

**MECHANICAL, THERMAL AND PHYSICAL PROPERTIES OF CHITOSAN  
AND CHITIN FILLED COMPATIBILIZED POLYAMIDE-  
6/POLYPROPYLENE COMPOSITES**

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MECHANICAL, THERMAL AND PHYSICAL PROPERTIES OF CHITOSAN  
AND CHITIN FILLED COMPATIBILIZED POLYAMIDE-6/POLYPROPYLENE  
COMPOSITES

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*I dedicate my thesis for my beloved*  
*DAD, HJ. ABD HAKIM ABAS*  
*MOM, HJH. CHE ZAHARAH CHE SU*  
*SIBLINGS*  
*FRIENDS*

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## ABSTRACT

Chitosan (CSN) is one of the natural fillers that offer various advantages due to its biodegradability, non-toxic and absorption properties. The presence of hydroxyl and amino group in chitosan molecules, which is a derivative obtained through alkaline deacetylation of chitin (CN), offers wide possibilities to be blended with other polymers to form new material with better properties. Polymer blending of polyamide-6 (PA6)/polypropylene (PP) incorporated with maleated polypropylene (MA-g-PP) as compatibilizer has been studied by many researchers. The present study investigates the performance of chitosan as filler incorporated into compatibilized PA6/PP blends. Throughout the study, the weight ratio of PA6/PP and compatibilizer was fixed at 70:30 weight percent of PA6/PP and 5 phr of MA-g-PP. All blends with different contents (0, 10, 20, 30 phr) of chitosan were compounded using co-rotating twin-screw extruder followed by injection moulding into test samples. Mechanical properties of the blends were studied through tensile, flexural and impact tests. It was found that the flexural strength and modulus were highest at 30 phr of chitosan. Since chitin is cheaper than chitosan and is also a biodegradable and non-toxic polymer, chitin was chosen to partially replace chitosan in the PA6/PP blends. Moreover, chitin contains amide group which is similar to PA6, and is expected to improve the composites properties. Results showed that tensile strength of PA6/PP/CSN/CN composites did not have significant difference with PA6/PP/CSN at 30 phr. However, the impact strength increased with increasing chitin content until it reached 20 phr. Furthermore, impact strength of mixed chitosan/chitin content is higher as compared to single fillers in the composites. The comparison between composites containing virgin chitosan and virgin chitin at 30 phr were made and results showed that the tensile strength, flexural strength and modulus, and impact strength of chitin composites were higher. Thermal analysis using thermogravimetry and differential scanning calorimetry showed that thermal stability of PA6/PP blends were not much affected with incorporation of chitosan or chitin. However, the incorporation of chitosan at 30 phr has increased the percentage of water absorption of blends to 66% with incorporation of chitosan at 30 phr which is in contrast with the addition of chitin. In conclusion there is no clear advantage of using chitosan over chitin or a mixture of both.

## ABSTRAK

Kitosan (CSN) adalah salah satu daripada pengisi semula jadi yang menawarkan pelbagai kelebihan kerana sifatnya yang boleh dibiodegradasi, tidak beracun dan kebolehan menyerap. Kehadiran kumpulan hidroksil dan amino dalam kitosan, iaitu satu terbitan yang diperolehi melalui pendeasetilan berkali kitin (CN), membolehkan ia untuk dicampur dengan polimer lain bagi membentuk bahan baru dengan ciri yang lebih baik. Pencampuran poliamida-6 (PA6)/polipropilena (PP) bersama dengan polipropilena termaleat (MA-g-PP) sebagai penserasi telah banyak dilakukan oleh penyelidik. Penyelidikan ini bertujuan mengkaji prestasi kitosan sebagai pengisi dalam PA6/PP. Dalam semua kajian ini, nisbah berat PA6/PP ditetapkan pada 70:30 dan MA-g-PP pada 5 phr. Semua adunan dengan kandungan kitosan yang berbeza (0,10,20,30 phr) disebutkan menggunakan penyemperitan skru berkembar diikuti oleh pengacuan suntikan untuk membentuk sampel ujian. Sifat mekanik telah dikaji melalui ujian tegangan, lenturan dan hentaman. Hasil kajian mendapati bahawa kekuatan lenturan dan modulus adalah tertinggi pada 30 phr kitosan. Oleh kerana kitin adalah lebih murah daripada kitosan dan boleh terbiodegrasi serta tidak toksik, kitin telah dipilih untuk menggantikan sebahagian kitosan dalam adunan PA6/PP. Kitin juga mengandungi kumpulan amida yang sama dengan PA6 dan dijangka menambahbaik sifat komposit. Keputusan menunjukkan bahawa kekuatan tegangan komposit PA6/PP/CSN/CN tidak mempunyai perbezaan yang signifikan dengan PA6/PP/CSN pada 30 phr. Walau bagaimanapun, ia memberi kesan peningkatan kepada kekuatan hentaman dengan peningkatan kandungan kitin sehingga mencapai 20 phr. Tambahan pula, kekuatan hentaman campuran kitosan/kitin adalah lebih tinggi berbanding dengan hanya pengisi tunggal di dalam komposit. Perbandingan antara komposit yang mengandungi hanya kitosan atau kitin sahaja pada 30 phr telah dibuat dan keputusan menunjukkan bahawa kekuatan tegangan, kekuatan lenturan dan modulus, dan kekuatan hentaman untuk komposit yang mengandungi kitin adalah lebih tinggi. Analisis terma menggunakan termogravimetri dan kalorimeter pengimbasan perbezaan menunjukkan kestabilan terma PA6/PP tidak banyak terjejas dengan penambahan kitosan atau kitin. Walau bagaimanapun, penambahan kitosan pada 30 phr telah meningkatkan peratusan penyerapan air kepada 66% berbeza dengan penambahan kitin. Kesimpulannya penggunaan kitosan dan kitin atau campuran kedua-duanya tidak memberikan kelebihan yang jelas.

