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2019

Liu, B., Liu, C., De Luca, H. G., Raman Pillai, S. K., Anthony, D. B., Li, J., . . . Chan-Park, M. B. (2019). Synthesis of epoxidized poly (ester carbonate)-b-polyimide-b-poly (ester carbonate) : reactive single-walled carbon nanotube dispersants enable synergistic reinforcement around multi-walled nanotube-grafted carbon fibers. *Polymer Chemistry*, 10(11), 1324-1334. doi:10.1039/C8PY01465E

<https://hdl.handle.net/10356/138616>

<https://doi.org/10.1039/C8PY01465E>

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Synthesis of epoxidized-poly(ester carbonate)-b-polyimide-b-poly(ester carbonate): reactive single-wall carbon nanotube dispersants enable synergistic reinforcement around multi-wall nanotube grafted carbon fibers†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Polyimides (PI) generally have high affinity for single walled carbon nanotubes (SWNTs), but suffer from poor solubility in most low boiling point organic solvents and low compatibility with common resins (such as epoxy) used in composites, limiting their suitability as dispersants. PI block copolymer systems containing reactive poly(ester carbonate)s have not yet been reported and are expected to act as effective reactive dispersing agents of SWNTs. Herein, PI derived block copolymers are synthesized via ring-opening copolymerization of lactide (LA) (a control monomer) and allyl-bearing 2 methyl 2 (allyloxycarbonyl)-propylene carbonate (MAC) from the OH-terminal ends of the PI block to produce PLA-PI-PLA (TB1, a control) and PMAC-PI-PMAC (TB2). The allyl pendant group of TB2 allows further facile functionalization to form a third series of epoxidized (EP) derivatives, i.e. PMACEP-block-PI-block-PMACEP (TB3). TB3 copolymer when mixed with a conventional structural epoxy resin forms blends that do not show inferior tensile properties compared with the epoxy, which is unusual. Further, the mixing solvent tetrahydrofuran (THF) can be readily evaporated off after forming the blends. TB3-dispersed (2 wt.%) SWNTs added to epoxy increased the tensile strength, modulus, and elongation to break of the resulting nanocomposite films by 40%, 34%, and 26% respectively, compared to the baseline epoxy resin. Furthermore, when TB3b triblock-dispersed SWNT in epoxy was combined with fuzzy carbon fibers, i.e. carbon nanotube-grafted-carbon fibers (CNT g CF), a synergistic interfacial strength reinforcement was observed, together with shifting the failure mode from the matrix interphase to the carbon fiber-grafted nanotube interface. The ultimate interfacial shear strength between TB3-dispersed SWNT-epoxy matrix and the fuzzy carbon fibers (i.e. fibers having carbon nanotubes grown on them) measured via single fiber pull-out tests, was 100 MPa, which was ca. 11% improvement over the baseline unsized carbon fiber in neat epoxy. To our knowledge, this is the first evidence of a synergistic enhancement in interfacial properties when fuzzy carbon fibers are combined with a SWNTs-reinforced epoxy using the new epoxidized TB3 nanotube dispersing agent that forms strong covalent TB3-epoxy interface. The new functionalizable TB3 synthesis route introduced here is generalizable to other PI-based copolymers with diverse functionalities and solvent compatibilities.

1 Introduction

Carbon nanotubes (CNTs), and especially single walled carbon nanotubes (SWNTs), have received much attention due to their outstanding intrinsic mechanical, electrical and thermal properties.¹⁻³ Their addition to conventional carbon fiber reinforced composites has shown great promise, notably by

addressing matrix and interface dominated failures.⁴⁻⁶ CNTs incorporation in hierarchical composites follows two main routes. The first method consists of grafting CNTs directly on the carbon fibers, with recent progress allowing for the continuous CNT synthesis and production of these hierarchical fibers, also known as “hairy” or “fuzzy” fibers.^{7,8} The second, is to incorporate the CNTs into the bulk matrix, which often involves shear-mixing prior to infiltration into carbon fiber fabrics, but this approach is generally limited to low loadings due to significant increase in matrix precursor viscosity. Moreover, CNTs in the matrix tend to form aggregates which are detrimental to the final composite mechanical performance. We predict that the combination of both approaches, i.e. embedding carbon nanotube-grafted-carbon fibers (CNT-g-CFs) into a SWNT-reinforced epoxy resin system, thus simultaneously reinforcing the interface and the interphase, should provide a synergistic reinforcing effect to enhance interfacial strength. For this, it is of utmost

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Scheme 1 Synthesis of PLA-PI-PLA (TB1), PMAC-PI-PMAC (TB2), and PMACEP-PI-PMACEP (TB3) triblock copolymers.

