Online available since 2012/Jun/04 at www.scientific.net
© (2012) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/KEM.512-515.1746

Fabrication and Mechanical Properties of Chitosan-Montmorillonite Nano-composite

Z. J.Shou[1], H.R.Le[2, a], S.Y.Qu[1], R. A. Rothwell[2], R.E.Mackay[3]

[1]School of Engineering, Physics and Mathematics, University of Dundee, Dundee, DD1 4HN, UK

[2]School of Marine Science and Engineering, University of Plymouth, Plymouth, PL4 8AA, UK

[3]Centre for Electronic Systems Research, School of Engineering & Design, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

[a]Corresponding author: huirong.le@plymouth.ac.uk

Keywords: Chitosan, Montmorillonite, Mechanical Properties

Abstract: Chitosan has found various applications in medical implants as well as heavy metal absorbent in waste water treatment. However, the material suffers from low strength and large shrinkage upon dehydration. The current project is aimed to develop a process to fabricate chitosan composites with the addition offunctionalised montmorillonite nanoparticles and to examine the effect of ceramic content on the mechanical behavior of the composites. This paper describes the fabrication of chitosan withmontmorrillonite composites, the mechanical testing of the samples and the mechanical behaviourof the composites. The effects of composition and microstructure on the mechanical properties of the composite are investigated. The results indicate that the nanoparticles are dispersed uniformly in the matrix up to 40wt% using high-speed homogeniser. The elastic modulus increases monotonically with the addition of nanoparticles, but the fracture strength drops due to the defects introduced by the nanoparticles.

Introduction

Chitosan is a natural polycationic polysaccharide obtained by deacetylation of its parent polymer chitin, which is found in the crustacean's shells, insect's cuticle and cell wall of fungi [1-3]. Chitosanexhibits a unique set of physicochemical and biological characteristics, such asbiocompatibility, biodegradability, antimicrobial activity, nontoxicity, physiological inertness, hydrophilicity, remarkable affinity to proteins and high flexibility [2, 4-5]. Hence, chitosan has found numerous applications in various fields such as medical implants, pharmaceutical products, tissue engineering scaffolds, agriculture, nutritional enhancement and food processing [3, 5-6]. Chitosan is insoluble in neutral or alkaline condition. Chitosan is an excellent viscosity-modifying agent in acidic environments due to its high molecular weight and a linearunbranched structure [5].The viscosity of chitosan solution increases with increasing degree of deacetylation, which influences physiochemical properties such as the molecular weight, the elongation at break and the tensile strength [5,7]. Viscosity also has an impact on biological properties such as wound-healing properties and osteogenesis enhancement as well as biodegradation [5,8].

Montmorillonite (MMT) takes a layered structure consisting of an octahedral sheet of alumina or magnesia that is surrounded by two tetrahedral sheets of silica [9-10]. MMT can significantly improve thermal stability and mechanical properties when dispersed in a polymer matrix with a low content, and exerts special behaviour towards chemical species present in water and can also be used to fasten flocculation and improve the flake's textures [9,11]. This paper is aimed to perform mechanical testing on the samples and investigate the effect of different MMT ratio on the mechanical properties.

Materials and methods

Preparation of pure chitosan. Chitosan flakes (provided by Sigma-Aldrich) was dissolved in distilled water (100 ml) added with acetic acid (2 ml) and was agitated using a magnetic stirrer at 500 rpm for 90 min. The temperature was set at 60°C. 12 g of the yielded viscous gelwas poured into anopen mould (52 mm x 30mm x 8mm), which was manufactured using a rapid prototyping machine withABS plastic (uPrint SE). The mould was then placed on a shaking machine for 10 min to remove air bubbles. The samples were kept at room temperature for 48 h to let them dry completely.The thickness of the samples was roughly 2 mm. The dry samples were kept in the distilled water for later mechanical tests before they were dipped in the 5% (w/v) sodium hydroxide solution for 10 min.