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**LIST OF ABBREVIATIONS AND SYMBOLS**

|                     |   |
|---------------------|---|
| 3-APE               | 3-Aminopropyltriethoxysilane                                |
| ASTM                | American Society for Testing and Materials                  |
| CN                  | Chitin  |
| CSN                 | Chitosan  |
| DA                  | Degree of acetylation                                       |
| DD                  | Degree of deacetylation                                     |
| DSC                 | Differential Scanning Calorimetry                           |
| ENR                 | Epoxidized Natural Rubber                                   |
| HDPE                | High Density Polyethylene                                   |
| MA-g-PP             | Maleated Polypropylene                                      |
| MAH                 | Maleic Anhydride  |
| MFI                 | Melt Flow Index   |
| MMT                 | Montmorillonite   |
| PA6                 | Polyamide-6   |
| PCL                 | Poly( $\epsilon$ -caprolactone)                             |
| PDLLA               | Poly(DL-lactide)  |
| PHB                 | Poly(3-hydroxybutyric acid)                                 |
| PLA                 | Poly(lactic acid)   |
| POE-g-MA            | Polyethylene octane elastomer grafted with maleic anhydride |
| PP                  | Polypropylene   |
| PS                  | Polystyrene   |
| PVC                 | Polyvinyl chloride  |
| SDS                 | Sodium dodecyl sulfate                                      |
| SEM                 | Scanning Electron Microscope                                |
| $T_{10\text{wt}\%}$ | Temperature at 10% weight lost                              |
| $T_c$               | Crystallization temperature                                 |
| $T_m$               | Melting temperature   |

|                            |   |
|----------------------------|---|
| $T_{\max}$                 | Maximum decomposition temperature           |
| TGA                        | Thermogravimetric analysis                  |
| $X_c$                      | Degree of crystallinity                     |
| W                          | Weight fraction                             |
| $\Delta H_{\text{sample}}$ | Measured enthalpy of melting                |
| $\Delta_{100\%}$           | Ideal enthalpy of melting a perfect crystal |



## CHAPTER 1

### INTRODUCTION

#### 1.1 General introduction

There is a continuous demand for improved materials that are able to meet stringent conditions but at the same time not expensive and environmental friendly. For mechanical properties efforts have done to develop polymer composites which are balance in strength, modulus and toughness to meet the needs of the applications (Chow *et al.*, 2004; Hassan *et al.*, 2011).

One of the ways to enhance the properties of polymers is through the incorporation of additives. Plastics additives such as impact modifiers, heat stabilizer, fillers and others have become very important in modifying polymer properties and assist in processing (Murphy, 1996). In the present research fillers are being used to improve certain mechanical properties, reduce cost and enhance biodegradability (Salmah *et al.*, 2012; Zakaria *et al.*, 2013).

Chitosan (CSN) and Chitin (CN) will be used as fillers in the current study. CN is a long-chain polymer of a *N*-acetylglucosamine, and are produced mainly from crab and shrimp waste (Ravi Kumar, 1999). CSN is produced from deacetylation of CN under alkaline condition. However, this reaction is rarely conducted to full completion where some of *N*-acetyl which is abundant in CN is also present in CSN, hence the term degree of deacetylation (DD) (Aranaz *et al.*, 2009).

CN and CSN has excellent properties such as biodegradable, biocompatibility and non-toxicity (Dutta *et al.*, 2004), making both good candidates as fillers to produce new polymer composites with different properties. Compared to CN, CSN has gained more attention because it is soluble in aqueous acidic media due to its free amino groups thus allowing protonation of these groups to dissolved in aqueous acidic solutions, making it applicable in solutions, gels, films and fibers (Aranaz *et al.*, 2009; Rinaudo, 2006).

Polyamides (PA) is one of the outstanding thermoplastics which has found a steadily increasing applications where their toughness, rigidity, abrasion resistance, good hydrocarbon resistance and reasonable heat resistance are important. However due to their high cost, they have not become general purpose materials such as polyethylene (PE) and polystyrene (PS) which prices are about a third of the price of the PA. Besides that, PA is hygroscopic and the absorbed water has a plasticizing effect which will cause a reduction in tensile strength and modulus but an increase in impact strength.