1 importance to reduce CNTs aggregation in the matrix
 2 precursor and the use of a dispersant to achieve an
 3 appropriate dispersion, and ideally individualization, of
 4 SWNTs should facilitate optimal nano-reinforcement in the
 5 composite. Further, the dispersing agent should covalently
 6 link to the epoxy-based resin to maximize interfacial strength.
 7 Polyimides (PI) are a class of widely used high-
 8 performance polymers with outstanding thermal,
 9 mechanical, physicochemical, and dielectric properties.⁹⁻¹⁴
 10 PI-derived block copolymers have been used as dispersing
 11 agents for carbon nanotubes to more fully exploit them as
 12 reinforcements in nanocomposites. In order to transfer the
 13 outstanding properties of nanotubes in nanocomposites, the
 14 nanotubes must be fully dispersed, and the nanotube/matrix
 15 interfacial strength ought to be high. Often, a dispersing
 16 agent is used but it can be a source of weak interphase. We
 17 have previously designed various dispersing agents for
 18 nanotubes to be applied in nanocomposites, but the solvents
 19 used for those dispersions typically have high boiling points
 20 (e.g. dimethylformamide (DMF)). We recently reported block
 21 copolymers of PI and polycaprolactone (PCL), i.e. PCL-PI-PCL,
 22 that can disperse nanotubes in low boiling organic solvent
 23 (tetrahydrofuran, THF) but the blends of the block copolymer
 24 with epoxy, a common resin used for nanocomposites,
 25 resulted in inferior mechanical properties compared to
 26 epoxy.¹⁵ We hypothesize that in addition to strong linkage of
 27 the dispersing agent to carbon nanotubes through the PI
 28 component of the agent, better compatibility and covalent
 29 linkage of the dispersing agent to the resin are necessary but
 30 missing from our previous nanotube dispersing agents.¹⁵
 31 Synthesis of block copolymers derived from PI and poly(ester-
 32 carbonate) (including functionalizable ones) have not yet
 33 been reported. Poly(2-methyl-2-(allyloxycarbonyl)propylene
 34 carbonate) (PMAC), is a type of poly(ester-carbonate) with

35 pendant allyl group that allows post-functionalization.¹⁶⁻¹⁸ We
 36 hypothesize that block PI-poly(ester-carbonate) copolymers
 37 may act as effective dispersants of single-walled carbon
 38 nanotubes (SWNTs) since aromatic PIs have good π - π
 39 interaction with SWNTs while the PMAC block has good
 40 solubility in low boiling point solvents such as tetrahydrofuran
 41 (THF), chloroform (CHCl₃) and dichloromethane (CH₂Cl₂).
 42 Further, the PMAC block is relatively polar, like epoxy, and can
 43 be post-epoxidized into novel epoxidized(EP)-PMAC-PI-
 44 epoxidized-PMAC triblock copolymers (denoted hereafter as
 45 PMACEP-PI-PMACEP). We hypothesize that blends of epoxy
 46 with the new PMAC-PI-PMAC and PMACEP-PI-PMACEP block
 47 copolymers may have improved mechanical properties
 48 compared with previously reported PCL-PI-PCL, which
 49 degrades the neat epoxy/PCL-PI-PCL tensile properties. We
 50 also synthesize PLA-PI-PLA block copolymers (PLA standing
 51 for poly(lactic acid)) as controls in this paper to compare
 52 against previously reported less polar PCL-PI-PCL copolymers.
 53 This paper reports our design, synthesis and application of
 54 3 series of novel triblock (TB) copolymers (Scheme 1) of (i)
 55 polylactide-block-polyimide-block-polylactide (PLA-PI-PLA)
 56 (TB1a and TB1b with different PLA block lengths), (ii)
 57 PMAC-PI-PMAC (TB2a and TB2b), and (iii) epoxidized (EP)
 58 derivatives of PMAC-PI-PMAC (hereafter referred to as
 59 PMACEP-PI-PMACEP) (TB3a and TB3b, Table S1). The triblock
 60 copolymers were synthesized through the addition of
 61 hydroxyl (-OH) groups at polyimide terminals, followed by
 62 ring-opening polymerization of lactide and functional
 63 carbonate (Scheme 1). The copolymers were used as
 64 dispersing agents for single walled carbon nanotubes
 65 (SWNTs) in THF. Epoxy was then added to the dispersion and
 66 mixed to prepare nanocomposite films by solvent casting. In
 67 order to confer reactivity of the TB copolymer dispersing
 68 agent with the epoxy resin matrix, and thus improve the

Table 1 Synthesized triblock copolymers initiated by polyimide homopolymer.

Sample	Monomer	Design [I]:[M] ^a	Initiator (Da)	M _n (Da) ^b	PDI ^b	Actual Ratios of m:n ^c
TB1a	<i>rac</i> -LA	1:80	PI (6900)	9780	1.55	10:20
TB1b	<i>rac</i> -LA	1:100	PI (6900)	15500	1.59	10:60
TB2a	MAC	1:110	PI (6900)	11000	1.78	10:20
TB2b	MAC	1:150	PI (6900)	15000	1.90	10:40

^a Mole ratio of polyimide macroinitiator and *rac*-LA/MAC monomers for ring-opening polymerization.^b Determined from GPC using polystyrene standards as references.^c Calculated from the molecular weight of polymers and single units (see Scheme 1 for the definition of m and n).

transfer of stress through the resin to SWNTs, the vinyl groups of PMAC-PI-PMAC copolymers were epoxidized with 3-chloroperbenzoic acid (m-CPBA) to obtain pendant epoxy-containing copolymers (TB3a and TB3b, Scheme 1). The copolymers were characterized by NMR, FTIR and GPC. The neat (i.e. without SWNTs) blends of TB1 (control TB) and TB3 with epoxy have similar tensile properties compared to neat epoxy and this is significant since previously reported less polar and non-reactive PCL-PI-PCL resulted in reduction of the block copolymer/epoxy blend tensile properties.

SWNT dispersions in THF were examined by UV-VIS-NIR and Raman spectroscopy. The SWNT/matrix interaction was investigated by FE-SEM and TEM, to determine the effectiveness of TB1b, TB2b and TB3b triblock copolymers as dispersants. We also measured the tensile properties of the nanocomposite films. The optimized triblock copolymer (TB3b)-dispersed SWNTs (2 wt.%) increased the tensile strength, modulus, and elongation of epoxy nanocomposites by 40%, 34%, and 26% respectively over that of neat epoxy. Lastly, we demonstrate that SWNTs dispersed by TB3b in epoxy resin increase the interfacial strength between the blended resin matrix and carbon fibers (CFs), which is relevant for improving the mechanical properties of CF-reinforced epoxy composites. We further demonstrate that the matrix-CF interfacial strength can be further increased using fuzzy carbon fibers which have surfaces grafted with in-situ grown multi-walled carbon nanotubes.