The pH of the solution was tested by the pH test strip before it was decanted into the mould and the pH was approximately 4. In terms of the influence of pH on the mechanical properties, some samples needed to be prepared at neutral pH. In order to prepare the neutral pH samples, 5% (w/v) NaOH solution was added drop-wise to the chitosan solution to adjust pH until reaching the neutral whilst agitating samples.

Preparation of chitosan with MMT. Chitosan flakes and appropriate proportions of MMT clay were dissolved in distilled water (100 ml) added with acetic acid (2 ml) and were agitated with a magnetic stirrer at 600 rpm for 90 min. The following procedures were identical with that of pure chitosan preparation.

Table1: The mixture ratio of chitosan and MMT

Samples	Porportion of MMT(%)	weight of chitosan(g)	weight of MMT(g)
Pure Chitosan	0	2	0
Chitosan/MMT	10	1.8	0.2
Chitosan/MMT	20	1.6	0.4
Chitosan/MMT	30	1.4	0.6
Chitosan/MMT	40	1.2	0.8

Mechanical test. The dried samples were cut into standard dog-bone configuration with wide ends and a narrow middlesection using a stamp for mechanical tests (Fig. 1). The wide ends were held firmly by the grips of the Tinius Olsens H5KS machine. The midsection of the specimen with a narrower width (10mm) is expected to fracture would fracturedue to higher stress.

Figure 1: Test sample

The specimen was kept straight by the grips before it was tested at the speed of 30 mm/s. The initial stress range was given from 0-10 MPa, and the gauge length was 50 mm. The software of QMAT would analyse the testing data and calculate the elastic modulus and strength in the form of stress-strain curve.

Microstructure observation. A small piece was cut from the sample and coated with a thin layer of a conductive material (palladium/gold, 20nm thick) as the samples were not naturally conductive. The specimen was placed on a stage which was fixed in the chamber of anenvironmental scanning electron microscope.

Table 2: E-modulus of chitosan-MMT (pH=4 or 7)

Percentage of MMT (%)	E-Modulus/MPa(pH=4)	E-Modulus/MPa(pH=7)
0	8.21	9.74
10	8.45	10.16
20	9.19	11.36
30	10.13	15.89
40	11.29	21.53

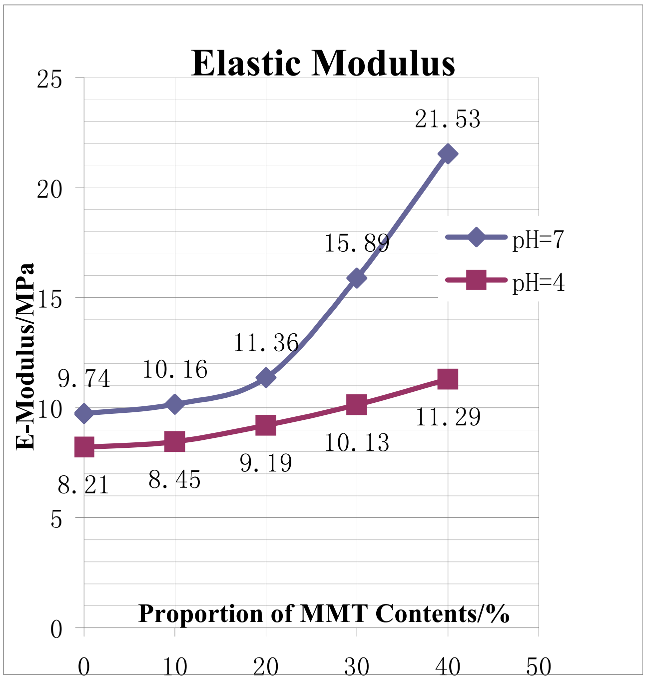

Figure 2: Elastic modulus of chitosan-MMT nano-composite

Results and analysis

Elastic modulus. The elastic moduli of different chitosan-MMT nano-composite made in acidic environment are all calculated to be around 10 MPa, and the value increase with the proportion of MMT in the nanocomposites. Table 2 shows the effect of MMT on the elastic modulus of the chitosan-MMT nano-composites.

