

# Study of Using Chitosan Fiber to Reinforce PSTG

B. Meng, Y. Zhang, F.Z. Cui\*

## ABSTRACT

In the present work, we use chitosan fiber to reinforce PSTG, copolymer based on poly(ethylene glycol) terephthalate (PEGT), poly(butylene terephthalate) (PBT) and poly(butylene succinate) (PBS). Elastic modulus ( $E$ ) of the samples were obviously improved. The method may overcome the disadvantage of thermoplastic elastomers, which are easily distorted.

**Keywords:** Chitosan, Fiber reinforcement, Thermoplastic elastomers

## INTRODUCTION

Among synthetic biomaterials, thermoplastic elastomers based on poly(ethylene glycol) terephthalate and poly(butylene terephthalate) segments (PEGT/PBT) have drawn much attention for their unique physical properties, good biocompatibility and adjustable biodegradability. Extensive research on copolymers as biomedical materials has been carried out in the last 10 years /1-4/. Aromatic segments of PBT provide mechanical properties in the backbone /5,6/. However, whether the aromatic oligomers through the cleavage of ester bonds by enzymatically or chemically catalyzed hydrolysis have side effects *in vivo* is still a matter of controversy, although Witt and co-workers recently reported that the lower ones with short segment length ( $DP < 3$ ) can be assimilated by microorganisms and the

longer ones have no acute toxicity /7,8/. With regard to the possible inflammatory response caused by highly crystalline debris of hard segment, the material with a short average block length of PBT is recommended in the case of an implant made of PEGT/PBT copolymer /6/.

Recently, polymer-composite materials have been investigated to adjust the mechanical properties of biomaterials /9,10/. Y. Zhang *et al.* have synthesized a new copolymer PSTG, by incorporating biodegradable poly(butylene succinate) (PBS) into the backbone of PEGT/PBT /11/. However, mechanical properties of the polymers were still poor, especially in elastic modulus ( $E$ ), compared with popularly used PLLA.

In the present work, fiber reinforcement strategy was used to adjust PSTG with adjustable mechanical properties without adjustment of length and content of hard segments. Mechanical properties of the sample were characterized by tensile test. The samples were destroyed by fiber pull-out.  $E$  was greatly increased with slight decrease of tensile strength ( $\sigma_b$ ). The composite may be useful in some field demand small distortion under certain force.

## MATERIALS AND EXPERIMENT

PSTG was synthesized by the School of Materials Science and Technology, Beijing Institute of Technology. Chitosan fiber and chitosan nonwoven was bought from Tianqing Company, Shanghai. Chloroform was purchased from Beijing Chemical Company.

\* Corresponding author name and address:

Dr. Cui Fuzhai

Department of Materials Science & Engineering, Tsinghua University, Beijing 100084, P.R. China

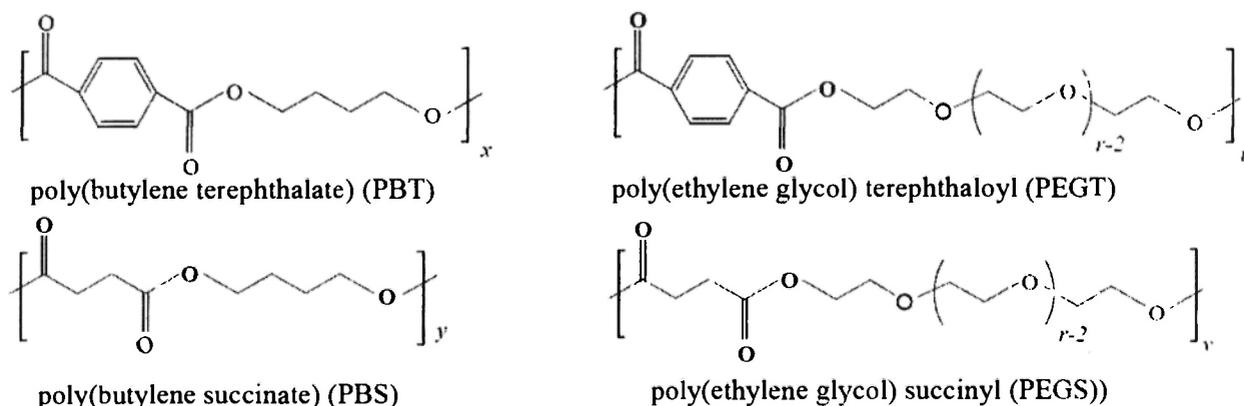
Tel.: +86-10-62772850; Fax: +86-10-62771160; E-mail: [cuifz@mail.tsinghua.edu.cn](mailto:cuifz@mail.tsinghua.edu.cn) (F.Z. Cui)

