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Reactive Coagulation of Single-Walled Carbon Nanotubes for Tougher Composites – Solution Processing and Assembly

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Abstract. The injection of reduced single-walled carbon nanotubes into a coagulation bath of polyvinyl chloride (PVC) solution leads to the formation of nanocomposite fibres with polymer covalently bound to the nanotubes. The influence of PVC concentration and molecular weight, and the extrusion diameter on the nanocomposite fibre tensile properties and composition have been examined. The nanocomposite fibres produced have strengths as high as 480 MPa and modulus of 15 GPa, making them the strongest and stiffest PVC composites recorded to date.

BACKGROUND

Single-walled carbon nanotubes (SWCNTs) are ideal fillers for nanocomposites owing to their high intrinsic mechanical properties, low weight, and high aspect ratio.[1] However, SWCNTs dispersed at high weight loadings through shear based approaches tend to form bundled agglomerates in the final composites which act as defects in the resulting composite. Instead, reduction to 'nanotubide' anions[2] can be performed generating salts which are spontaneously soluble as individualised SWCNTs[3] at high concentrations. The approach relies on stabilization through Columbic repulsion, and avoids damage more typically induced during shear dispersion or acid oxidation. Nanotubides are highly reactive, opening the possibility of a family of functionalisation reactions, most commonly through addition of alkyl halides. The high concentration nanotubide solution can be used as a dope for coagulation spinning of pure SWCNT fibres,[4] though their mechanical properties are relatively poor. 'Reactive coagulation spinning', using a polymer coagulant that is reactive towards nanotubide, such as polyvinyl chloride (PVC), allows formation of stronger composites with matrix covalently grafted onto the filler. In this approach, the SWCNTs are wrapped in polymer, as evidenced by their lack of electrical conductivity and high composite dielectric constant, even at high loadings.[5] The composite mechanical properties can be modulated by SWCNT selection: longer SWCNTs give higher strain-to-failure and more crystalline nanotubes provide higher strength. Nevertheless, while the mechanical properties of these composites are higher than nanotubide-derived pure SWCNT fibres, their performance is limited by poor processing and has significant scope for improvement. Here, the effects of coagulant concentration, polymer molecular weight and extrusion cannula diameter are examined to improve the reactive coagulation fibre spinning of nanotubide.

EXPERIMENTAL

Materials

Sodium (99.99 % ingot), N,N-dimethylacetamide (DMAc, 99 %), naphthalene (99 %) and PVC were purchased from Sigma Aldrich Ltd. (U.K.). PVC was purchased at three different molecular weights: M_w 43 kDa (M_n 22 kDa),

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M_w 80 kDa (M_n 47 kDa), M_w 233 kDa (M_n 99 kDa). Polymers are referred to by weighted average molecular weights throughout. Methyl isobutyl ketone (MiBK, 99.9 %), ethanol (96 %), and water (HPLC grade) were purchased from VWR (U.K.). SWCNTs (Elicarb, P929, Batch K108511/g) were provided by Thomas Swan (U.K.) and purified before use through a previously reported reductive route.[6]

Characterization

Thermogravimetric analysis (TGA) was performed on a Pyris 1 (Perkin Elmer, U.S.A.), under 60 sccm nitrogen flow on 0.5 - 1 mg samples. The samples were held at 100 °C for 90 min to dry the sample and degas the furnace, weights are normalized to the weight at, and are presented from, the end of this drying step. The samples were then heated at 10 °C min^{-1} to 700 °C. Single fibre tensile tests were adapted from BS ISO 11566 with fibres mounted to a card template using Araldite Rapid (Huntsman, U.S.A) for ease of handling, and tested at 15 mm gauge lengths at a cross head displacement of 15 µm s^{-1} on a TST350 Tensile testing stage (20 N load cell, Linkam U.K.). The fibre cross-sectional area was assumed to be circular at fracture site, with true stress provided accordingly, and standard error is provided from at least 10 samples tested for each sample set.

Processing

Nanotubide solutions were made using a previously reported technique;[7] in short, in a glovebox, sodium (2.3 mg, 0.1 mmol) and naphthalene (12.8 mg, 0.1 mmol) were dissolved in dry DMAc (3.4 mL) through stirring with a glass stirrer bar for 1 h to give a deep green solution, before dried SWCNT powder (12 mg, 1 mmol, 3.5 mg mL^{-1}) was added and stirred overnight to give a viscous black solution. Reactive coagulation spinning was performed according to previously reported procedure.[5] PVC was dissolved in boiling MiBK at a desired concentration and cooled to room temperature before use, poured into a crystallization dish on a rotating platform. The nanotubide dope was drawn into a syringe in the glovebox and capped before removal to limit exposure to non-ambient conditions before spinning. The cap was replaced by a z-shaped cannula allowing the dope to be injected parallel to the flow of the rotating bath and was injected via syringe pump at a gauge-dependent rate (Table 1) into a bath traveling at 20 cm s^{-1} at the point of injection. The extruded fibres were removed from the coagulation bath and dried under tension (0.49 mN) before soaking in fresh MiBK (5 min, 50 °C) to remove adsorbed PVC, and dried at room temperature.