With the chitosan-MMT nano-composite prepared at neutral pH condition with different ratios of MMT content, the elastic modulus increases asthe proportion of MMT increases. The elastic modulus of the 40% chitosan-MMT nano-composite is 2.2 times higher than that of the pure chitosan.

The effects of MMT contents and pH on the elastic modulus are shown in Figure 2. Within the composition range investigated, the elastic moduli of acidic and alkaline chitosan-MMT nano-composites increase with the MMT contents, reaching their maxima at an MMT proportion of 40%. This is owing to the dispersion toughening of the clay particles. The nano-composites prepared at higher pH yield better elastic moduli. The higher elastic moduli of composites prepared at neutral condition, when compared to that at acidic condition, is associated with the cross-linking of chitosan molecules with the addition of sodium hydroxide.

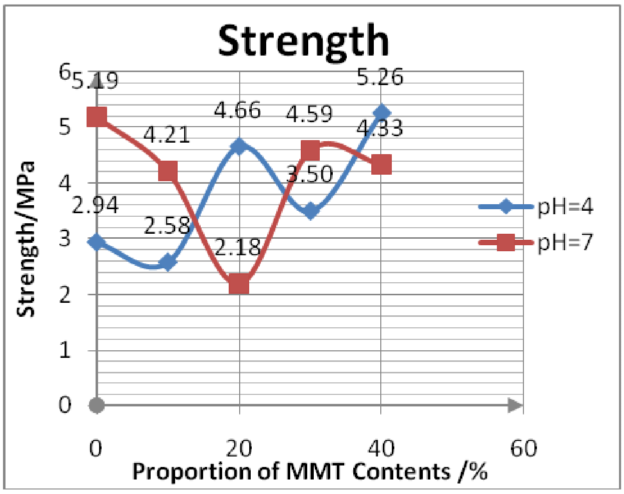

Figure 3: Strength of chitosan-MMT nano-composite

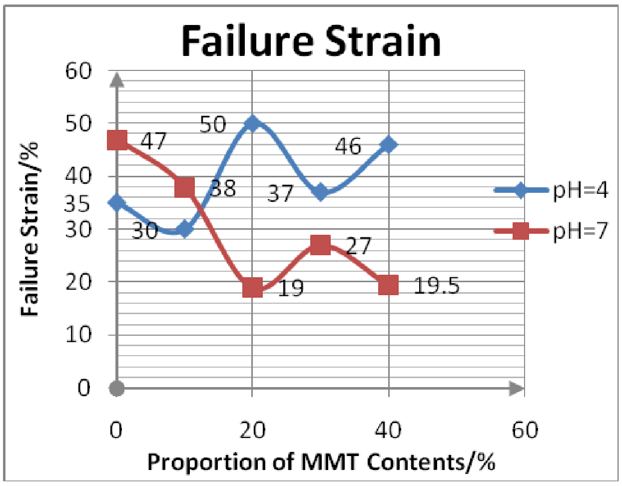

Figure 4: Failure strain of chitosan-MMT nano-composite

Strength and failure strain. The effects of MMT contents and pH on other mechanical properties such as strength and failure strain are shown in Figure 3 and Figure 4. Under the compositions investigated, the strength of the acidic chitosan-MMTnano-composite fluctuates with the proportion and reaches its maxima at 40% of MMT, while the strength of the more alkalinenano-composite reaches its maxima at 0% and touches the bottom at 20% of MMT. With regard to the nano-compositeprepared in acidic pH, the strength of 40% MMT composite is almost 2 times higher than that of 10% MMT composite.Except for the 20% MMT contents, the strengths of nano-composite prepared in neutral pHare within a small range from 4.21 MPa to 5.26 MPa. The general trends of the strength of composites prepared under different pH are distinctive.

Similar to the strength changing trend, the strain-proportion curves are also undulant. With the nano-compositepreparedin acidic pH, the failure strain can reach a maximum value of 50% at a content of 20%, where the strength is highest. The general trend of alkaline nanocomposite failure strain decreases with the MMT content, bottoming at an MMT content of 20%.

