

WET SPINNING OF POLYMERIC FIBERS WITH HIGH LOADING OF CARBON NANOTUBES

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Introduction

Single-walled carbon nanotubes (SWCNTs) are well known for their excellent mechanical and conductivity properties. These properties make SWCNTs ideal candidates as reinforcement elements in polymer composites [1]. In composite manufacturing, the main problem is the SWCNTs agglomeration in polymer matrix. This phenomenon limits the SWCNTs loading in composite fibers to 2-5 wt % of SWCNTs. For many applications such as artificial muscles, biosensors or support for biomedical devices one requires high electrical and thermal conductivity for fibers. Hence there is a need to further increase the SWCNT loading in the fibers [2].

Several methods for spinning of highly loaded SWCNT fibers have been reported in the literature [2-4]. Typically, prior to fiber spinning, the nanotubes are coated with surfactant, Sodium dodecyl sulphate (SDS). Recently, we proposed to take advantage of an industrially available technology called wet spinning technology [5, 6]. We successfully produced fibers with 23% weight concentration of carbon nanotubes in the fiber. In our approach, the SWCNT- SDS dispersion is mixed with the aqueous solution of sodium alginate followed by its wet spinning into calcium chloride (CaCl_2) coagulation bath. We have shown that these fibers are comparable to best textile fibers. However, it was observed that ionic bonding of alginate through calcium bridges is not sufficient for chemical stability of fibers: when this fiber comes in contact with a stronger metal ion, the calcium ion has a tendency to be replaced and the fiber loses its integrity. Here we suggest to covalently cross-link the alginate chains thus improving the fiber stability.

Experimental

Fibers with different concentration of SWCNTs (up to 23 wt %) were produced and characterized for mechanical and morphological properties as reported previously [5, 6]. In order to improve the chemical stability of these fibers we propose to use a method developed in bioengineering [7, 8]. As reported in Refs. [7, 8], 1-ethyl-3-(3-dimethylamino-propyl) carbodiimide hydrochloride (EDAC) and N-hydroxysulfosuccinimide (Sulfo-NHS) can be used in alginate-based materials as catalysts needed for crosslinking some enzymes with amine groups. The steps in the chemical modification of calcium alginate involves (a) pretreatment with ethylenediamine tetraacetic acid (EDTA) to free some of the carboxylic acid ($-\text{COOH}$) groups of alginate by leaching out some of the Ca^{+2} -ions, (b) binding of EDAC to the

pretreated polymer which forms an unstable complex (c) stabilization of the complex by treating with sulfo-NHS (d) addition of enzyme (that need to be attached with polymer) solution, and (e) post treatment of this treated polymer with enzyme attached using calcium chloride solution to again impart Ca^{+2} ionic bonding for the uncross-linked $-\text{COOH}$ groups.

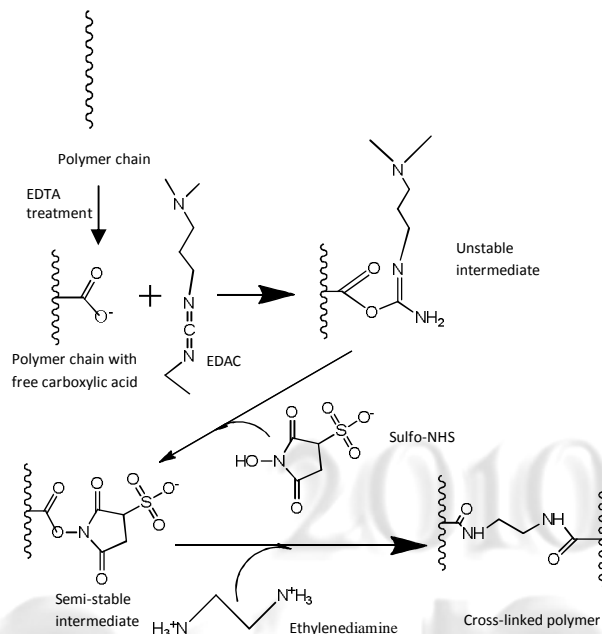


Fig. 1 The steps of chemical modification of calcium alginate by using ethylenediamine as cross-linker

Considering similar chemistry, we choose to use ethylenediamine (ED) instead of enzyme. ED has two amino groups, so assuming two of these react with free $-\text{COOH}$ groups of different polymer chains, it is possible to achieve chemical cross-linking between alginate polymer chains. Experimental procedure followed is the same as that reported in Ref [8]. One only needs to replace enzyme solution in step (d) with the ED aqueous solution. The chemical modification steps are shown in Fig. 1.

Based on molar value, ED was added at different ratios depending on the amount of $-\text{COOH}$ groups available in alginate and assuming that only $-\text{COOH}$ groups cross-link with ED. Three ratios were chosen (i) 50 % - meaning that ED is able to cross-link only 50 % of free $-\text{COOH}$ alginate groups, (ii) 100 % - meaning ED will cross-link all the free $-\text{COOH}$ groups in alginate, (iii) 200 % - meaning we twice exceeded the necessary concentration of ED to cross-link all free $-\text{COOH}$ in alginate; this ensures better cross-linking.. After modification, these fibers were kept in mixture of 0.01 M PBS buffer and 0.1 M KCl aqueous solution to check the time of their disintegration.

Similarly, instead of ED, triethylenetetramine (TETA) [Fig.2] was also used as the cross-linker. All other modification steps were kept same as in case of (iii).

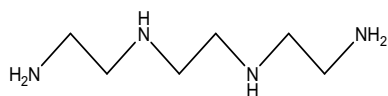


Fig.2 Chemical structure of TETA

Results and Discussion

Table 1 represents the improvement in the stability of the fiber by the proposed method of covalent cross-linking. As can be seen from Table 1, the chemical modification of alginate improves the chemical stability of alginate fibers.

Table 1. Improvement of fiber stability based on the cross-linker amount

Sample	% modification of alginate	Amount of cross-linker (g)/0.1 gm Na-alginate	Time of disintegration in PBS buffer and KCl solution
Pure alginate	0	0	5 min
ED modified	50	0.0075	15 min
	100	0.015	25 min
	200	0.03	1 hr
TETA modified	200	0.37	4 hr

As compared to unmodified alginate fiber, the modified fibers show longer stability in the buffer and salt solutions. Again, the higher the amount of cross-linker the better is the stability. In the case of TETA, the stability has been very much improved. This can be explained by a higher functionality of TETA. However, one drawback of the TETA-treated fibers is that they become brittle after modification. As one TETA molecule now reacts with four of alginate monomeric units, the fiber loses its flexibility. Again covalent cross-linking is present but the fiber still disintegrates. This can be explained by insufficient penetration of TETA in the fiber core: most likely, only surface modification of alginate fiber has been done. There are some chances that one cross-linker might react with the same alginate chain.

Conclusion

We showed promising method of covalent cross-linking of alginate fibers. This method results in the fibers which demonstrate the chemical stability in the harsh base environment. Amount of cross-linker added during the modification process has prominent effect on the fiber stability. Use of TETA provides much better stability but compromises the fiber flexibility. Some results on the covalently modified SWCNT-alginate fibers will be shown in the talk.

Acknowledgement

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