PSTG was dissolved in chloroform at a concentration of 2% (g/ml). Composites were prepared by three methods: (a) 3cm long chitosan fiber was laid in a module with unique orientation. PSTG solution was cast on in the module to evaporate. (b) Chitosan nonwoven was laid in a module, PSTG solution was cast on in the module to evaporate. (c) Chitosan fibers were cut into different lengths, and mixed with PSTG solution. Then the mixture was cast into a module. All the samples were dried in a vacuum desiccator for 72h and cut into standard shape for tensile test.

Tensile test was carried out on an electrical universal tester (Shimadzu, AGS-10KNG). Gauge length was 54mm and crosshead speed was 10mm/min. Five specimens of each type of sample were tested and the average data are calculated. For samples prepared by method (a), the tensile force was along the orientation of the fibers. The fracture surface and fibers of the samples were characterized by scanning electrical microscopy (SEM) (Hitachi, S-450, Japan).

## RESULT AND DISCUSSION

As illustrated in Scheme 1, in PSTG there were two sorts of hard segments, PBT ( $M_n = 220$  g/mol) and PBS ( $M_n = 172$  g/mol), and two types of soft segment, PEGT ( $M_n = 1132$  g/mol) and PEGS ( $M_n = 1084$  g/mol). PBS is 5% mol fraction of the hard segment, and the soft segment is 20% fraction of whole monomers.



Scheme 1: PEG/PBT/PBS segmented copolymer (where  $u, v=1$ )

Some figures representing mechanical properties of the composites are listed in Table 1. The fiber content was calculated from the initial fiber and PSTG weight that were used in the preparing process. All the samples reinforced by fibers are greatly improved in  $E$ , while there is a slight decrease in  $\sigma_b$ . In the samples series prepared by method (a), numbered from 2 to 4, chitosan fiber length and fiber orientation were fixed. As fiber contents increased,  $E$  of the samples increased obviously. Sample 4, that contains 15.3% fiber in weight, has  $E$  about eight times of sample without the addition of chitosan fiber. Chitosan nonwoven is also effective in increasing  $E$  of the composite, as shown in Table 1. But  $E$  value of non-woven reinforced composite is much smaller than the value of the fiber reinforced composite with the same fiber content. This is caused by non-preferred orientation of nonwoven.

We have also fixed fiber content and changed fibers length. The cut fibers were mixed with PSTG solution and cast in module. The composite was slightly improved in  $E$  with addition of 0.3mm fibers. When fibers length changed to 0.5mm, the  $E$  increased, as well. 1mm fibers were too long and they entangled together and not dispersed very well. Therefore, the composite reinforced by 1mm chitosan fiber has lower  $E$  than the one reinforced by 0.5mm fibers.

All the fiber reinforced composites have lower tensile strength ( $\sigma_b$ ) than the initial polymer. Elongation at break  $\epsilon_b$  (%) of all composite was also decreased. As more fibers were added or fibers became longer,  $\sigma_b$  and

