THE EFFECT OF FIBRES CONTENT ON COTTON REINFORCED ALBUMEN COMPOSITES

Y. YUSLIZA AND A. ZURAIDA

Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic University Malaysia (IIUM), Jalan Gombak, 53100 Kuala Lumpur, Malaysia.

zuraidaa@iium.edu.my

ABSTRACT: The effect of fibres content on mechanical properties and thermal stability of the cotton/albumen composites (CAC) were investigated and presented in this paper. The composites having 0%, 3%, 6%, 10%, 13 %, and 16% w/w of cotton fibres were considered. Hands lay-up technique was used to prepare the CAC specimens which were dried for 24 hours before being characterised and evaluated for their mechanical performance. The thermal stability of the composites were characterised by thermogravimetry analysis. The tensile strength and impact resistance of CAC were found to be maximum at 8.7 MPa and 19.0 kJ/m^2, respectively. Analysis on the morphological structure by scanning electron microscope (SEM) revealed that the mechanical properties of the composites depend on good wettability and adhesion between fibres/matrix.

ABSTRAK: Kesan kandungan gentian keatas sifat mekanikal dan kestabilan termal diselidiki dan dibentangkan dalam kertas ini. Komposit yang mengandungi 0%, 3%, 6%, 10%, 13 %, dan16% peratus berat gentian kapas telah diambil kira. Teknik *"hands lay-up'* telah digunakan untuk menyediakan spesimen komposit kapas/ albumin ini, dimana ianya telah dikeringkan selama 24 jam sebelum dilakukan pencirian dan penilaian mekanikal. Kestabilan termal komposit ini diuji melalui analisis temogravimetri. Kajian mendapati nilai kekuatan regangan dan penyerapan hentaman adalah maksima masing-masing pada 8.7 MPa dan 19.0KJ/m^2. Analisis struktur morfologi melalui Mikroskop Imbasan Electron (SEM) menunjukkan bahawa sifat mekanik komposit ini bergantung kepada penyelaputan dan pelekatan diantara gentian dan matriks.

KEYWORDS: *Composite, fibres, lay-up, mechanical properties, thermal stability.*

INTRODUCTION

The depletion of petroleum resources coupled with increasing awareness of environmental issues; provide the impetus for new engineered materials and products that are independent of fossil fuels and compatible with sustaining the environment. Recent attention has focused on the development of environmentally friendly natural composites derived from natural or synthetic resin materials reinforced with natural fibres. Natural cellulose fibres have been replacing synthetic fibres in many composite applications due to their biodegradability, improved products' acoustics, higher processing and operational safety, higher strength and stiffness, lower weight and lower production cost [1-2].

For many years, numerous researches have focused on introducing matrix materials from biopolymer resources, such as proteins, lipids and polysaccharides. Protein-based biopolymers in particular have the advantage of biodegradability and higher degradation rates among the other fast-degrading polymers. A wide variety of proteins are produced at huge scale, for instance, wheat gluten, soy and pea proteins from vegetables resources; egg albumen, fish myofibrillars and wool keratin proteins from animal resources [3]. In addition, the protein networks have an important role in providing mechanical properties of the encapsulating matrix. The strength of a protein network could be manipulated during the structuring process, or gelation, by balancing the attractive and repulsive forces among polymer molecules, polymer network and surrounding solvent [4].

Egg white proteins (egg albumen) are highly functional food proteins and are frequently used in food matrix applications due to their ability to form gel networks, increase solution viscosity, and stabilize emulsions and foams [5]. Egg albumen consists mainly of 10-15% numerous proteins dissolved in water and is 95.5% protein on dried weight basis [4]. However, for non-food applications, protein denaturation turns out to be a further thrust for the design of new materials. Protein denaturation takes place when the protein loses its native state and thus ceases to be biologically active. It involves the disruption of both its secondary and tertiary structures. Denaturation may occur because of changes of several external parameters, such as increasing temperature, pressure, denaturant concentration and pH, or the presence of salts, acids, alkalis, alcohols, or denaturing agents like urea [2-5].

Cotton can be categorized as a natural cellulose fibre that is a highly crystalline with high-molecular weight biomaterial [6]. A new method of fabricating biodegradable cellulosic composite nonwoven materials based on cotton and natural fibres has been prepared by sandwiching and hot pressing [7]. Another recent article reports on the use of cotton fibres with a plant-oil to produce a polymer material made of triglycerides and polycarbon acid anhydrides (PTP) that enables the combination of thermoset composites with high stiffness values and improved glass transition temperature as well as good impact properties [8].

The objective of this paper is to investigate the thermal stability and mechanical properties of the CAC. The mechanisms of reinforcement in the composites are analysed in terms of tensile strength, elastic modulus, elongation at break and impact strength. Scanning electron micrographs on the cross-sectioned surfaces are examined and discussed to correlate with the composite's strength.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Composites Preparation

Fresh eggs were obtained from Farm Sdn Bhd (Malaysia). A hen's egg albumen contains approximately 10% protein mixture dispersed in water with specific gravity (relative) density of 1.03. The natural fibres of cotton (*Gossypium hirsutum*) with a density of 1.51 g/cm^3 were purchased from Able Enterprise (M) Sdn Bhd (Malaysia). In this work, the fibres were used without further chemical treatment.

