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Reinforced Films Based on Cross-Linked Water-Soluble Sulfonated Carbon Nanotubes with Sulfonated Polystyrene

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Reinforced films based on sulfonated polystyrene cross-linked with water-soluble sulfonated carbon nanotubes were fabricated using a free-standing film-making method. Transmission and scanning electron microscopy (TEM and SEM), and X-ray photoelectron spectroscopy (XPS) were used to verify the cross-linking reaction. The mechanical properties of these films demonstrated that the tensile strength increases with an increase in the sulfonated nanotube concentration. At 5 wt% nanotube loading, the tensile strength increased 84% compared with polymer containing no nanotube loading. The relationships between structure and mechanical properties are discussed and a possible direction for making ultra thin and ultra lightweight film is proposed.

Keywords: Single-Walled Nanotube, Sulfonated Polystyrene, Polymer Reinforced Membrane.

1. INTRODUCTION

The discovery of carbon nanotubes (CNTs) can be traced back to the origin of fullerene chemistry in 1985.¹ CNTs have attracted a great deal of attention because of their unique structural, electronic, mechanical, and optical properties.²⁻⁴ The single walled nanotubes (SWCNTs) are believed to be the ideal mechanical reinforcement materials for lightweight systems. They have been known to have an elastic modulus of up to 1 TPa and a tensile strength close to 60 GPa. These values are in the range of five to ten times greater than those for steel, respectively, at just 1/6 the weight. Recently, Rice University and Oak Ridge National Laboratory scientists claimed that the tensile strength of the carbon nanotube was 100 times than that of steel.⁵

However, the studies and applications of CNTs are hindered by processing and manipulation difficulties, which lead to their insolubility or poor dispersion in common solvents and polymeric matrixes.⁶ Since CNTs are generally insoluble in common solvents and polymers, they tend to aggregate and disperse poorly in polymer matrix, resulting in deteriorative effects. To overcome these difficulties,

several methods have been developed to disperse CNTs in host polymers. For example, CNTs could be dispersed in certain polymer solutions via ultrasonication⁷⁻¹⁶ or in the presence of surfactants.¹⁷⁻²² Another way is polymer wrapping on the wall of CNTs through noncovalent functionalization, which enables CNTs to disperse in polymers.²³⁻²⁷ Along with the rapid development of carbon nanotube chemistry, the direct polymerization of CNTs with specific molecules has also been achieved.²⁸⁻³³ A key alternative approach of carbon nanotube chemistry is to make CNTs soluble in aqueous and/or nonaqueous solvents,³⁴⁻³⁶ which could allow homogeneous dispersion of CNTs in the host polymer matrix.

Recently, Billups et al.³⁷ synthesized water-soluble SWCNTs with pendent sulfonated phenyl group (SSWCNTs). Water soluble polymers and SSWCNTs may form well dispersed polymeric-nanotube reinforced films.

In the present study, water-dispersible SSWCNTs and sulfonated polystyrene (SPS) were used to make reinforced composite films. Cross-linking agents were also applied in the mixture to provide covalent linkages between sulfonic groups on the polymer and the SSWCNTs. This approach provides a strong interface between the nanotube and polymer through chemical bonding.

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2. EXPERIMENTAL DETAILS

2.1. Materials

Synthetic details for making water-dispersible single-walled carbon nanotubes (SWCNTs) with pendent sulfonated phenyl groups (SSWCNTs) were previously reported by Billups³⁷ and the degree of sulfonation is about 18 (carbon/phenyl ratio). The chemical structure of SSWCNTs is represented in Figure 1. HiPco SWCNTs used in this study were purchased from Beijing Boda Green High Tech. Co. Ltd. (China) (purity > 90%). Sulfonated poly(styrene-*ran*-ethylene) (SPS) is also shown in Figure 1. Cross-linkable, 5 wt% solution in 1-propanol (Contains <0.5% vinyl silane cross-linking agent, Styrene 76 wt%, Sulfonated styrene units 32–38%), and glycerin were purchased from Aldrich and used as received. All other chemicals were commercially available reagent grade and were used as received.

2.2. Film Making

Films of SSWCNT/SPS composite were made by drop-casting iso-propanol solutions of the mixture onto clean glass substrates. The SSWCNT contents in all mixture samples were in the range of 1 wt% to 5 wt%. The cross-linker glycerin content in the mixture was 5 wt% for each sample. Uniform black films were formed after drying. The films become cross-linked with 800–1000 mJ/cm² UV exposure after drying at 110 °C for 10–15 min, then at 140–150 °C for 1 min. Treat with 0.5 M Sulfuric acid for 20 min to strengthen after cross-linking. The average thickness of the films was around 100 μm.