Polypropylene (PP) is one of the important commercial thermoplastics where its consumption is still increasing more rapidly than the total for all thermoplastics. The excellent combination of processing and mechanical properties was exploited in a variety of applications. In recent past few years, the increase in prices and possible shortage of petroleum in future has increased the need to incorporate more fillers into PP.

Blending PA6 with PP can close the property gap between these two polymers where PA6 has better mechanical properties but expensive and hygroscopic. Meanwhile PP is not hygroscopic and also low cost, but has lower mechanical properties. Thus by blending PA6 with PP can balance properties in mechanical strength and hygroscopicity while reducing cost.

The incorporation of fillers into plastic can extend the available volume of resin while improving properties. Polymer composites with different properties can

be produced by incorporating various types of fillers into the polymer matrix. Recently, replacing inorganic fillers in thermoplastic with natural fillers derived from agricultural by-product has attracted great interest (Biagiotti *et al.*, 2004). Investigations on the application of CSN as natural fillers to modify the properties of PP have also been reported (Amri *et al.*, 2011; Salmah *et al.*, 2011b; Salmah *et al.*, 2012; Faisal Amri Tanjung *et al.*, 2013; Amri *et al.*, 2013).

Blending two or more polymers together can produce new material with better properties where PA6 acts as the matrix with PP as the dispersed phase. Studies by Hassan *et al.* (2011) has shown that the optimum condition for blending PA6 with PP is at 70wt% and 30 wt% respectively due to highest impact strength obtained. However, due to immiscible system between the blends could results in production of new material with poor mechanical properties. PA6 and PP is one example of immiscible blend and addition of compatibilizer agent can improve poor interfacial adhesion between the dispersed and continuous phase. Maleated polypropylene (MA-g-PP) (Chow *et al.*, 2003) and polyethylene octane elastomer grafted with maleic anhydride (POE-g-MA) (Othman *et al.*, 2004) are among the compatibilizers used for the blends.

## 1.2 Problem statement

Blending of polymers has gained much attention as it produces materials with better properties and bridges the property gap between the polymers. Many studies on PA6 and PP blends have been done. PA6 has outstanding mechanical properties but expensive and hygroscopic. Meanwhile PP is lower in mechanical properties compared to PA6, but lower cost and not hygroscopic. It has been proven by other researchers that blends of PA6/PP will result in a material that has balanced properties in terms of mechanical strength and hygroscopicity while reducing the cost (Holsti-Miettinen *et al.*, 1995). Many studies on incorporation of inorganic fillers into PA6/PP blends have been reported. However, the use of organic materials into PA6/PP blends such as chitin and chitosan has yet to be explored.

Since no literature on the study on incorporation of chitin and chitosan as fillers into PA6/PP has been found yet, this study will analyze the effects of chitin and chitosan as fillers on mechanical, morphological and thermal properties of MA-g-PP compatibilized PA6/PP composites. CN was obtained from prawn waste while CSN can be produced through deacetylation process of CN using autoclave method. CN and CSN have good properties such as biodegradability and biocompatibility, thus making it interesting to be studied. CN and CSN are incorporated into PA6/PP blends with the presence of maleated PP as compatibilizer. CN has amide functional group similar to PA6 while CSN has an amino group which can form hydrogen bonding with PA6. From this viewpoint, it would be expected that CSN would performed better in improving the properties composites compared to CN. Therefore it would be interesting to compare the effectiveness of CN with CSN in improving the properties of PA 6/PP composites. Besides, since CN is relatively cheaper than CSN, production on composites from CN would be of an advantage from economic point of view if the good properties can be maintained. The effect of partial replacement of CSN with CN on properties of PA6/PP composites would be interesting to investigate since it would reduce the overall cost.

### **1.3 Objectives of the study**

The overall objective of the current is to use CSN and CN as fillers in PA 6/PP blends to produce new polymer composites with good balance of mechanical properties, cheap and enhanced biodegradability.

The overall objective can be further divided into:

1. To investigate the effect of CSN content on mechanical and thermal properties of PA6/PP blends.
2. To study the effect of partial replacement of CSN with CN on mechanical and thermal properties of CN filled PA6/PP composites.

## 1.4 Scope of the study

1. Incorporation of CN and CSN as fillers and maleated polypropylene (MA-g-PP) as compatibilizer into PA6/PP blends.
2. Compounding process of PA6 and PP blends with the presence of maleated polypropylene, CN and CSN using twin screw extruder and molded by injection molding.
3. The blends will be characterized for morphological, thermal and mechanical properties.
  - 3.1 Characterization and morphological study
    - i. Scanning Electron Microscopy (SEM)
    - ii. Fourier Transform Infrared Spectroscopy (FTIR)
  - 3.2 Thermal properties analysis
    - i. Thermogravimetric Analysis (TGA)
    - ii. Diferential Scanning Calorimeter (DSC)
  - 3.3 Physical and mechanical analysis
    - i. Water absorption test
    - ii. Tensile properties
    - iii. Flexural properties
    - iv. Izod impact properties

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