The matrix preparation of the aqueous albumen was obtained by separating the egg white from egg yolk and chalazae. The aqueous albumen was denatured by beating for 5 minutes into froth and left for 24 hours at room temperature before the remaining dirty froth was removed. The albumen was filtered through muslin to get a yellowish and homogeneous albumen solution with a pH value of 9.0. The CAC with different fibres content of 0%, 3%, 6%, 10%, 13 %, and 16% w/w were fabricated by hands lay-up technique and were subjected to load of 100 N for 30 minutes. The samples were dried at room temperature (25°C) for 14 days and conditioned for at least 24 hours at 20$\pm$ 2% relative humidity before the samples were carried out for mechanical testing.

2.2 Materials Characteristics

The morphology of raw albumen before beating and after beating was observed using an Inventor Contrast Phase Microscope. The density of raw albumen and cotton fibres were measured in accordance to ASTM D3800. The structure and diameter of the fibres were examined using the scanning electron microscope (SEM).

2.3 Analysis and Testing

The structures of the samples were examined with X-ray diffraction experiments using a XRD Shimadzu 6000 diffractometer. The X-ray diffraction patterns were performed with the CuKα radiation (λ = 0.154 nm) operated at 40 kV and 30 mA, with scanning 2θ angles from 5° to 30° at a scanning rate of 2° min^{-1}.

Thermal degradation studies were performed by thermogravimetric measurements using a Pyris Diamond TG/DTA thermal analysis controller. Samples with the weight of 8-10mg were heated from 25 to 900°C at a heating rate of 10°C/min under air atmosphere. The mass loss was recorded as a function of temperature.

Tensile test of the samples were conducted in the strain rate of 50 mm/min by using a universal testing machine (Instron Model LLOYD instruments). The tensile tests were performed in accordance to ASTM D3039. Charpy impact tests were carried out using an Advanced Pendulum Impact Dynosco (model API-230-0) in accordance to ASTM D256. The test results were typically the average of five specimens of each test.

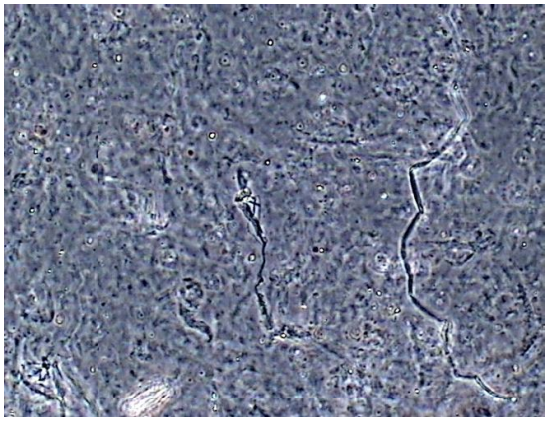
Morphological examinations of the samples were carried out using a scanning electron microscope (SEM model Hitachi S-2500) with an operating voltage of 15kV. Surface of the samples were sputter-coated with gold-palladium prior to SEM observations and mounted on aluminium holders using double-sided electrically conducting carbon adhesive tabs. This is important to prevent electrical charging during examination, and to get better resolution as well as quality image for the non-conducting materials.

3. RESULTS AND DISCUSSION

Morphology structures of the pristine albumen were examined using an Inventor Contrast Phase Microscope. The micrograph in Fig. 1(a) shows that before the albumen was beaten during the matrix preparation, the three dimensional shape of albumen protein

showed "globular" conformation in its native state. The globular proteins are composed of a rounded, compact mass of intertwined protein chains due to the interrelations of the amino acids that always exist in the lowest free energy state [9]. In this state, the hydrophobic (molecule that is repelled from a mass of water) amino acid side chains would cluster in the centre of the molecules, away from the watery environment, while the hydrophilic (molecule that can bond with water through hydrogen bonding) amino acid side chains are attracted to the outside of the molecules, near the watery environment.

a)



b)

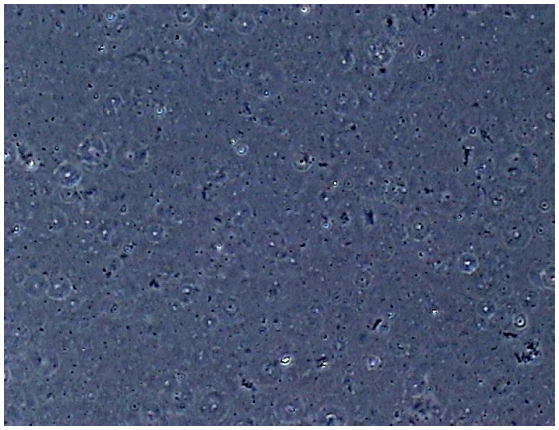


Fig. 1: Micrograph of pristine albumen at 100X magnification showing (a) the folded structure of proteins before beating, and (b) the unfolded structure after beating.