2.3. Characterization Methods

Transmission electron microscopy (TEM) analysis was conducted on a JEOL JEM-2010 system operated at a voltage of 200 kV. Scanning electron microscopy (SEM) was performed using a Hitachi S-4300F system. Specimens were cryogenically fractured in liquid nitrogen and the fracture surface was investigated. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra XPS equipped with a monochromated Al X-ray source. Mechanical tensile strength measurements were conducted on a MTS QTest Elite QT/10 Mechanical Testing System. Three samples were tested for each weight percentage and the average value was adopted.

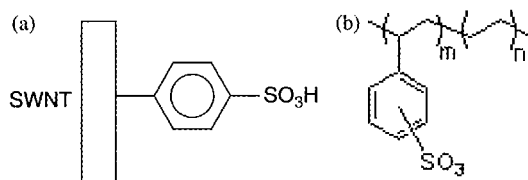


Fig. 1. Chemical structure of functionalized SSWNT (a) and SPS (b).

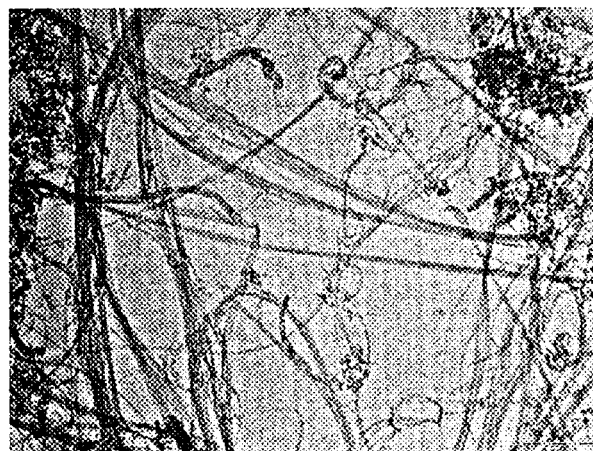


Fig. 2. TEM of SSWNT in water (scale bar: 200 nm).

3. RESULTS AND DISCUSSION

The approach of this work is to create covalent linkages between functional groups on the SWNT and the polymer using a cross-linking agent, ensuring a strong and defect-free interface between the nanotube and polymer. Compatibility between the two components at the interface is a crucial factor that determines the mechanical property of the polymer/nanotube composite material. The cross linking strategy significantly reduces defects at the polymer/nanotube interface that would otherwise lead to inferior mechanical properties.

3.1. TEM of SSWCNT

The water-dispersible property of SSWCNTs was reported in Ref. [37]. Figure 2 shows a typical large-scale TEM image of the SSWCNTs used in our experiments. It can be seen clearly that functionalized SSWCNT disperses very well in water. No agglomeration or nanotube bundles are observed in the image.

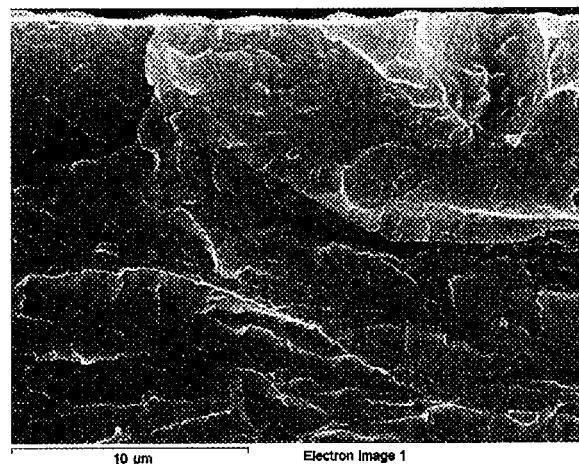


Fig. 3. SEM images of fracture surfaces SPS/SSWNT composite film (scale bar: 10 μm).

3.2. SEM of SPS/SSWCNT Composite Film

SEM was employed to investigate the micro-scale homogeneity of the films at the fracture surfaces of the composites. The SEM of the composite (5 wt% SSWCNT content, Fig. 3) shows clearly that SSWCNTs are enveloped by the polymer matrix, which indicates good adhesion between SSWCNTs and matrix polymer SPS. This implies that a homogeneous dispersion of SSWCNTs can be achieved in the SPS matrix. The introduction of -phenyl-SO₃H on the surface of SWCNTs serves to compatibilize the SWCNTs with the polymer matrix and the cross-linking agent covalently bonds the two components together.