Results and discussion

Design and Synthesis of PLA-PI-PLA, PMAC-PI-PMAC and PMACEP-PI-PMACEP Copolymers

The α,ω -dihydroxy-polyimide macroinitiator (OH-PI-OH) was prepared according to our previous work.¹⁵ Briefly, the polyimide macroinitiator was synthesized by condensation of a dianhydride (specifically 2,2-bis[4-(3,4-dicarboxyphoxy)phenyl] propane anhydride (BPADA)), diamine (specifically 3,3'-dihydroxy-4,4'-diamino-biphenyl (HAB) and 4-aminophenethyl alcohol (APA)) (molar ratio [BPADA]/[HAB]/[APA] = 4:3:2). The ¹H NMR spectrum of OH-PI-OH is shown in Figure S1: the resonances at 10.17 ppm ('a') are assigned to the hydroxyl protons of the polyimide block; the resonance at 4.82 ppm ('b') is attributed to the hydroxyl protons at the two ends. The ratio of the areas of 'a'

and 'b' indicates the number of repeat units in the OH-PI-OH ("m" in Figure S1) to be around 4. The number-average molecular weight (M_n) and molecular weight distribution (PDI) of the synthesized OH-PI-OH precursor measured by gel-permeation chromatography (GPC) was 6900 Da (with PDI of 1.32), thus m=6900/690=10 (690 is the M_n of single repeat unit), which is somewhat higher than that from the NMR results. The OH-PI-OH precursor was then mixed with tin(II) 2-ethylhexanoate (Sn(Oct)₂) which catalyzed a ring opening polymerization that is not living,¹⁹ to yield an α,ω -OSn(Oct) terminated PI macroinitiator, which can undergo further ring-opening polymerization with lactide (LA) and 2-methyl-2-(allyloxy-carbonyl)propylene carbonate (MAC). We synthesized two PLA-PI-PLA triblock (TB1a and TB1b, Scheme 1) and two PMAC-PI-PMAC triblock copolymers (TB2a and TB2b, Scheme 1) with varying macroinitiator to monomer ratios (Table 1). The PMAC-PI-PMAC polymer was also epoxidized, with m-chloroperbenzoic acid, to produce PMACEP-PI-PMACEP (TB3a and TB3b, Scheme 1).

All copolymers were characterized by NMR and GPC. ¹H NMR spectra of TB1a and TB1b (Figures S2 and S3) have resonances at 7.17, 7.38, 7.97 and 10.14 ppm assigned to the polyimide block, while the resonances centered at 1.41 ('e') and 5.12 ppm ('g') are attributed to the methyl and methyne protons of the PLA block. For TB2b (and also TB2a) (Figures 1, S4 and S5), the resonances at 1.23 ('e') and 5.94 ppm ('h') are methyl and methyne protons of the PMAC block, and the resonance at 3.48 ppm ('f', Figure S5) is the methylene protons next to benzene rings of PI, indicating the successful synthesis of TB2b. Epoxidation of TB2a leads to the copolymer TB3a with new signals at 2.34 and 2.71 ppm ('q' and 'p', Figure S6) due

Fig. 1 ¹H NMR of TB2b (d₆-DSMO, 25 °C).

Fig. 2 FTIR spectra of (a) macroinitiator OH-PI-OH and (b) triblock copolymers.

1 to the protons of epoxy groups. The ratio of the areas of 'h'
2 (refers to methyne proton of vinyl group) and 'q' (refers to
3 methyne proton of epoxy group) is approximately 1:1,
4 indicating conversion of approximately half of vinyl groups to
5 epoxy groups (Figure S6). Similarly, the ratio of the vinyl to
6 epoxy group of TB3b is around 3:1~4:1 based on the NMR
7 spectrum (Figure S7).

8 The FTIR spectra of the OH-PI-OH precursor and the
9 synthesized triblock copolymers (TB1b, TB2b, and TB3b)
10 (Figures 2a and 2b) confirm these findings. The signals around
11 1700 cm^{-1} (C=O stretching) and 1400 cm^{-1} (C-N stretching) are
12 attributed to the imide groups on the OH-PI-OH backbone
13 (Figure 2a). The triblock copolymers (Figure 2b) have bands
14 around 2950 cm^{-1} (C-H stretching) and 1720 cm^{-1} (C=O
15 stretching), which can be assigned to characteristic absorption
16 bands of PLA and PMAC components. The peaks around
17 980 cm^{-1} can be attributed to the double bonds ($-\text{CH}=\text{CH}_2$) on
18 MAC components. Further, the characteristic bands of
19 polyimide around 1750 cm^{-1} (C=O stretching) and 1380 cm^{-1}
20 (C-N stretching) are also observed in all copolymers (Figure
21 2b).

22 The M_n and PDI values of the triblock copolymers were
23 determined by GPC (Figure 3 and S8), and compared to the
24 precursor homopolymer OH-PI-OH. The molecular weights of
25 all the triblock copolymers exceed that of the polyimide
26 macroinitiator (OH-PI-OH). The molecular weights of TB1a,
27 TB1b, TB2a and TB2b are 9780, 15500, 11000, and 15000 Da,
28 respectively, and PDIs are in the range 1.55 to 1.90 (Table 1).
29 We have calculated the repeat units of MAC of TB2b as
30 follows: $n = (15000 - 6900) / 215 \approx 40$.