After the beating process the molecules unfold until they stretch-out with no specific shapes, as shown in Fig. 1(b). As beating is increased the air is entrapped, further stretching the albumen. This shows that the albumen was denatured by the shear forces of mechanical energy during whipping. The shear can cause the proteins to unfold, thus exposing its hydrophobic groups to the non-aqueous phase. The presence of shear force helps to accelerate the denaturation process and introduce more air into the solution, leading to the formation of froth. This is because of the major protein in albumen – ovalbumin's sensitivity to the shear forces applied during whipping [9].

Denaturation of proteins involves disruptions of both the secondary and tertiary structures from the normal alpha-helix and beta sheets into a random shape. The primary

structure of proteins consisting of sequence of amino acids however, remains the same due to the lack of reactions that is not strong enough to break the peptide bonds [10]. In addition, this unfolding protein would lead the hydrophobic groups present to insert into the non-polar phase and causing an increase in water binding. Water binding is the ability of protein to entrap water (H_2O) molecules due to the interaction of the hydrophobic and hydrophilic amino acids and polar groups with water. As reported in previous study, the water binding capacity of a denatured protein is generally about 10% greater than that of the native protein [11].

An important factor influencing reinforcement effect of natural fibres used is due to their high fibres aspect ratio (length/diameter). The aspect ratio of most typical cotton fibres is approximately 2000 [2]. The high aspect ratios would give rise to greater reinforcement of the cotton fibres reinforced albumen composites. In addition, cotton fibres are also hydrophilic in nature due to their high cellulose content (85-90%). Due to the nature of cellulose structure, many hydroxyl (OH) groups are available for interaction with water molecules via hydrogen bonding [2]. These hydroxyl groups form hydrogen bonds inside the macromolecule itself (intramolecular) and between other cellulose macromolecules (intermolecular). The result of the density test of the cotton fibres measured by densitometer is 1.5-1.6 g/cm^3. SEM of the cotton fibres as shown in Fig. 2 shows that a single cotton fibre has widths in the range of 8.0 to 12.0 μm, and lengths in the range of 2.0 to 5.0 cm.

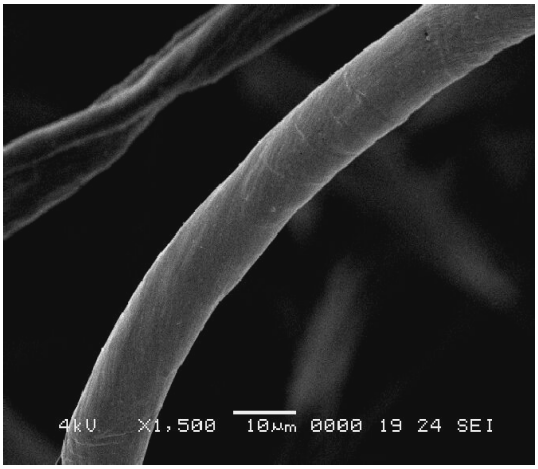


Fig. 2: SEM showing the image of single cotton fibres.

The thermogravimateric analysis (TGA) was employed in the composites to determine both the degradation temperatures and the decomposition behaviour of inorganic and organic components in the materials. The TG curves obtained for the CAC, cotton fibres and pristine albumen are presented as in Fig. 3. It is observed that the TG curve of the pristine albumen as in Fig. 3a shows a weight loss of water vaporization (drying) at T≤100°C and thermal decomposition at T>250°C. In the second region from 250 to 450°C, the albumen experiences a small weight loss due to thermal decomposition of the protein into volatiles. In the third region at temperature range of 450 to 600°C, the albumen continues to decompose slowly with 10% of the weight loss and the trend remains constant.

The degradation of cotton fibres at T≤100°C as in Fig. 3b also corresponds to water evaporation and at 250°C where the decomposition of the fibres begins. Since the cotton fibres consist of 85-90 % weight of cellulose, thus the first degradation step involves formation of 'active' cellulose. As mentioned by Spoljaric et al. [12], this is believed to be associated with scission of the glycosidic bonds, caused by transglycosylation. The second step consists of dehydration of pyranose rings, producing anhydrocellulose and resulting in mass loss. Further degradation of pyranose produces CO_2, various volatile gases and unsaturated cyclic compounds.

Figure 3c also shows that the CAC two-step degradation below 600°C, in the ranges 50-250°C and 250-350°C corresponds to the removal of water and degradation of the cotton. It can be seen that the weight loss of CAC due to water evaporation was slightly greater than the cotton fibres because of its higher water content. Thermal stability of the CAC was significantly increased to 475°C, which is higher than that of pristine albumen though slightly lowered compared to the cotton fibres by 125°C.

The stress-strain curves of the CAC having different cotton fibres content are shown in Fig. 4. When the fibres content increases the composite strengthens and becomes stiffer but more ductile when compared to the pristine albumen. The addition of cotton increases the ability of the weak albumen to stretch and carry a load. The stress-strain behaviour of the CAC initially consists of linear region (elastic behaviour), then elongates with further increase in stress and finally fails almost without necking behaviour. In comparison, the pristine albumen shows less glassy and rubbery characteristics.