Table I. XPS results of SPS-SSWCN composite films.

Name	Position	FWHM	Line shape	R.S.F.	Area	(%) Conc.
O 1s/8	532.44	1.408	GL(30)	2.93	17462.8	22.40
O 1s/8	533.62	1.468	GL(30)	2.93	2685.1	3.44
N 1s/9	400.33	1.336	GL(30)	1.8	222.7	0.47
N 1s/9	402.21	1.562	GL(30)	1.8	200.7	0.42
C 1s/10	285	1.281	GL(30)	1	12605.2	47.37
C 1s/10	286.64	1.441	GL(30)	1	1540.7	5.79
C 1s/10	288.11	1.324	GL(30)	1	346.5	1.30
C 1s/10	289.27	1.14	GL(30)	1	402.4	1.51
S 2p/12	168.85	1.6	GL(30)	1.68	320	0.72
S 2p/12	170.03	1.6	GL(30)	1.68	159.9	0.36
Si 2p/13	102.88	1.512	GL(30)	0.817	2351.4	10.82
Si 2p/13	103.48	1.512	GL(30)	0.817	1175.2	5.41

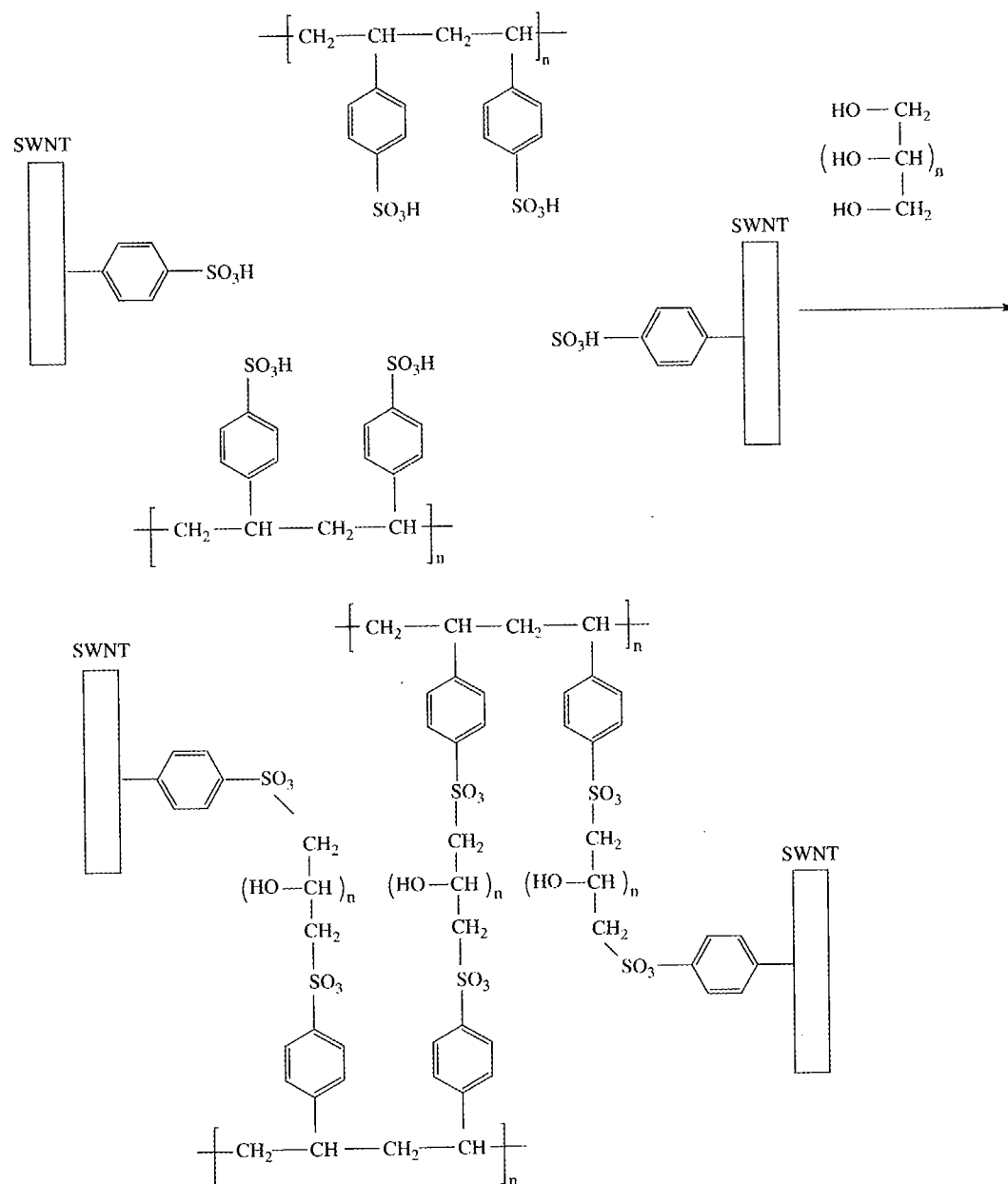


Fig. 4. The possible cross link reaction.

3.3. Solubility of SPS/SSWCNT Film

The crosslink reaction between SSWNTs and SPS through glycerin is accrued in Figure 4. The cross-linked films were insoluble in the solvents such as water, alcohol, toluene and THF, tested, suggesting that the degree of cross-linking was sufficient.

3.4. X-ray Photoelectron Spectroscopy Results

XPS results of SPS-SSWCNT composite films are listed in Table I and shown in Figure 5. The sulphur 2s peak was measured as opposed to the S 2p peak. This is because S 2p overlaps with Si 2s. Regardless, the sulphur peak at 232.9 eV is consistent with that of oxidized sulphur, $-\text{SO}_2-$.

Three carbon peaks have been fitted to the C 1s profile as binding energies of approximately 285.0, 286.3 and 289.1 eV. With the exception of the first peak at 285.0 eV, placement of the C 1s peaks in organic species is best done with a reference spectrum. The first peak at 285.0 eV is likely C-H, C-H₂. These two species overlap and, as a result, are virtually impossible to distinguish.³⁸ The second peak (286.6 eV) is consistent with a C-O-H or C-O-S bond while the third peak (289.1 eV) is most likely to be doubly-bonded carbon. It is common for many carbon species to have very similar binding energies.