TABLE 1. Injection rates for varying diameter cannulas, calculated to give flow velocity of 15 cm s^{-1}.

Cannula Gauge	Cannula Diameter (µm)	Cross-Sectional Area (m^2)	Injection Rate (mL h^{-1})
24	311	7.54×10^{-8}	41
27	210	3.46×10^{-8}	19
29	184	2.66×10^{-8}	14

RESULTS AND DISCUSSION

Extrusion Cannula Diameter

It is a common adage within the materials community that smaller is stronger: by decreasing the cross sectional area of a material, the probability of the material containing a weakening flaw is decreased. In coagulation spinning, decreasing the extrusion diameter will not only decrease the fibre diameter, but is also expected to increase the SWCNT alignment in the composite due to higher shear of the dope. Here, three cannulas (24 gauge, 27 gauge, 29 gauge) were used to a spin nanotubide dope into a 5 wt% $PVC_{(MiBK)}$ (43 kDa) coagulant. Final fibre diameter followed the same trend as the cannulae diameter (Table 2). As the fibre diameter reduced, strength (143 MPa to 234 MPa) and modulus (7.8 GPa to 17.3 GPa) increased substantially, whilst strain-to-failure (4.5% to 2.5%, Fig 1) decreased. This trend is consistent with increasing alignment of SWCNTs within the nanocomposite fibre. Increasing the initial alignment of SWCNTs increases their contribution to reinforcement along the fibre axis but reduces the capacity to realign under tension, subsequently reducing the strain-to-failure of the nanocomposite fibres. As the PVC content is similar between all samples (26.7 wt% to 32.9 wt%, Fig 1d) and independent of cannula diameter, the mechanical differences can be attributed to the fibre hierarchy. The consistency in composition also demonstrates that

the fibre formation is not hampered by PVC diffusion which might have been expected to decrease PVC content for larger diameter fibres.

TABLE 2. Diameters and mechanical properties of SWCNT/PVC composite fibres coagulated using differing gauge dope injection cannulae. † Values in parentheses represent standard deviations. * SWCNT content calculated at 600 °C from TGA. ‡ Calculated average value from mean strength and mean diameter.

Cannula Gauge	Fibre Diameter (µm) †	SWCNT (wt%) *	Strength (MPa)	Young's Modulus (GPa)	Strain-to-failure (%)	Breaking Force (mN) ‡
24	34.0 (± 14.6)	32.9	143 (± 25)	7.8 (± 0.4)	4.5 (± 0.2)	519
27	31.2 (± 9.9)	26.7	163 (± 11)	10.2 (± 1.0)	2.8 (± 1.8)	498
29	24.7 (± 7.8)	26.8	234 (± 17)	17.3 (± 1.3)	2.5 (± 0.7)	448

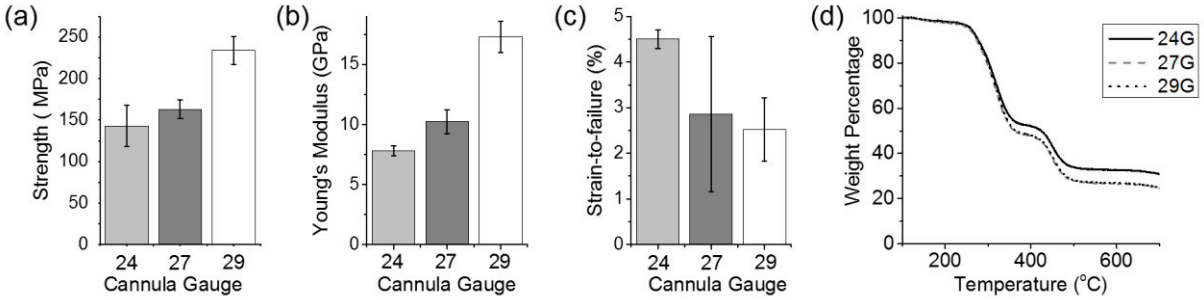


FIGURE 1. Left: Mechanical properties of SWCNT/PVC fibres created using Elicarb nanotubide dope and PVC solution (M_w = 43 kDa, 5 wt% in MiBK) as coagulant. Right: TGA of SWCNT/PVC composite fibres coagulated using differing gauge dope injection cannulae 5 wt%, 43 kDa PVC coagulant.