The ultimate tensile strength of the CAC having various cotton fibres (0%, 3%, 6%, 10%, 13 %, and 16% w/w) is presented in Fig. 5. The results show that there is an increase in tensile strength with increasing fibres content. Maximum variation was observed for the composite having a fibres' loading of 10% w/w cotton. Unsupported albumen is soft with a tensile strength of about 0.3-0.7 MPa and a modulus of about 14-28 MPa [12]. It shows that the tensile strength of the CAC is increased at least by 10 times than that of the pristine albumen. The reinforcement effect concerning stiffness of the composite displays the highest Young's modulus of 404 MPa at 10 % w/w cotton. The increase indicates that the cotton has good reinforcement ability on the matrix albumen.

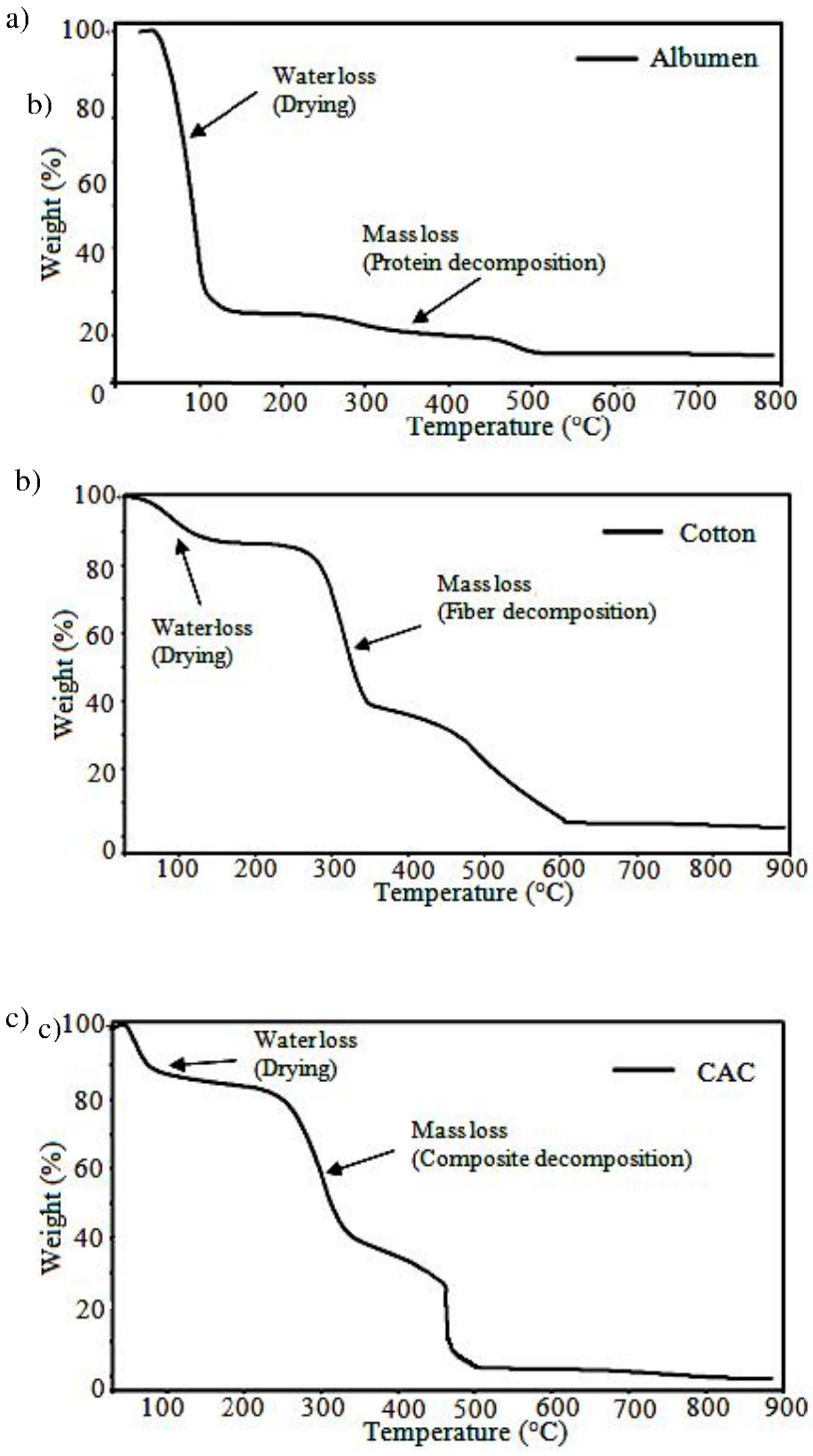


Fig. 3: (a)-(c) Thermogravimetric curves obtained for pristine albumen, cotton fibres, and CAC having 10 % cotton fibres.