The silicon spectrum initially appears to be made up of one species; however, peak fitting with only one Si 2p curve yielded a poor fit. For this reason, 2 curves, one at 103.3 eV and another at 102.6 eV were fitted. The peak

Table II. The tensile strength data of SPS/SSWCNT composite film.

Film	Tensile stress (MPa)	Increase (%)
PS ^a	19	0
PS-5% MWNT ^a	26	37
SPS	21	10
SPS crosslink	21	10
SPS/SSWCNT, 1.5%	23	21
SPS/SSWCNT, 3.0%	28	47
SPS/SSWCNT, 3.5%	30	58
SPS/SSWCNT, 5%	35	84

^aSafadi et al., *J. Appl. Polym. Sci.* 84, 2660 (2002).

at 103.3 eV is consistent with that of SiO₂. The origin of peak at 102.6 eV is less certain. Typical Si-C peaks are found in the neighbourhood of 100.0 to 101.0 eV. A search of the NIST data base reveals that Si 2p peak at 102.6 eV would be consistent with a silicon-bearing organic complex but not Si-C. Silicon carbide could be present in the sample but at a depth too great to be detected (>7 nm) by XPS. There is small peak of N which must left from purification procedure.

3.5. SPS/SSWCNT Film Mechanical Properties

It is quite interesting to explore how the concentrations of SSWCNT in the composite influence the mechanical properties (tensile strength) of SSWCNT/SPS composites films. Table II lists the tensile strength data of different SPS/SSWCNT films. In order to exclude the concern that SPS self cross link reaction may enhance the tensile strength of the film and therefore confuse the results discussion, the SPS self cross link film is made and the