32 SWNTs Dispersion and Interfacial Bonding with Triblock 33 Copolymers

34 The dispersion of SWNTs in THF was evaluated by UV-Vis-
35 NIR absorption spectroscopy. In order to calibrate the
36 concentration of the SWNTs in the THF solvent, a series of
37 known concentrations of SWNTs was prepared (0, 0.02, 0.04,
38 0.1, and 0.15 mg/mL) and the absorbance at 500 nm
39 measured. The slope of the absorbance versus concentration

40 (Figure 4a) was used to calculate the extinction coefficient
41 ($\epsilon = 23.2\text{ mL/mg/cm}$), for the back-calculation of the
42 concentrations of SWNTs in other samples. The
43 concentrations of SWNTs dispersed with and without TBs prior
44 to centrifugation were determined with increasingly stringent
45 centrifugal forces (Figure 4b). Immediately after sonication, all
46 specimens have a concentration of ca. 0.15 mg/mL. After

Fig. 3 GPC curves of OH-PI-OH, PLA-PI-PLA (TB1a, TB1b), PMAC-PI-PMAC (TB2a, TB2b) and PMACEP-PI-PMACEP (TB3a, TB3b).

Fig. 4 (a) Absorption spectra of SWNTs/TB1b dispersant (mass ratio = 1:2) at different nanotube concentrations. Inset shows the absorbance of the dispersion at 500 nm. The straight line is a linear-least-squares fit to the data. (b) SWNTs concentrations of TBs dispersed in THF under different conditions: immediately after sonication, after centrifugation at 6000 rpm for 10 min, and after centrifugation at 10000 rpm for 10 min.

Fig. 5 Photographs of SWNTs dispersed in THF without any dispersants and using different TBs (a) immediately after sonication; and (b) after centrifugation at 10000 rpm for 10 min.

Fig. 6 TEM images of dispersed SWNTs with (a) TB1b (b) TB2b (c) TB3b at different magnifications.

1 centrifugation at 6000 rpm and 10000 rpm for 10 min, the
 2 concentrations without any dispersing agents are quite low
 3 (< 0.01 mg/mL). For TBs, the concentrations decrease as some
 4 of the SWNTs settled, especially for the TB3a solution. In TB2b
 5 and TB3b, the concentrations maintain a relatively high value;
 6 for TB2b, the supernatant still has 0.11 mg/mL and 0.09
 7 mg/mL after centrifugation at 6000 rpm (3743 RCF) and 10000
 8 rpm (10397 RCF), respectively. For TB3b, the supernatant still
 9 has 0.10 mg/mL and 0.07 mg/mL at 6000 rpm and 10000 rpm
 10 respectively, indicating that TB2b and TB3b are dispersants
 11 superior or comparable to TB1b. Comparing the same kind of
 12 copolymer with different molecular weights (TB2a versus
 13 TB2b, and TB3a versus TB3b, respectively), increased end
 14 block length improves dispersion. For example, the CNT
 15 concentration of TB2a (0.08 mg/mL and 0.04 mg/mL at 6000
 16 rpm and 10000 rpm, respectively) with short chains is much
 17 lower than that of TB2b with longer chains (0.11 mg/mL and
 18 0.09 mg/mL) at both 6000 rpm and 10000 rpm. Increasing the
 19 length of the end blocks leads to a more stable SWNTs
 20 dispersion due to the enhanced solubility in the chosen
 21 solvent (THF). TB1a and TB1b behave differently in that their
 22 dispersion efficacies are quite similar at 10000 rpm; this may
 23 be due to the higher solubility of PLA in organic solvents. The
 24 visual appearance of dispersed SWNTs in different TB
 25 solutions corroborates the UV-VIS measurements (Figure 5).
 26 Immediately after sonication, all the solutions are black. After

27 high-speed centrifugation, some SWNTs settled, especially
 28 with TB3a where the remaining SWNTs in the supernatant are
 29 scarce.

30 In order to examine the nature of the dispersed material,
 31 the morphologies of SWNTs dispersed by TB1b, TB2b and
 32 TB3b in THF were characterized by TEM (Figure 6). From the
 33 TEM images, all three copolymers disperse SWNTs well,
 34 showing no obvious signs of aggregation.

35 Raman spectra of pristine and copolymer-dispersed
 36 SWNTs indicate the degree of structure perturbation
 37 (Figure 7). The peaks at around 1326 cm^{-1} and 1590 cm^{-1}
 38 correspond to the defect-induced (D band) and graphitic (G
 39 band) modes, respectively. I_D/I_G ratios of the
 40 copolymer-dispersed SWNTs are similar though slightly lower
 41 than for the pristine SWNTs (Table S3), indicating that the
 42 SWNT/dispersant interaction does not introduce defects to
 43 the SWNT sidewalls, which is characteristic of noncovalent
 44 interaction. The slight reduction in D/G ratio may indicate

modest selective dissolution or purification effects, as observed for other SWNT-polymer dispersants. The RBM peaks of the polymer-dispersed SWNTs ($156.7\text{ cm}^{-1}/173.8\text{ cm}^{-1}$) are upshifted by $\sim 7\text{--}9\text{ cm}^{-1}$ from the RBM peaks of pristine SWNTs ($149.3\text{ cm}^{-1}/164.8\text{ cm}^{-1}$). The G bands of the polymer-doped SWNTs (1592.0 cm^{-1}) are upshifted by around 1.1 cm^{-1} from the G band of pristine SWNTs (1590.9 cm^{-1}). The 2D Raman band of pristine SWNTs is at 2628.8 cm^{-1} , while those of the TB-dispersed SWNTs are upshifted from 2634.9 cm^{-1} to 2638.3 cm^{-1} (Table S3). The upshift of G bands and 2D bands of the polymer-dispersed SWNTs is due to $\pi\text{--}\pi$ interaction between the copolymers and the SWNTs. The noncovalent attachment does not affect the structure of SWNTs but the strong $\pi\text{--}\pi$ interaction between wrapped polymer chains and the nanotubes leads to the upshift.²⁰ Also, the RBM peaks are generally broadened due to the interaction between SWNTs and the dispersants.