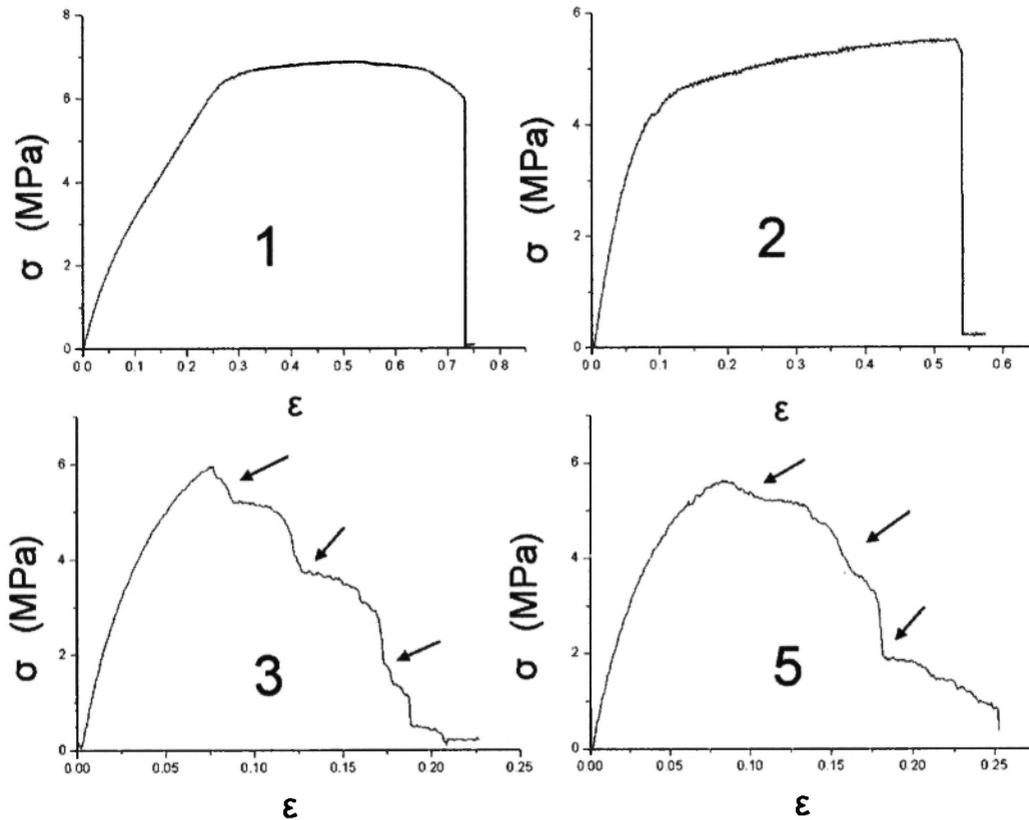
**Table 1**  
Mechanical properties of the fiber reinforced polymers

Sample No.	Fiber length	Fiber content (by weight)	Elastic Modulus, E(MPa)	Tensile strength, $\sigma_b$ (MPa)	Elongation at break, $\epsilon_b$
1	--	0	31.1	7.19	0.91
2	3cm	2.5%	54	5.54	0.77
3	3cm	7.41%	105.1	6	0.187
4	3cm	15.3%	243	5.9	0.158
5	Non-woven	15.3%	102.5	5.5	0.17
6	0.3mm	7.41%	37.4	5.99	0.99
7	0.5mm	7.41%	59.05	5.39	0.666
8	1mm	7.41%	41.1	4	0.557

$\epsilon_b$  decreased.

To make clear the mechanical performance of the samples during tensile test,  $\sigma$ - $\epsilon$  curves of sample prepared by method (a) and (b) are shown in Fig. 1.

PSTG sample without addition of chitosan fibers demonstrates that the composite cracked rapidly as the curve reaches maximum elongation point. With low fiber content of 2.5%, that is sample 2, the  $\sigma$  quick



**Fig. 1:**  $\sigma$ - $\epsilon$  curves of samples reinforce by 3cm long fibers with unique orientation and by nonwoven during tensile test.