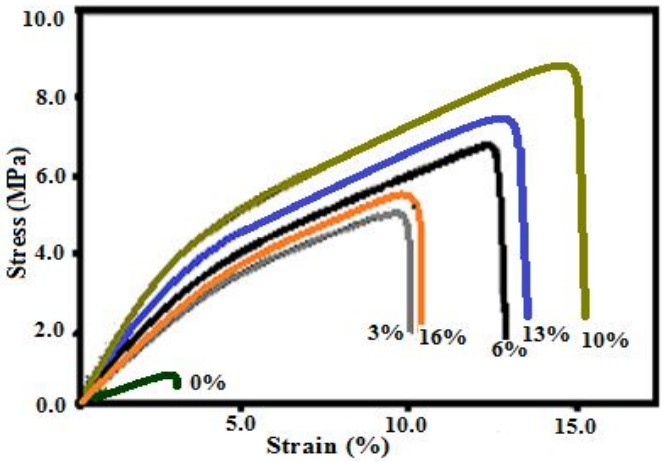


Fig. 4: Stress-strain curves obtained from CAC having various cotton fibres content.

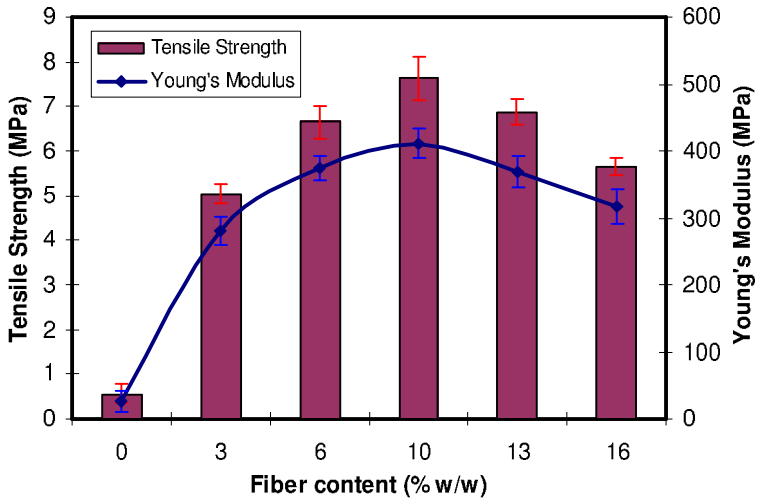


Fig. 5: The effect of fibres content on tensile strength and Young's modulus of the CAC having various fibres content (0%, 3%, 6%, 10%, 13 %, and 16% w/w).

The compatibility and hydrophilic similarity of the cotton and albumen strengthens the interaction between fibres/matrix interfaces. This good adhesion at the interface of fibres/matrix is effective for the stress transfer and load distribution, and improves mechanical properties of the composites [14]. The incorporation of further fibres content causes the composite to experience a critical drop in strength possibly because of insufficient flow of albumen matrix around the fibres, and thereby introducing more voids. In addition, at higher fibres content the fibres act as flaws and crazing occur, thereby forming stress concentration area that lowers stiffness of the composite

Elongation at break of the pristine albumen and CAC are shown in Fig. 6. It illustrates that the composites show the strength-elongation characteristics with the same trends as when the cotton fibres content is increased. In this case, a lower tensile strength and comparatively higher elongation at break, characterizes the material behaviour of applied

albumen as matrix. As depicted from earlier study [13], the pristine albumen was found moderately extensible with a 1.5-3.4 % of strain. On the other hand, the elongation of typical raw cotton fibres is 7-8% of strain [2]. As expected, the incorporation of cotton fibres increases the CAC's elongation at break varying from 10-16% of strain. The same strength-elongation characteristic of the CAC seems to have a considerable influence in good impact resistance at higher fibres content. This can be observed from Fig. 7, wherein the trend for impact strength also increases by a higher elongation at break attributing to the high elongation characteristics particularly at room temperature.