Effects of SWNT dispersion on mechanical properties of TB/epoxy films

TB/THF solvent was prepared at a concentration of 1 mg or 2 mg TB per mL of THF and SWNTs were added to achieve a concentration of 1 or 2 mg SWNTs per mL solvent. The dispersions were sonicated with a tip-sonicator until homogeneous. The SWNT/polymer dispersion in THF was added to pre-mixed epoxy resin/hardener mixture. After thorough agitation by bath sonication, the reinforced resin was cast on a flat substrate and the solvent evaporated at room temperature. The films were then transferred to a vacuum oven and fully dried at $40\text{ }^{\circ}\text{C}$ for 24 h . After peeling from the substrate, the films were cured at $130\text{ }^{\circ}\text{C}$ for 3 h . The produced films have a homogeneous appearance (Figure S9) with no obvious aggregation of the nanofiller at all concentrations of SWNTs (0.5 , 1 , and $2\text{ wt.}\%$) and with all dispersants. Under FE-SEM (Figure 8), the SWNTs appeared well dispersed in the matrix and no aggregation was observed with $0.5\text{ wt.}\%$ SWNT loading (Figure 8b to 8d), for all three

Fig. 8 FE-SEM images of fracture surfaces of (a) SWNT/epoxy; (b) SWNT/TB1b/epoxy; (c) SWNT/TB2b/epoxy and (d) SWNT/TB3b/epoxy with $0.5\text{ wt.}\%$ SWNTs loading and at different magnifications ($\times 10000$, $\times 20000$, and $\times 30000$).

Fig. 7 Raman spectra of pristine SWNTs and polymer-dispersed SWNTs using 633 nm laser.

polymer dispersants. However, without TB there is clear evidence of aggregation (Figure 8a); the SWNTs are not evenly dispersed in the epoxy resin.

The tensile properties (strength, modulus, and elongation at break) of composite films were compared with the base epoxy system (see Table 2). The stress-strain curves (Figure 9) retain a similar shape in all cases, showing plastic failure. The data indicate that TB ($2\text{ wt.}\%$)/EP blends (samples #2-4, Table 2) have tensile properties generally better than or similar to neat epoxy resin, which indicates good compatibility between the TB dispersant and the epoxy resin. From the tensile strengths, it appears that TB3b has good compatibility with the epoxy resin while TB2b and TB1b exhibit poorer compatibility. Since PLA is more polar than PMAC, TB1b has better compatibility than TB2b, while the epoxy groups in TB3b allow it to link covalently to the base resin.

At $1\text{ wt.}\%$ SWNT loading (samples #5-7, Table 2), all three SWNTs/TB/epoxy films have improved tensile properties when compared to the neat epoxy (sample #1, Table 2) and the epoxy resin/TB blends (samples #2-4, Table 2). Amongst the samples #5-7 with $1\text{ wt.}\%$ SWNTs, TB1b (sample #5) has slightly better tensile strength and modulus than the other two composites (samples #6 and #7). However, at $2\text{ wt.}\%$ SWNT loading, the properties of SWNTs with TB1b and TB2b (samples #8 and #9, Table 2) are inferior to the $1\text{ wt.}\%$ samples (#5 and #6, Table 2). The reduction in tensile properties at $2\text{ wt.}\%$ loading for TB1b and TB2b (samples #8 and #9, Table 2) may be due to nanotube bundling and/or relatively weak nanotube/matrix interfacial bonding for the non-covalently functionalized SWNTs. At high SWNT concentration, there may be more voids and more free volume introduced by SWNTs affecting the composite films, thereby impairing the tensile properties of the nanocomposites.^{21, 22}

Table 2 Mechanical Properties of neat EP and SWNT/TB/EP Composite Films with standard deviation provided.

No.	Sample	Strength (MPa)	Modulus (GPa)	Elongation at maximum stress (%)
1	Neat EP	47.8±4.2	1.9±0.2	4.19±0.75
2	TB1b(2 wt.%)/EP	53.5±7.4	2.5±0.4	3.31±0.81
3	TB2b(2 wt.%)/EP	45.1±4.4	2.3±0.3	2.84±0.29
4	TB3b(2 wt.%)/EP	50.1±5.4	2.3±0.2	3.26±0.45
5	SWNTs(1 wt.%)/TB1b/EP	63.3±4.1	2.6±0.4	4.79±0.80
6	SWNTs(1 wt.%)/TB2b/EP	61.2±5.5	2.1±0.2	5.16±0.46
7	SWNTs(1 wt.%)/TB3b/EP	60.3±2.2	2.1±0.3	5.82±1.12
8	SWNTs(2 wt.%)/TB1b/EP	13.6±1.7	0.5±0.09	4.43±1.59
9	SWNTs(2 wt.%)/TB2b/EP	55.1±4.4	2.2±0.3	5.29±1.45
10	SWNTs(2 wt.%)/TB3b/EP	66.9±2.8	2.6±0.4	5.26±1.08

Epoxy functionalization of the dispersant (TB3b) avoids the impairment of the tensile properties at 2 wt.% SWNTs loading (sample #10, Table 2). Among all the composite films, the SWNTs (2 wt.%)/TB3b/EP (sample #10, Table 2) has the best properties. Its tensile strength is 66.9±2.8 MPa, which is 40% above that of the neat epoxy (47.8±4.2 MPa); whilst its modulus reaches 2.6±0.4 GPa, which is 34% higher than neat resin (1.9±0.2 GPa) and the elongation to break is 26% higher. The highest and lowest values of the mechanical properties on the composite films beside the average values are given in Table S4.