Microstructural observation. Figure 5 shows that the MMT particles disperse effectively in the matrix. The particles in the Chitosan-MMT nano-composite display tight contact. A possible consequence of this layered structure is the improved retardation to deformation. The densest surface structure is found in composite with 40 wt% MMT. This microstructure is correlated with the increase in elastic modulus and strength of chitosan composites prepared under acidic conditions.

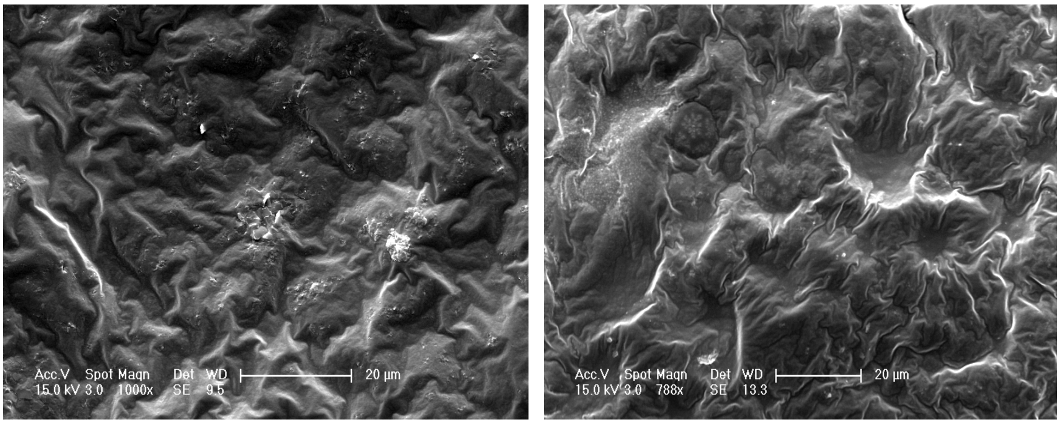

Figure 5: Microstructure 2wt% Chitosan with MMT (pH=4) (a, left) 10% and (b, right) 40%.

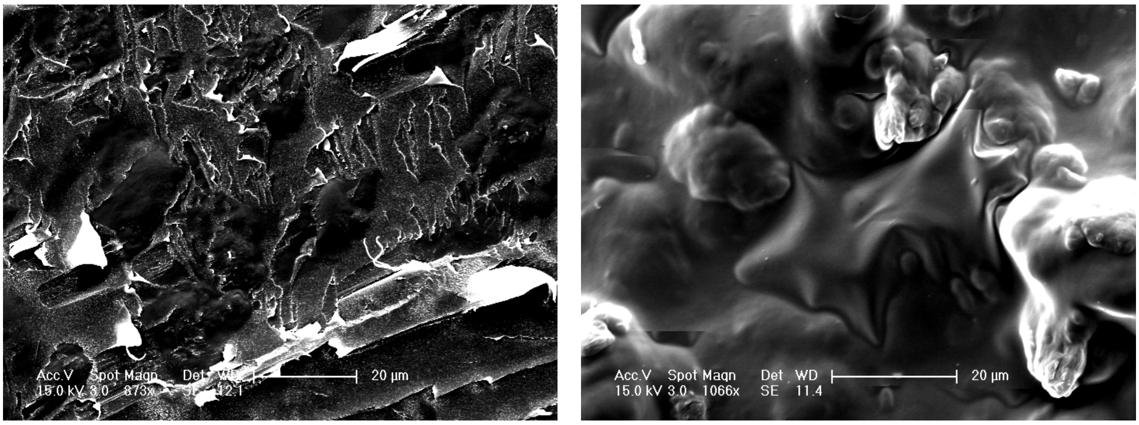

Figure 6: Microstructure of Chitosan with MMT (pH=7) (a, left) 10% and (b, right) 40%.