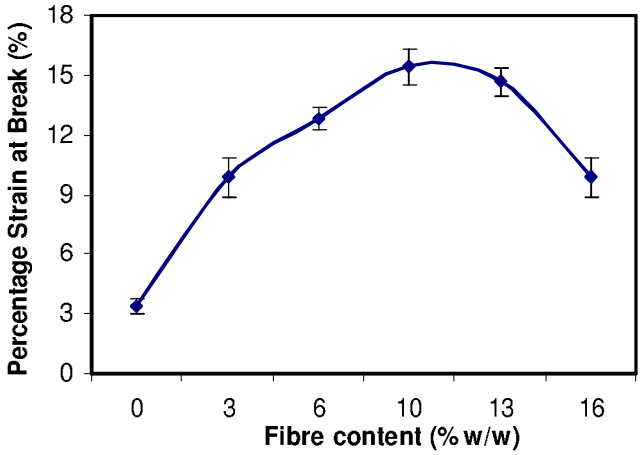


Fig. 6: Elongation at break of the CAC having different fibres content

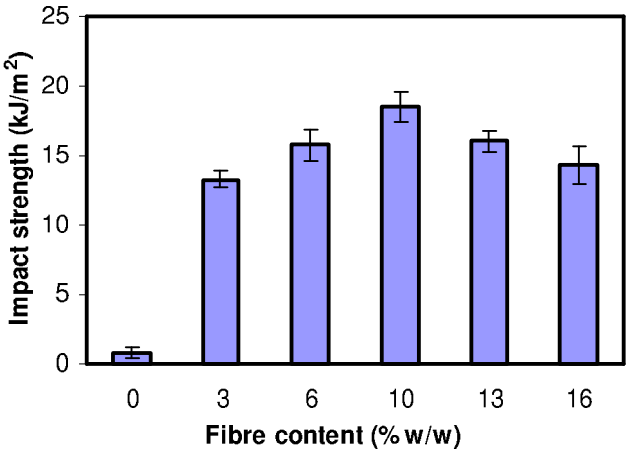


Fig. 7: Impact strength of CAC with various fibres content

The maximum of impact strength is observed with the CAC having a fibres content of 10% w/w. The impact strength of the pristine albumen increases with increasing fibres content from 0 to 10% in the range of 1.0 to 19.0 kJ/m^2. Similar trend is found in other studies when the incorporation of cotton fibres possibly increase the impact resistance of composites structures [8,15,16]. In addition, another study shows that fibres' fineness also plays a key role in the impact strength properties of composites Typical cotton fibres' widths average between 12.0 -15.0 µm in diameter, almost three times finer than kenaf

fibres (43.0 µm) [17]. Fibres with small diameters always lead to an improvement in their surface to volume ratios, which increases the contact surface between fibres and matrix [18]. Utilization of fine cotton fibres increases the number of actually embedded fibres and offers the advantage of an increasing absorption for impact energy.

Microscopic examination on the cross sections of the CAC was carried out by using SEM. The microstructure of the composites as can be seen in Fig.8 reveals that the cotton fibres are well embedded in the albumen matrix. This phenomenon is due to a strong interaction between cellulose fibres and the protein matrix, as established in the literature reviewed [19]. In addition, the cotton fibres have high degree of crystallinity (65-70%) that is hydrogen bonded to each other. As elucidated from a previous related study [13], when the fibres are in contact with aqueous albumen solution, the inter-fibre hydrogen bonds are disrupted by water. Upon drying, the water is removed and the albumen dries across the inter-fibre bonding sites. The result is a fibre-adhesive-fibre composite consisting of inter-fibre albumen bonds. Though the pristine albumen is weak, the albumen adhesive holding the inter-fibre sites together is stronger than the equivalent made of hydrogen bonds. A strong inter-fibre albumen bond at the interface of fibres/matrix is effective for the stress transfer and load distribution that attributed to the substantial increase in mechanical properties of the CAC with increased fibres content.

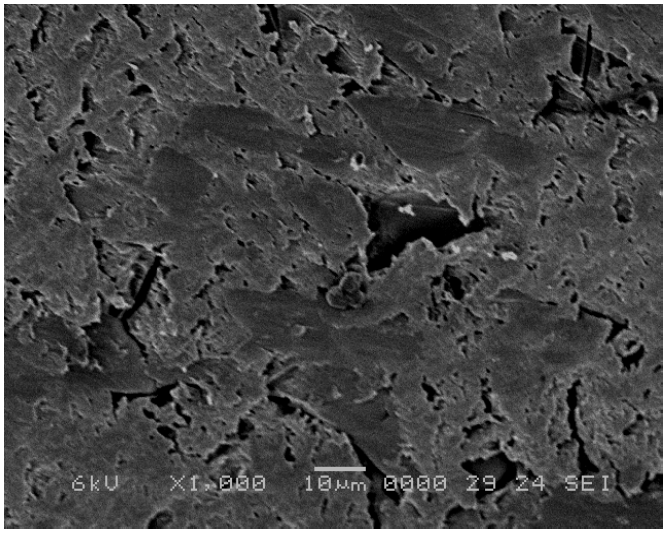


Fig. 8: SEM showing the fibres embedded into the albumen composite.

SEM examinations on the CAC display the phenomenon of matrix cracking as in Fig. 9. Albumen cracking results when humidity or water content changed slowly. In this case, the cracked albumen acts like rubber, offering low resistance to stress or strain and yielding a normal amount before failure [13]. In fact physical handling of the pristine albumen has pronounced rate of strain dependent properties. In the fast strain rate, albumen is brittle, and in the slow it is rubbery. Thereby faster drying would presumably result in greater cracking. The typical cotton fibres swell and shrink no more than 1-2% when wet and dried [13]. Therefore when the CAC shrinks upon drying, the strain limit of the albumen would be exceeded, which results in matrix micro-cracking.