The three new PI-derived block copolymer dispersants that can disperse SWNTs in the low boiling point solvent THF. Epoxidized TB3b is the best dispersant among the three copolymers for SWNT/epoxy nanocomposites. It appears that TB3b with epoxy groups has good interaction with SWNTs and good compatibility and reactivity with the epoxy resin; the covalent bonding between the TB3b dispersant and epoxy

25 Interfacial shear strength of single fiber model composites

The effect of SWNT reinforcement in the epoxy resin (hereafter denoted as “matrix”) on interfacial strength of the matrix with micron-sized continuous carbon fibers was also investigated. We determined the apparent interfacial shear strength, a measure of adhesion, between a single carbon fiber embedded in epoxy matrix (both neat and SWNT/TB3b reinforced). In single fiber pull-out tests, typically, upon displacement of the piezo-translator axially with respect to the fiber, the load increases linearly in the elastic regime until one of the three following events occurs; for excessive embedding lengths, the load may exceed the fiber strength leading to fiber failure. For non-ductile/-compliant matrices, the fiber could prematurely debond, initiated at a localized high stress region, leading to a sudden load drop (brittle failure). Finally, for ductile matrices, plastic yielding of the resin would lead to a rearrangement of the shear stresses along the fiber (ductile failure) with the load progressively levelling off until complete debonding occurs. In this study, the latter case was observed for all resin systems, emphasized by the independence of the apparent shear strength from embedded length (ESI Figure S10).

We also explored fuzzy carbon fibers in which the fibers were modified with an in-situ grown layer of multi-walled

Fig. 9 Typical Stress-Strain Curves of TBs/epoxy/SWNT composite films.

resin could cause improved stress transfer between matrix and nanofillers, without impairment of the neat matrix properties.

Fig. 10 SEM images of (A, B) as-received unsized carbon fibers and (C, D) CNT-g-CFs with 1 μm scale bars.

carbon nanotubes. The carbon fibers were successfully grafted with a uniform coating of CNTs, around 200 nm long and 10 nm in diameter (Figure 10). As found previously,⁸ this nanostructured interphase increased the interfacial shear strength by 7.5% (to 96.7 MPa) when compared to the virgin carbon fibers (89.4 MPa) in neat epoxy (Figure 11, first 2 columns). The slight increase in apparent interfacial shear strength on adding 0.1 wt.% SWNT is not statistically significant (comparing first and third columns, or 2nd with 4th columns); however, on increasing the SWNT loading to 1.0 wt.% (using TB3b as the dispersing agent), IFSS increased to 95.6 ± 2.7 MPa (fifth column, Figure 11) compared to neat resin (89.4 ± 1.3 MPa). The interfacial shear strength (IFSS) increased further when combining CNT-grafted-carbon fibers (CNT-g-CFs) with a SWNT/TB3b-reinforced epoxy resin matrix by 10.8% increase over the baseline (100.2 ± 1.5 MPa, Table S5 and Figure 11). Fracture surfaces (Figure 12) of unsized carbon fibers in neat epoxy are relatively clean; no epoxy residue can be seen on the fiber surface. CNT-g-CFs, on the other hand, have rougher fracture surfaces when pulled-out from neat epoxy, consistent with the increased interfacial shear strength, and deflection of the failure to the CNT-epoxy interface. However, when the epoxy matrix is further reinforced with 1.0 wt.% SWNTs, CNT-g-CFs show a different failure mechanism (Figure 12); the absence of epoxy residue suggests that the failure is at the CNT/carbon fiber interface. The epoxy system reinforced with 1.0 wt.% SWNTs seems to result in a fracture of the CNTs grafted to the carbon fiber

Fig. 11 Single fiber pull-out test results for carbon fibers without (unhatched) and with CNTs grafted (hatched) on the surface embedded in (A) neat epoxy, (B) 0.1 wt.% TB3b dispersed SWNTs reinforced epoxy and (C) 1.0 wt.% TB3b-dispersed SWNTs reinforced epoxy. Error bars represent standard errors associated with the measurement.

surface rather than failing at the grafted CNT/matrix interface as observed for unreinforced epoxy, thus confirming a synergistic interaction between the nano-engineered epoxy and the CNT-grafted carbon fibers.

Experimental

Materials

P2-SWNTs (purity = 90%, diameter 4-5 nm, length 0.5-1.5 μm) is a kind of SWNT, which are purified by air oxidation and subsequently treated to remove the catalyst. They were

Fig. 12 Fracture surfaces after single fiber pull-out tests for; (A) unsized carbon fiber, and (B) CNT-g-CF in neat epoxy; (C) unsized carbon fiber and (D) CNT-g-CF in TB3b-dispersed SWNT (0.1 wt.%) reinforced epoxy; (E) unsized carbon fiber and (F) CNT-g-CF in TB3b-dispersed SWNT (1.0 wt.%) reinforced epoxy with 2 μm scale bars.

obtained from Carbon Solutions, Inc., and used as received. Polyacrylonitrile (PAN)-based unsized carbon fibers (AS4-12K-7D, HS-CP-5000 grade, 7.1 μm diameter) were supplied by Hexcel Composites, UK, and used as received from the supplier as a whole tow. α,ω -dihydroxy-polyimide macroinitiator (OH-PI-OH) was synthesized according to previous work.¹⁵ D,L-lactide was purchased from Sigma-Aldrich and recrystallized in anhydrous ethyl acetate (EtOAc). m-Chloroperbenzoic acid (m-CPBA), 2,2-bis(hydroxymethyl) propionic acid, allyl bromide and tin (II) 2-ethylhexanoate ($\text{Sn}(\text{Oct})_2$) were purchased from Sigma-Aldrich. Epoxy resin (Part A: EPR L20 and Part B: EPH 161) was supplied by R&G Faserverbundwerkstoffe GmbH. Dimethylacetamide (DMAc) and dimethylformamide (DMF) were purchased from Sigma-Aldrich, dried over calcium hydride and distilled before use. Other chemicals were used without purification.