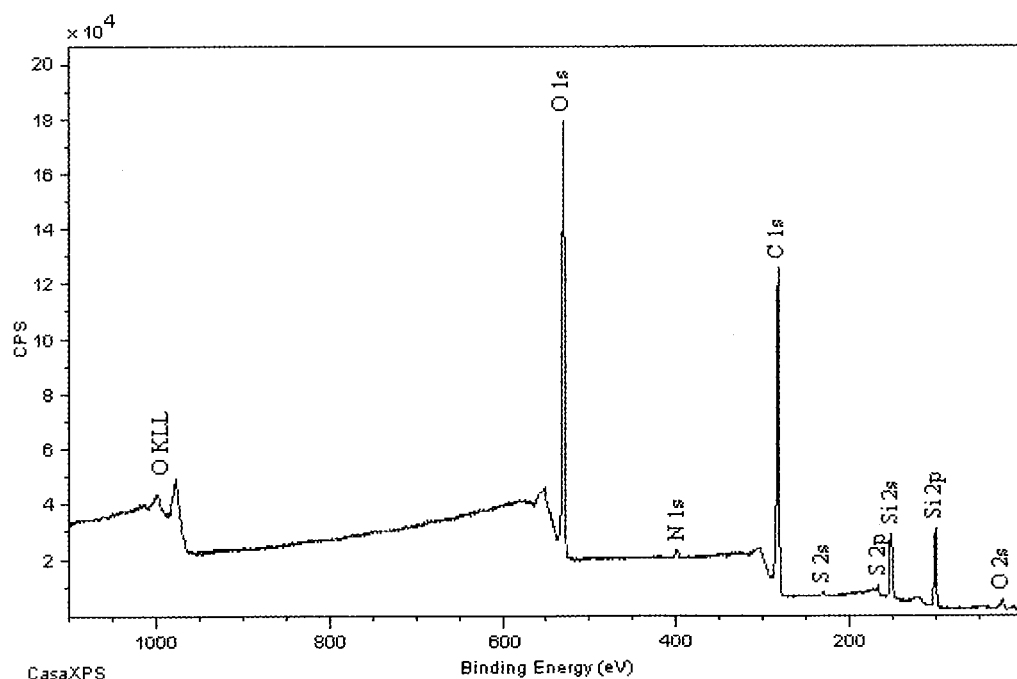


Fig. 5. XPS result of SPS/SSWCNT composite film.

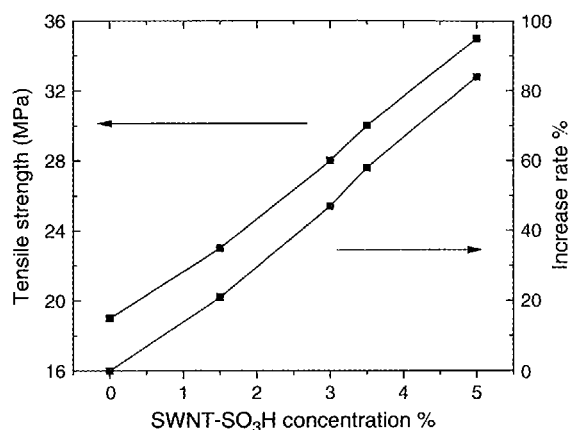


Fig. 6. The tensile strength data of SPS/SSWNT composite film.

measured mechanical strength is the same as that of non cross link film (21 Mpa). It is also clearly seen that the addition of SSWCNTs increased the tensile strength of composite films. Addition of 5 wt% SSWCNTs increases the film's tensile strength by 84%, from 19 MPa (neat polystyrene) to 35 MPa. Also, Figure 6 shows that the increase of tensile strength is linear, indicating that when the weight percentage of SSWCNT is increased, tensile strength also increases.

The tensile increase ratio (84%) could be further enhanced with quality improved film. Films of SSWCNT/SPS composite were made by drop-casting solutions of the mixture onto clean glass substrates and dried in the air. The rate of solvent evaporation influences the homogeneity of the film. Figure 7 shows the SEM image of 5 wt% SSWCNT/SPS composites films (quickly dried in air) (scale bar: 60 μ m). It is clearly seen that film is not uniform. A lot of holes and defects occur gradually. Fast evaporation of solvents ruins the homogeneity of the film.

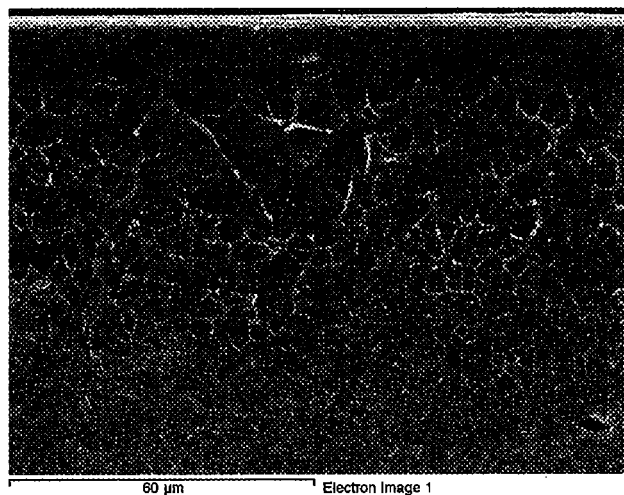


Fig. 7. SEM of 5 wt% SSWCNT/SPS composites films (quickly dry in air) (scale bar: 60 μ m).