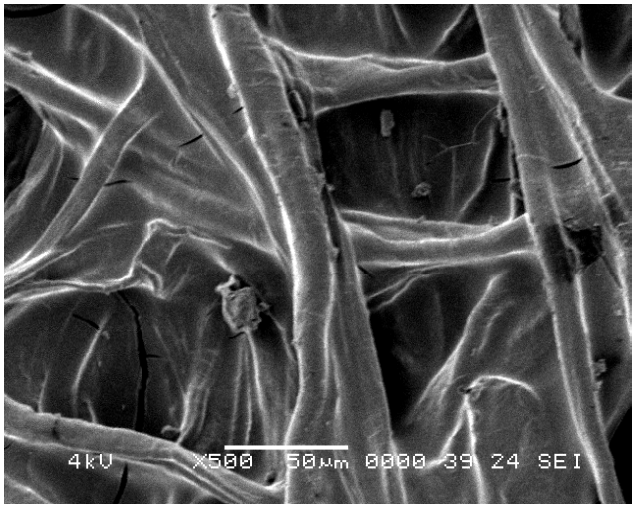


Fig. 9: SEM showing the matrix encapsulation and the phenomenon of matrix cracking.

The development of strength in the composite generally depends on the existence of strong fibres-matrix interface, which is enhanced with the interlocking and entanglement of the cotton fibres. Thus Fig. 10a – c demonstrate the observations of the morphological structure of the CAC with increasing cotton fibres content of 3%, 10% and 16% w/w respectively.

At low fibres content of 3% w/w cotton fibres (Fig. 10a), the fibres act as a flaw causing highly localized strains to occur in the matrix even at low stress, resulting in poor mechanical performance due to the embrittlement of the albumen. The clear surface observed in the composite demonstrates the presence of excess albumen in comparison to the cotton fibres. At 10% w/w of cotton SEM observation reveals the optimization of mechanical strength of the CAC due to the close packing and entanglement of the fibres, as well as sufficient wettability of albumen onto the cotton fibres (Fig. 10b). Nevertheless, as more (greater than 10% w/w cotton fibres) get incorporated (Fig. 10c), less albumen matrix is available to provide complete wetting onto the cotton fibres surface, resulting in the formation of some pores, which in turn leads to poor fibres-matrix interphase thus reducing the mechanical performance. The fibres act as flaws causing crazing to occur, thereby forming stress concentration areas that reduce the mechanical strength of the composite [20].

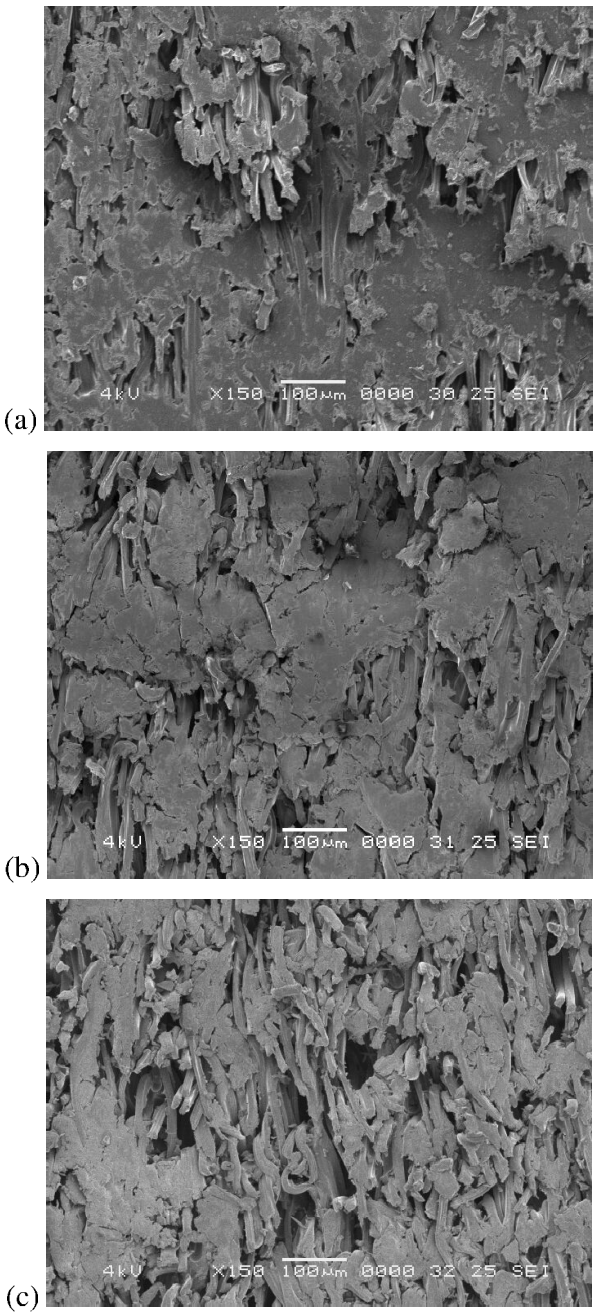


Fig. 10: SEM micrographs of the CAC show cross sections with different fibres loading (a) 3% cotton, (b) 10% cotton, and (c) 16% cotton.