PVC Coagulant Control

To measure the influence of the PVC coagulant, three commercial PVC samples (M_w 43 kDa, 80 kDa, and 233 kDa) were dissolved in MiBK at two different concentrations: 1 wt% and 3.5 wt%. The 'high' concentration was decreased from the 5 wt% used for the previous experiments as 233 kDa PVC forms gels at ≥4 wt% at room temperature (Fig 2). Fibres were spun with 24 gauge cannula to increase handleability, as in spite of the increased mechanical performance from narrower cannulas/fibres, the absolute breaking force of the thicker fibres is still higher (Table 2).

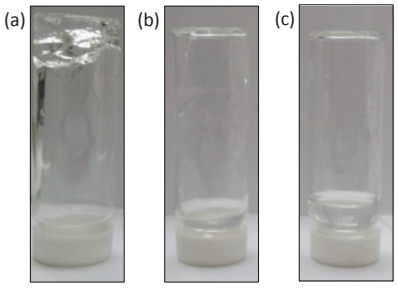


FIGURE 2. PVC (Mw 233 kDa) in MiBK at varying concentrations. 5 mL of solution at (a) 5.0 wt%, (b) 4.0 wt%, and (c) 3.5 wt% after inverting and leaving to stand for ~5 seconds.

The molecular weight of the PVC in the coagulation bath was inversely related to the percentage of polymer within the final composite fibre (Fig 3), *i.e.* the heaviest 233 kDa PVC leads to the lowest PVC content for both coagulant

concentrations likely due to the increased diffusion times required for the polymer into the coagulating fibre, akin to the effects seen by Mercader *et al.*[8] for coagulation SWCNTs in polyvinyl alcohol solutions. Decreasing the concentration of the polymer decreased the loading of polymer in the final composite for all PVC molecular weights. While increasing the polymer concentration could be thought to increase the quantity of polymer which can diffuse into the coagulating fibre, as shown for varying gauge nanocomposite fibres, the composition is not diffusion controlled. Instead it is thought that the number of grafting sites for distinct PVC molecules along each SWCNT is increased with increasing polymer concentration. A single PVC molecule contains thousands of C-Cl bonds capable of reacting with a nanotubide, with each reaction depleting the finite number of reactive charges on the nanotubide.[9] If one PVC molecule grafts to a nanotubide, it will, given time, eventually wrap the SWCNT, covalently bonding at many sites along the surface, depleting charge and sterically occluding the grafting of additional PVC molecules. By increasing the polymer concentration, the number of distinct PVC molecules which can react to each nanotubide, before the surface is occluded/the charge depleted, is likely increased.

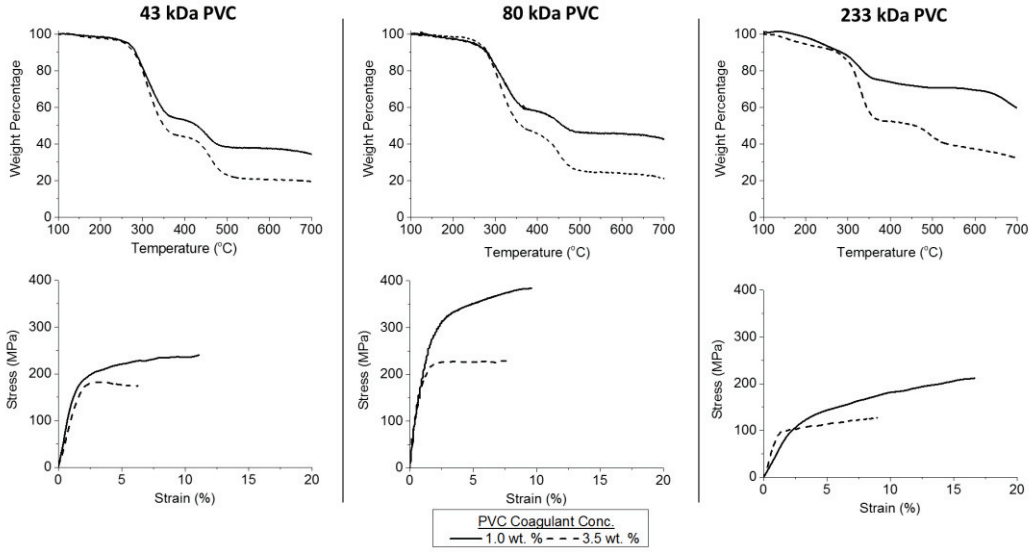


FIGURE 3. Thermograms (top) and representative stress-strain diagrams (bottom) for SWCNT/PVC nanocomposites fibres.

