that CS, AG and/or PVA form highly compatible blends and their films displayed homogenous and smooth surface properties compared to their individual pure components. Studying the mechanical properties of the films showed some improvement in tensile strength (TS) with respect to CS/PVA and CS/AG/PVA blended films with respective increase in AG and /or PVA contents, but a decrease in the TS of CS/AG blended films with increasing AG content was observed. Blending of AG and/or PVA with CS at all proportions was found to enhance the swelling of the obtained films compared to the pure CS film. Static water contact angle measurements confirmed the affinity of the blended films towards water, which demonstrates that blending with AG and/or PVA can improve the wettability of the blended films. Based on the findings of this study, it can be suggested that blending of AG and/or PVA with CS brings about new biomaterials with improved tensile strength, swelling and enhanced wattability while maintaining similar thermal properties as the main component (CS).

ABSTRAK

Penyelidikan ini melibatkan adunan kitosan (CS) dengan agar (AG) dan/atau polivinal alcohol (PVA) pada kadar yang berlainan dalam bentuk larutan dan filem pepejal. Tujuan penyelidikan ini adalah untuk menyediakan adunan biopolimer dengan sifat-sifat rheologi, mekanikal,terma, pembengkakan dan permukaan yang mantap. Di bahagian pertama kerja ini sebilangan adunan larutan daripada (CS/AG), (CS/PVA) dan (CS/AG/PVA) pada kadar yang berlainan (dengan mengira kitosan sebagai komponen utama) disediakan. Kesan suhu, kadar ricih, masa ricihan dan masa storan ke atas sifat-sifat rheologi ketiga-tiga adunan larutan berhubung dengan kelikatan yang diperhatikan dan regangan ricih dikaji seiring dengan kadar ricih. Keputusan rheologi menunjukkan bahawa kelakuan ala Newton diperhatikan pada suhu dari 40 ke 55^{o}C untuk adunan larutan CS/AG pada kepekatan AG rendah, manakala kelakuan penipisan ricih (kelakuan pseudoplastik bukan Newton) diperhatikan dengan jelas pada kepekatan AG yang tinggi. Kelakuan ala Newton diperhatikan pada julat suhu yang sama untuk semua adunan larutan CS/PVA dengan nisbah berbagai. Sebagai tambahan, adunan larutan terner CS/AG/PVA didapati memperlihatkan kelakuan penipisan ricih hanya pada kepekatan AG dan PVA yang tinggi. Pertambahan kelikatan dan penjelmaan kelakuan penipisan ricih dengan peningkatan AG dalam adunan larutan CS/AG dan kedua-dua AG dan PVA dalam adunan larutan terner CS/AG/PVA mungkin disebabkan oleh kehadiran interaksi yang baik diantara komponen. Kelikatan ketiga-tiga adunan larutan didapati berfungsikan suhu dan menuruti persamaan Arrhenius. Kajian kesan masa ricihan ke atas kelikatan yang diperhatikan bagi kesemua adunan larutan tidak menunjukkan perbezaan signifikan pada semua masa ricihan yang dikenakan dalam kajian ini kecuali kadaran 50/50 untuk adunan larutan CS/AG dan nisbah yang mengandungi lebih daripada 15 % setiap AG dan PVA untuk adunan terner larutan CS/AG/PVA.

Sebagai tambahan, kelakuan yang berlainan diperhatikan untuk adunan larutan dimana tempoh storan diperpanjangkan kepada tiga minggu. Pada bahagian kedua kajian ini, adunan filem CS/AG, CS/PVA dan CS/AG/PVA di sediakan dengan mengandun kadaran yang berbagai sama seperti dalam adunan larutan. Struktur kimia dan morfologi adunan filem yang diperolehi telah dikaji menggunakan inframerah Fourier terubah (FTIR) dan mikroskop medan pancaran imbasan elektron (FESEM). Kestabilan terma filem yang diadun juga dikaji menggunakan analisis terma gravimetrik (TGA) dan kalometri imbasan pembezaan (DSC). Secara umum, didapati CS, AG dan/atau PVA membentuk adunan yang amat serasi dan filemnya memperlihatkan sifat-sifat permukaaan yang homogen dan licin berbanding dengan komponen individu masing-masing yang tulen. Kajian keatas sifat mekanikal filem menunjukkan sedikit kemajuan dalam kekuatan regangan (TS) berhubung dengan adunan filem CS/PVA dan CS/AG/PVA seiring dengan pertambahan dalam kandungan AG dan/atau PVA, tetapi pengurangan dalam TS untuk adunan filem CS/AG dengan pertambahan kandungan AG diperhatikan. Adunan AG dan/atau PVA dengan CS pada kesemua kadaran didapati membantu pembengkakan filem yang diperolehi berbanding dengan filem CS tulen. Pengukuran sudut sentuhan air yang static mengesahkan afiniti adunan filem terhadap air dan ini menunjukkan bahawa adunan dengan AG dan/atau PVA boleh meningkatkan pembasahan adunan filem. Berdasarkan kepada hasil kajian ini, bolehlah dicadangkan bahawa pengadunan AG dan/atau PVA dengan CS membawa kepada biobahan yang baru dengan kekuatan regangan, pembengkakan yang lebih baik, dan pembasahan yang meningkat sementara mengekalkan sifat-sifat terma yang serupa dengan komponen utama (CS).

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LIST OF SYMBOLS

E_a	Activation energy (J mol^{-1})
R	The gas constant (J mol^{-1} K^{-1})
T	The absolute temperature (K)
T_g	Glass transition temperature (^oC)
T_m	Melting temperature (^oC)
W_1	The weight of completely dried sample (g)
W_2	The weight of swelled sample (g)

LIST OF ABBREVIATIONS

AC	Acetic acid
AG	Agar
cP	Centipoise
CS	Chitosan
D	Dalton
DA	Degree of acetylation
DD	Degree of deacetylation
DSC	Differential scanning calorimetry
GPC	Gel permeation chromatography
MW	Molecular weight
PVA	Poly vinyl alcohol
POE	Poly ethylene oxide
SD	Standard deviation
SEM	Scanning electron microscopy
SF	Silk fibroin
TG	Thermogravimetric
TS	Tensile strength