4. CONCLUSION

Unsupported pristine albumen is very weak. Results of this study indicate that the use of cotton fibres could play an important role in optimizing the performance of albumen composite through enhancements of its morphological and mechanical properties. The addition of cotton fibres improves the mechanical properties of the pristine albumen with

increasing fibres contents with the optimum mechanical strength achieved with 10 % w/w cotton. The maximum tensile and impact strengths of CAC with 10 % w/w cotton were 8.7 MPa and 19.0 kJ/m^2 respectively. In this case, a moderate tensile strength and comparatively higher elongation at break of the CAC characterizes the material behaviour of applied albumen as matrix. In addition, the strength-elongation characteristics with high elongation ~~of~~ cotton fibres compared to pristine albumen yields in good impact properties of the CAC. Incorporation of cotton fibres in the albumen greatly increases the thermal stability of the composite to 475°C. Observations through SEM reveal that the mechanical performance of the CAC greatly enhanced the wettability and adhesion between fibres and matrix.

ACKNOWLEDGEMENT

The authors thank eScience Fund Research Grant (Project No. 03-01-08-SF 0039) from the Ministry of Science, Technology and Innovation (MOSTI) for their financial support.

REFERENCES

[1] S.A.R. Hashmi, U.K. Dwivedi and C. Navin. "Graphite Modified Cotton Fibres Reinforced Polyester Composites Under Sliding Wear Conditions". *Wear*, 262, 2007, pp. 1426-1432.

[2] A.K. Mohanty, M. Misra and L.T. Drzal."Natural Fibres, Biopolymers, and Biocomposites". Taylor & Francis Group. United States of America, 2005.

[3] A. Jerez, P. Partal, I. Martinez, C. Gallegos and A. Guerrero. "Egg White-based Bioplastics Developed by Thermomechanical Processing". *Food Engineering* 82, 2007, pp. 608-617.

[4] S. Wongsasulak, T. Yoovidhya, S. Bhumiratana and P. Hongsprabhas. "Physical Properties of Egg Albumen and Cassava Starch Composite Network Formed by a Salt-Induced Gelation Method". *Food Research International*, 40(2), 2007, pp. 249-251.

[5] S. Wongsasulak, K.T. Kit, D.J. McClements, T. Yoovidhya and J. Weiss. "The Effect of Solution Properties on the Morphology of Ultrafine Electrospun Egg Albumen-PEO Composite fibres". *Polymer* 48(2), 2007, pp. 448-457.

[6] L.A. White "Preparation and Thermal Analysis of Cotton-Clay Nanocomposites". *Applied Polymer Science*, 92, 2004, pp. 2125-2131.

[7] X. Zhang. "Investigation of Biodegradable Nonwoven Composites Based on Cotton, Bagasse and Other Annual Plants". Thesis, Louisiana State University, 2004.

[8] J. Mussig. "Cotton Fibres-Reinforced Thermosets Versus Ramie Composites: A Comparative Study using Petrochemical and Agro-based Resins". *J Polym Environ*, 16(2), 2008, pp. 94-102.

[9] P. Messier, "Protein Chemistry of Albumen Photograph". *Photographic Reservation*; 4, 1991, pp. 124-135.

[10] C.E. Ophardt, *"Denaturation of Protein"*. Virtual Chembook. Elmhurst College. c2003.

[11] O.R. Fennema, *"Food Chemistry"*. Third Edition. Food Science and Technology. New York, 1996.

[12] S. Spoljaric, A. Genovese, and R.A. Shanks. "Polypropylene-Microcrystalline Cellulose Composites With Enhanced Compatibilty and Properties". *Composites: Part A*, Available online 5 April 2009, in press.

[13] T. Vitale, and P. Messier. "Physical and Mechanical Properties of Albumen Photographs". *Journal of the American Institute for Conservation*, 3, 1994, pp. 279-299.

[14] L. Dobircau, P.A. Sreekumar, R. Saiah, N. Leblanc, C. Terrie, R. Gattin, and J.M. Saiter. "Wheat Flour Thermoplastic Matrix Reinforced by Waste Cotton Fibres: Agro-Green-Composites". *Composites: Part A*. 40 (4), 2009, pp. 329-334.

[15] U. Kukadia. "Room Temperature Curing of Bio-Based Resins and Preparation of Their Composites". Thesis. University College of Boras, Sweden. 2008.

[16] M.G. Kamath, G.S. Bhat, D.V. Parikh and D. Mueller. "Cotton Fibres Nonvowens for Automotive Composites". Peer-reviewed. *INJ Spring*, 2005, pp. 34-40.

[17] N. Graupner. "Application of Lignin as Natural Adhesion Promoter in Cotton Fibres-reinforced Polylactic Acid (PLA) Composites". *J Mater Sci*, 43, 2003, pp. 5222-5229.

[18] D.H. Mueller. "Improving the Impact Strength of Natural Fibres Reinforced Composites by Specifically Designed Material and Process Parameters". *INJ Winter*, 2004, pp. 31-38.

[19] C.M.O. Muller, J.B. Laurindo and F. Yamashita. "Effect of Cellulose Fibres on the Crystallinity and Mechanical Properties of Starch-Based Films at Different Relative Humidity Values". *Carbohydrate Polymers*, 77, 2009, pp. 293-299.

[20] M. Munirah, R. Abd. Razak and H. Azman. "Characterization and Treatments of Pineapple Leaf Fibres Thermoplastic Composite for Construction Application". Thesis, University Technology Malaysia, 2007.