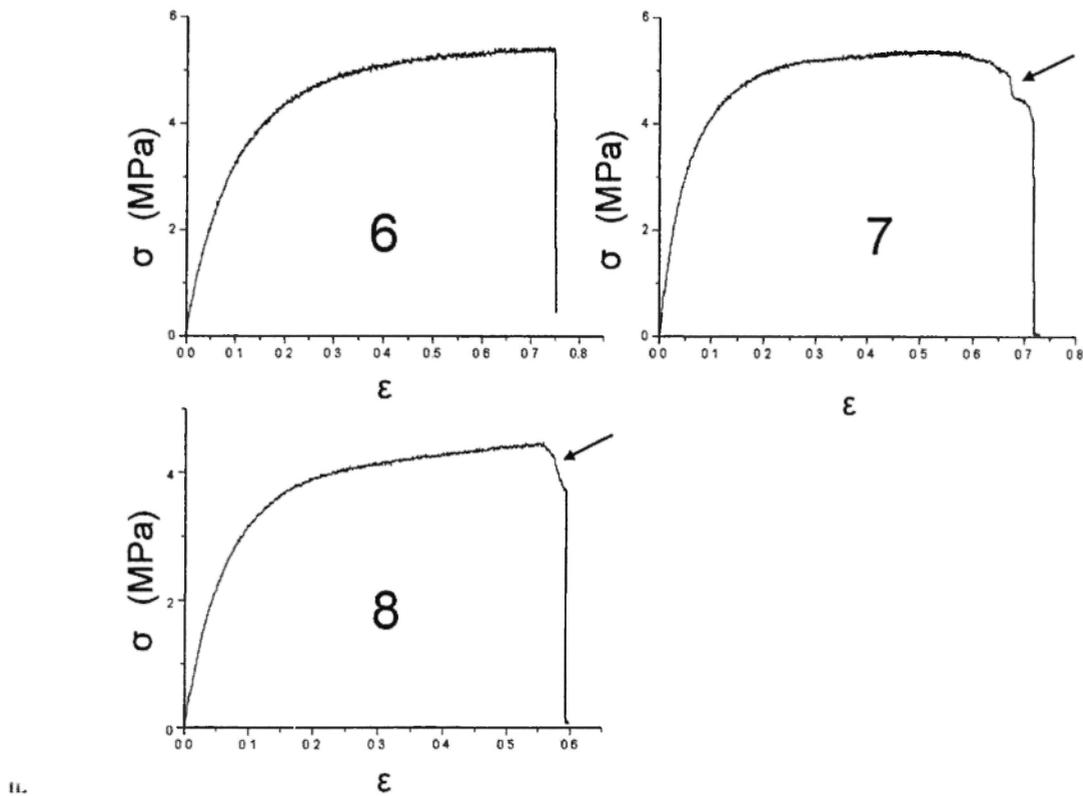
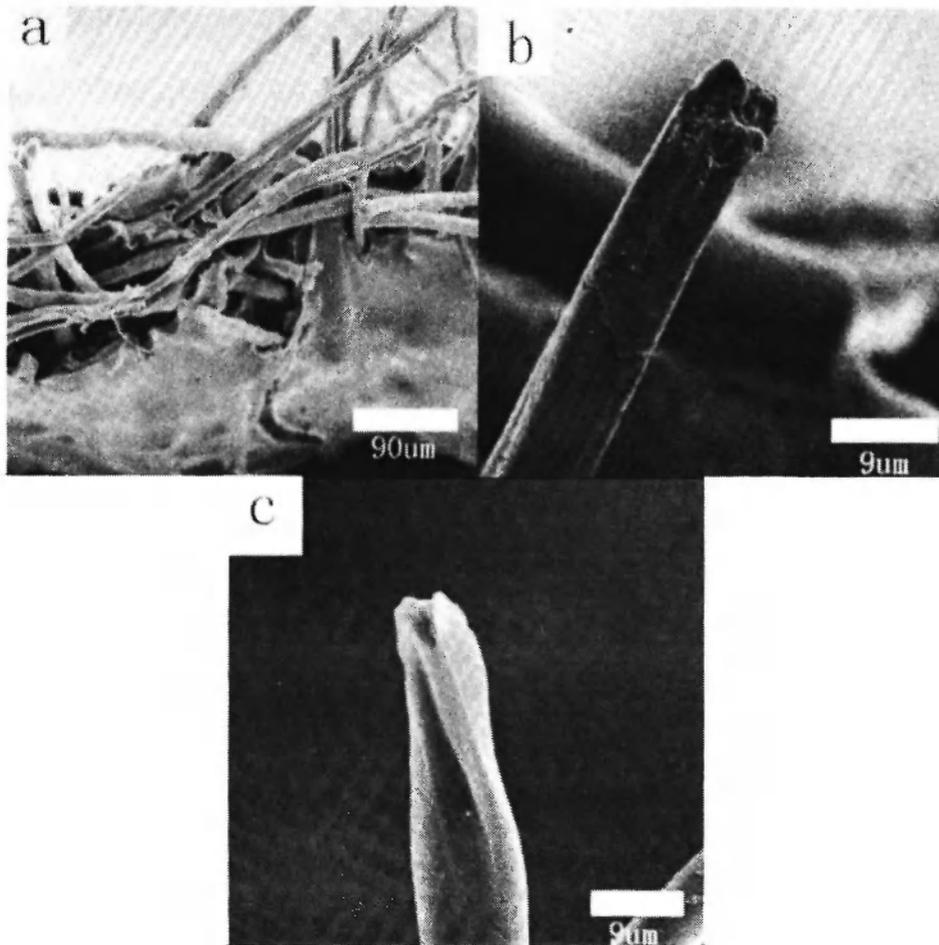