Figure 6 shows the microstructures of chitosan-MMT nano-composites with different contents of MMT prepared with the addition of NaOH. It is found that the surface textures are significantly different from that of the composites fabricated under acidic pH.It is believed that the addition of NaOH solution would cross-link the chitosan molecules, which is correlated with the increase in elastic modulus of the pure chitosan(c.f. Figure 2). On the other hand, the structures become more non-uniform than that of acidic composites. One possible reason for this is that the addition of NaOH solution affects the dispersion of MMTparticles adversely. More non-uniform surface texture was observed on chitosan-MMT composite. The particles are close to each other, leading to agglomerates. This is responsible the decrease in strength and fracture strain with increasing MMT content.

Conclusions

The proportion of MMT and pH of suspension play a significant role in the mechanical properties and microstructures of chitosan composites.From the research conducted, the chitosan composites with40% MMT possess the best elastic modulus both at acidic and neutral pH. The elastic modulus of chitosan sample with 40% MMT prepared at neutral pH was as high as 21.5 MPa. Generally, the samples at neutral pH have a higher Young's modulus than that at acidic pH. It is believed that sodium hydroxide led to the cross-linking of the chitosan matrix.

The microstructures of the samples were studied by the ESEM. The samples fabricated at acidic pH have more uniform surface textures. While composites prepared at the neutral pH exhibit different microstructure. With higher proportion of MMT in the sample, MMT agglomerates are more profound. Hence the sample with higher ratio of MMT possesses larger elastic modulus but lower fracture strength and strain due to larger structural defects.

References

[1] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Chitosan-A versatile semi-synthetic polymer in biomedical applications, Progress in Polymer Science36 (2011) 981–1014.

[2] A.P. Martínez-Camacho, M.O.Cortez-Rocha, J.M. Ezquerra-Brauer, A.Z. Graciano-Verdugo, F. Rodriguez-Félix, M.M. Castillo-Ortega, M.S. Yépiz-Gómez, M. Plascencia-Jatomea, Chitosan composite films: Thermal, structural, mechanical and antifungal properties, Carbohydrate Polymers, 82(2010) 305-315.

[3] J. Berger, M. Reist, J. M. Mayer, O. Felt, R. Gurny, Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications, European Journal of Pharmaceutics and Biopharmaceutics, 57 (2004) 35-52.

[4] X. Huang, D.Ge, Z. Xu, Preparation and characterization of stable chitosan nanofibrous membrane for lipase immobilization, European Polymer Journal, 43(2007) 3710-3718.

[5] S.Senel, S. J. McClure, Potential applications of chitosan in veterinary medicine, Advanced Drug Delivery Reviews, 56(2004) 1467-1480.

[6] T. Kean, M. Thanou,Biodegradation, biodistribution and toxicity of chitosan, Advanced Drug Delivery Reviews, 62(2010) 3-11.

[7] W. Wang, D. Xu, Viscosity and flow properties of concentrated solutions of chitosan with different degrees of deacetylation, Int. J. Biol. Macromol, 16 (1994) 149–152.

[8] P. Glerentes, L. Vachoud, J. Doury, A. Domard, Study of a chitin-based gel as injectable material in periodontal surgery, Biomaterials, 23 (2002) 1295–1302.

[9] S. Zhu, J. Chen, Y.Zuo, H. Li, Y. Cao,Montmorillonite /polypropylene nanocomposites: Mechanical properties, crystallization and rheological behaviors, Applied Clay Science,.52 (2011) 171-178.

[10] M. Xia, Y. Jiang, L. Zhao, F. Li, B.Xue, M. Sun, D. Liu, X. Zhang, Wet grinding of montmorillonite and its effect on the properties of mesoporousmontmorillonite, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 356 (2010) 1-9.

[11] E. Assaad, A. Azzouz, D. Nistor, A.V. Ursu, T. Sajin, D.N. Miron, F. Monette, P. Niquette, R. Hausler, Metal removal through synergic coagulation–flocculation using an optimized chitosan–montmorillonite system, Applied Clay Science, 37 (2007) 258-274.

High-Performance Ceramics VII

10.4028/www.scientific.net/KEM.512-515

Fabrication and Mechanical Properties of Chitosan-Montmorillonite Nano-Composite

10.4028/www.scientific.net/KEM.512-515.1746