As previously reported,[5] SWCNT/PVC nanocomposite fibres behaved elastically to a yield point at 1% - 2% strain, however, after yield, the mechanical behavior was dependent on the SWCNT loading. Composites spun using 1 wt% PVC coagulant (*i.e.* with higher SWCNT loadings, Fig 3) displayed noticeable strain hardening. In the 3.5 wt% PVC samples, only the 233 kDa sample (which also indicated high CNT loading) showed a strain hardening response (Fig 3, right); the rate of strain hardening was noticeably higher for the 1 wt% PVC samples containing the higher SWCNT content (69.5 wt% vs 37.3 wt%). The dependence on SWCNT loading combined with the lack of strain hardening seen intrinsically for PVC leads to the conclusion that the strain hardening is a SWCNT effect, tentatively assigned to reorientation. It is worth noting that these trends are consistent with the 5 wt%, 24 gauge experiments (*vide supra*) which show lower strength, modulus, strain-to-failure (Fig 1) than either of the 1 wt% and 3.5 wt% PVC concentration coagulant based nanocomposite fibres.

TABLE 3. Properties of SWCNT/PVC composite fibres from varying coagulants * Calculated from TGA at 600 °C.

Mw (kDa)	PVC Coagulant (%)	SWCNT (wt%) *	Strength (MPa)	Young's Modulus (GPa)	Strain-to-failure (%)
43	1.0	37.7	217 (± 25)	11.0 (± 1.1)	8.0 (± 3.1)
43	3.5	20.7	183 (± 10)	10.0 (± 1.1)	4.6 (± 2.6)
80	1.0	45.7	295 (± 19)	15.0 (± 0.3)	8.9 (± 1.9)
80	3.5	23.8	253 (± 19)	15.0 (± 1.2)	7.7 (± 2.5)
233	1.0	69.5	211 (± 17)	5.98 (± 0.8)	12.3 (± 6.3)
233	3.5	37.3	122 (± 14)	8.90 (± 1.0)	7.5 (± 2.1)

The molecular weight of the coagulant polymer has a strong influence on the composite's mechanical properties (Fig 4). The 80 kDa PVC shows the best strengths (295 MPa for 1 wt% PVC, max 482 MPa measured) and moduli (15.0 GPa). The increase in strength versus the 43 kDa PVC composites can be either attributed to the higher SWCNT loading, or the higher inherent strength of longer polymers due to heightened intermolecular bonding. The 233 kDa PVC composites have the highest SWCNT loading but the lowest average strengths and moduli. Combined with their high strain-to-failures, it is thought that the SWCNTs are very poorly aligned leading to high reorientation under tension but poor SWCNT contribution to strength due to their off axis loading orientation.

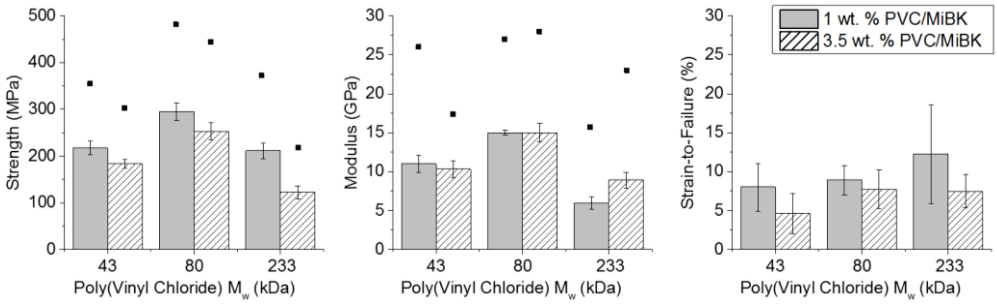


FIGURE 4. Tensile properties of Elicarb/PVC nanocomposite fibres with varied PVC coagulant concentrations and PVC molecular weights. Squares represent the highest measured values.

CONCLUSION

Reactive coagulation spinning of individualised, reduced SWCNT nanotubide ions into PVC solutions provides an effective new route to SWCNT composites. By examining the spinning parameters, the mechanical properties have been substantially improved, over the nanocomposite fibres reported initially. By decreasing the extrusion diameter, strength and modulus are increased, at the expense of strain-to-failure. By decreasing the concentration of the polymer in the coagulation bath, the loading of SWCNTs in the composite can be increased, subsequently increasing the strength and strain-to-failure of the nanocomposite fibres; at high SWCNT loadings, the toughness is further increased by introduction of a strain hardening mechanism. Finally, the matrix molecular weight has an important effect on the mechanical performance: an intermediate weight appears to maximise strength and stiffness by balancing the poor intrinsic properties of short polymers and the limited matrix loading obtained for larger polymers.

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