Fig. 2:  $\sigma$ - $\epsilon$  curves of samples reinforced by 0.3mm, 0.5mm and 1mm long fibers during tensile test.

decrease to zero as sample stretches to the longest, just like sample 1. However, as fiber content increases to 7.41%,  $\sigma$  decreases step by step after maximum  $\sigma$  is reached, as indicated by arrows. The phenomenon is also observed during tensile test of sample 4 (not shown) and sample 5, the nonwoven reinforced one. Fig. 2 is  $\sigma$ - $\epsilon$  curves of samples reinforced by short fibers. Curve of sample 6 shows no step decrease before fractured. As fibers became longer,  $\sigma$  decreased by two steps before drop to zero.

We also demonstrated the fracture surface of the sample 3 in Fig. 3, after tensile test. Fibers extended out

of the rupture. We can also note that the PSTG and fibers were not attached very well in the experiment, for gaps are observed from the SEM image between PSTG and fibers. One fiber is magnified and shown in Fig. 3b. The fiber has also unique diameter along the fiber and no necking phenomenon is observed. A chitosan fiber that directly snapped is shown in Fig. 3c as contrast. Obvious necking behavior was observed. Thus, during the tensile test of the composite, samples are cracked by fibers pull-out. The bonding strength between the PSTG and chitosan fiber is poor, which calls for further study.



**Fig. 3:** (a) SEM image of the fracture surface of the sample 3 after tensile test. (b) SEM image of one fiber at the fracture surface. (c) SEM image of a chitosan fiber that directly snapped.

### CONCLUSION:

Chitosan fibers were used to reinforce PSTG, as an alternative strategy for adjustment of PSTG mechanical properties without increment of hard segment. Tensile test demonstrated that  $E$  of the reinforced samples are greatly improved, with slight decrease of  $\sigma_b$ . The samples are destroyed by fiber pull-out, during the tensile test.

### ACKNOWLEDGMENT

This work is supported by the 973 program of Ministry of Science and Technology of China,

G199064207 and Analysis Foundation of Tsinghua University.

### REFERENCES

1. J.M. Benzemer, D.W. Grijpa, P. Dijkstra, C.A. Van Blitterswijk and J. Feijin, *J Controlled Release* **62**:393 (1999).
2. A.G.M.V. Drop, M.C.H. Verhoeven, H.K. Koerten and C.A. Van Blitterswijk, *J Biomed Mater Res* **47**:292 (1999).
3. C.A. Van Blitterswijk, J.V.D. Brink, H. Leenders and D. Bakker, *Cells Mater* **3**:23 (1993).
4. C. Due, G.J. Meijer, C. van de Valk, R.E. Haan,

- J.M. Bezemer, S.C. Hesselting, F.Z. Cui, K. de Groot and P. Layroole, *Biomaterials* **23**, 23, (2002).
5. G. Betolho, A. Queiros and P. Gijsman, *Polym Degrad Stab* **67**:13 (2000).
  6. A. Deschamps, D.W. Grijpma and J. Feijin, *Polymer* **42**:9335 (2001).
  7. U. Witt, M. Yamamoto, U. Seeliger, R.-J. Muller and V. Warzelhan, *Angew Chem, Int Ed Engl* **38**:1438 (1998).
  8. U. Witt, T. Einig, M. Yamamoto, I. Kleeberg, W.D. Deckwer and R.J. Muller, *Chemosphere* **44**:289 (2001).
  9. S. Ramakrishna, J. Mayer, E. Wintermantel and K.W. Leong, *Compos Sci Technol* **61**:9 (2001)
  10. A.L. Yang and R.J. Wu, *J Appl Polymer Sci* **84**:3 (2002)
  11. Y. Zhang, Z.G. Feng and A.Y. Zhang, *Polym Int* **52** :8 (2003)