Structure analysis and characterization

The molecular weights of the triblock copolymers and their molecular weight distributions were characterized by gel permeation chromatography (GPC) using DMF with 0.02 M LiBr as the eluent and polystyrene standards as reference. ^1H NMR spectra were measured using a Bruker AVANCE-300 (300 MHz) spectrometer in CDCl_3 or d_6 -DMSO as solvents and TMS as internal reference at 25 $^\circ\text{C}$. FTIR spectra were recorded using a Perkin Elmer Spectrum One at 4.0 cm^{-1} resolution. The absorption spectra of TB-dispersed SWNTs dispersions were recorded using a Cary 5000 UV-vis-NIR spectrophotometer. Raman spectra were collected using a He-Ne laser Renishaw

Raman scope at 633 nm excitation wavelength. The dispersions were prepared according to a previous report¹⁵ and then filtered through PTFE membrane and dried for Raman characterization. High-resolution transmission electron microscopy (TEM) images were acquired using a JEOL Model 3010F analytical electron microscope operating at an accelerating voltage of 200 kV. TEM samples were prepared by placing several drops of TBs/SWNT (mass ratio of polymer and SWNTs = 2:1) dispersion in THF on a 200 mesh carbon-coated copper grid (EasyLab) and drying. Tensile testing of the composite films was performed at room temperature on an Instron 5543 test frame equipped with a 100 N load cell at 2.5 mm/min crosshead speed. The dimensions of the coupons were 20 mm × 4 mm × 60 μm (length × width × thickness). Tensile properties of each composite film were measured on five to ten specimens. Field-emission scanning electron microscope (FE-SEM) images were obtained using a JEOL JSM-6700F microscope. The fractured surfaces of composite films were coated with a thin layer of gold before FE-SEM observation. The morphology of the CNT-grafted-carbon fibers and pull-out fracture surfaces were investigated through high-resolution field emission scanning electron microscopy (Leo Gemini 1525, Carl Zeiss NTS GmbH) at 5 kV at approx. 15 mm working distance, with consumables purchased from Agar Scientific, GB

27 Synthesis of Monomer MAC

The cyclic carbonate monomer 2-methyl-2-(allyloxycarbonyl) propylene carbonate (MAC) was prepared according to a previous work.²³ The final product was white crystals (yield: 50%). ¹H NMR (300 M, CDCl₃, 25 °C): δ [ppm] 5.91 (dd, 1H, CH₂=CH-), 5.30 (m, 2H, CH₂=CH-), 4.68 (d, 2H, =CH-CH₂-O-), 4.60 and 4.22 (d, 2H+2H, -C-CH₂-O-), 1.34 (s, 3H, -CH₃) (Figure S11).

36 One-pot synthesis of triblock copolymers PLA-PI-PLA and PMAC-PI-PMAC

In a glove box, OH-PI-OH (0.3 g, 50 μmol) (M_n = 6900 Da) was dissolved in 2 mL DMAc, and then Sn (Oct)₂ (74 mg, 60 μmol) in toluene was added. After stirring for 6 h, D,L-lactide (0.36 g, 2.5 mmol for TB1a and 0.54g, 3.8 mmol for TB1b) or MAC (0.80 g, 4 mmol for TB2a and 1.5 g, 7.5 mmol for TB2b) was added into the mixture at room temperature. A viscous solution formed after 4 h and the reaction was continued at 130 °C for 24 h. The crude product was poured into large amount of ethanol and the precipitate was filtered. To obtain pure copolymers, the precipitates were re-dissolved in DMAc and precipitated twice in methanol and dried at 70 °C overnight in vacuum oven (yield = 75%). Other triblock copolymers with different molecular weights (Table 1) were synthesized via similar procedure. The identification data of initiator and triblock copolymers are given. For initiator, ¹H NMR (300 M, d₆-DMSO, 25 °C): δ (ppm) 10.31 (s, Ar-OH), 7.88-8.04 (m, Ar-H), 7.40-7.21 (m, Ar-H), 7.21-7.02 (m, Ar-H), 4.76 (s, -CH₂-OH), 3.50 (tr, -CH₂-CH₂-), 2.77 (tr, -CH₂-CH₂-), 1.70 (s, -CH₃); FTIR (cm⁻¹) with KBr: 2920, 1730, 1360, 1200. For TB1: ¹H NMR

(300 M, d₆-DMSO, 25 °C): δ (ppm) 5.19 (m, -CH of LA), 1.47 (d, -CH₃ of LA), FTIR (cm⁻¹) with KBr: 2920, 1730, 1360, 1200, 1073. For TB2: ¹H NMR (300 M, d₆-DMSO, 25 °C): δ (ppm) 5.82 (m, -CH=CH₂ of MAC), 5.19 (d, -CH=CH₂ of MAC), 4.57 (d, -CH=CH₂ of MAC) 4.23 (s, -CH of MAC) 5.19 (s, -CH₃ of MAC); FTIR (cm⁻¹) with KBr: 2920, 1730, 1360, 1200, 1073, 900. For TB3: ¹H NMR (300 M, d₆-DMSO, 25 °C): δ (ppm) 2.75 (m, O-CH₂-CH- of MACEP), 2.28 (d, O-CH₂-CH- of MACEP); FTIR (cm⁻¹) with KBr: 2920, 1730, 1360, 1200, 1073, 900. GPC data are given in Table 1 and Figure S8.