With 10 wt% sulfonated SWCNTs added to the sulfonated polystyrene solution containing an appropriate cross link agent, a more significant tensile strength increase is expected. However, due to the high sulfonated nanotube weight percentage, the solution became very viscous and the quality of the film made by the free-standing method is relatively poor and non-uniform. The measured mechanical strength is much lower than expected.

Since carbon nanotubes increase the viscosity of fluids much more than other materials, such as polymer and metal oxide, due to its unique structure, it is hard to load them with large amounts of nanotubes. Hence, only limited improvements of the mechanical properties are observed. It is highly demanding to develop a clear scientific understanding of the main obstacles preventing ultrahigh CNT loading in composites and propose new methods or approaches to increasing the loading of well dispersed CNTs in structural composites.

3.6. Structure and Mechanical Properties

Normally, without a chemical reaction between nanotube and polymer and proper nanotube alignment, a 5 wt% nanotube loading in a polymer matrix only leads to a 30–50% increase in tensile strength. An interfacial problem between polymer and nanotube is the reason for this relative low tensile value because it is hard to transfer the force from polymer to the inorganic nanotube in such a situation. A combination of good dispersion and covalent cross-linking between polymer and nanotube significantly enhances the compatibility and strength of the interface, resulting in materials that show relatively high mechanical strength.

However, compared with the extremely high tensile strength of SWCNT (around 60 GPa), the strength value of our cross-link membrane (35 MPa) is still very low. Assuming that nanotubes disperse very well in the polymer matrix, ideally, a 5 wt% nanotube loading in a film would have a tensile strength of around ≈ 3 GPa. One possible explanation of the lower than expected values may be as follow: the insertion of functional group interferes with the conjugate structure of the nanotube, thereby reducing its macro-mechanical strength. The effective electrical conductivity measurement of SSWCNT solution³⁹ provides strong evidence and support to this assumption. No percolation threshold phenomenon is observed in the experiments. The linear conductivity increase versus the weight percentage indicates that the dominant conduction mechanism might be the ionic conduction, which is in agreement with the chemical structure of functional SSWCNT (anion SO_3^- group).

Many references^{19,31} reported that it is hard to get improved mechanical tensile strength, although a lot of efforts have been put to functionalize the nanotube and chemically bond with polymer matrix (co-valent bond).

These results might also be explained by our assumption that macro-mechanical strength is damaged by addition (insertion) of functional group.

Therefore, partially oxidizing (functionalizing) the nanotube might be a good direction for making the ultra thin and ultra light weight film. Functional groups would maximally reduce the interfacial influence and unbroken nanotube conjugate structure would maintain a high macro mechanical strength value. Electrical conductivity measurement could provide the information of nanotube structure. Kotov et al.⁴⁰ recently has discovered that slightly oxidized the SWCNTs could significantly increase the mechanical strength of layer-by-layer nanocomposite films. A tensile strength value of around 500 MPa could be reached, which is two times greater than the previous value without oxidation (160 MPa).

Nanotechnology is new and challenging, but the reward is also tremendous. The success of this research could lead to a thin, uniform, lightweight reinforced film which has great application in aerospace.

4. CONCLUSION

In summary, this study involved making a series of SPS/SSWCNT composite films with different weight percentage of SSWCNTs. The SEM images of these composite films showed that SSWCNTs disperse very well in a SPS polymer matrix. The composite films after cross link reaction were not dissolved in the solvents anymore, indicating that cross linking reaction did occur between SSWCNTs and SPS. XPS results verified this assumption. The cross link reaction is responsible for the substantial increase of the tensile strength of the composite film. At 5 wt% SSWCNT loading, the tensile strength increased by 84% compared with no nanotube loading. Normally, 5 wt% nanotube loading only leads to a 30–50% increase in tensile strength.

These mechanical enhancement results are very encouraging because they demonstrated a significant improvement in the tensile strength of the polymer composite. Relationship between structure and mechanical properties are discussed in the end and possible direction toward ultra thin and ultra lightweight film is proposed.

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