68 Epoxidation of PMAC-PI-PMAC with *m*-CPBA

PMAC-PI-PMAC (TB3a) (0.11 g, 10 μmol) was first dissolved in 5 mL CH₂Cl₂, and then 3-chloroperbenzoic acid (34.5 mg, 0.2 mmol) was added. The mixture was stirred for 12 h in darkness. The crude product was poured into a large excess of ethanol and the precipitate was filtered. The precipitates were dissolved in DMF again and dialyzed for two days. The transparent solution was re-precipitated in excess ethanol and the precipitate was dried overnight at 70 °C for 24 h at reduced pressure (yield = 70%). TB3b was synthesized by similar procedure. The degree of epoxidation was determined by ¹H NMR.

81 Dispersion of SWNTs with various dispersing agents in THF

The concentration of SWNTs in the dispersions was estimated from absorption measurements using the Beer-Lambert law.²⁴ To calibrate the relation between SWNT concentration and absorbance, the absorbance of known concentrations of SWNTs solutions (0, 0.02, 0.04, 0.1, 0.15 mg/mL) in THF with dispersing agent TB1b, prepared by tip sonication for 15 min (1 and 1 second on/off) was measured and the absorbance at 500 nm was plotted against SWNT concentrations. The slope of the plotted graph was used to calculate the concentration of other SWNTs samples from absorbance measurements. We prepared 0.15 mg/mL TBs/SWNT (mass ratio 2:1) in THF and tip sonicated (150 W, 60%) for 15 min (1 and 1 second on/off), after which the absorption was measured immediately. After centrifugation at 6000 rpm for 10 min and 10000 rpm for 10 min, the absorption value at 500 nm was recorded.

99 Fabrication of TBs/SWNTs/epoxy Films

Composite films reinforced with carbon nanotubes were fabricated using the solution casting method. L20 epoxy parts A and B at a ratio of 100:34, were mixed and heated at 40 °C for 30 min to pre-cure the epoxy mixture. TB/SWNTs dispersions (1 mg/mL, 2 mg/mL, etc.) in THF were prepared via tip sonication (150 W, 60%) for 15 min and then added to the calculated amount of pre-cured epoxy. After thorough mixing by bath sonication, the solution was cast on PET film. After evaporating the solvent at room temperature, the films were transferred into a vacuum oven and fully dried at 40 °C for 24 h. The films were then peeled off and cured at 130 °C for 3 h.

112 Grafting CNTs onto carbon fibers

The surface of the unsized carbon fibers was plasma treated prior to catalyst precursor deposition, using oxygen as feed gas, following a previously reported procedure.²⁵ CNTs were grown on the surface of catalyst precursor pre-deposited carbon fibers using a continuous hot-wall CVD set-up with an in situ potential difference of +300 V at a pull-through speed of 2.4 m/h, as previously reported in detail.⁸ The 3-zone tubular furnace (PTF15/-/610, Lenton, GB) heated an adjustable arrangement of quartz tubes, allowing the reduction and growth time to be altered depending on the specific length of tubes used. The set-up was flanked on either side with inert gas regions for reactor inlet/outlets to maintain an inert environment within the hot-zone. The carbon fibers decorated with catalyst precursors were exposed to both a mixture of 2.4 vol.% hydrogen in nitrogen (3400 sccm) and 1.3 vol.% acetylene in nitrogen (325 sccm), sequentially, at a temperature of 760 °C for 2 and 12 min, respectively.

Single fiber pull-out test

The interfacial shear strength (IFSS) between single fibers and neat/reinforced epoxy was assessed using a hand-built apparatus following procedures previously reported.^{26, 27} The method involves embedding a fiber in an epoxy filled aluminum screw using a fine vertical adjustment (ca. 40 - 100 μm), pre-curing the matrix (L20:EPH161, 1:0.25 by weight) at 100 °C for 20 min using a built-in heating stage and completing the cure cycle in an oven at 100 °C for 19 h 40 min. The cured specimen is attached to a piezo-force sensor, measuring the force with a resolution of 0.1 mN, the free fiber end (ca. 10 mm) is then attached to a needle which is fixed to a piezo-translator (resolution 1.8 nm) using cyanoacrylate adhesive (Figure S12). The pull-out test is conducted at a cross-head speed of 0.2 μm/s. The apparent fiber pull-out shear strength (tapp) is calculated from the peak force (Fmax) and the measured embedded fiber area (Ae):

$$\tau_{app} = F_{max}/A_e = F_{max}/\pi d_f l_e$$

where d_f is the fiber diameter (measured for each sample including any contribution from grafted CNTs) and l_e the fiber embedded length measured by scanning electron microscopy post-fracture. The average apparent interfacial shear strength was determined from at least 9 individual measurements, with a linear fit fixed at the origin of the population when peak force is plotted as a function of embedded fiber area.

Conclusions

In summary, we have successfully synthesized novel triblock copolymers of PLA-PI-PLA (TB1, control), PMAC-PI-PMAC (TB2) and the epoxidized-PMAC-PI-epoxidized PMAC (i.e. PMACEP-PI-PMACEP, TB3). These three block copolymers improve the dispersion of SWNTs in THF, a low boiling point solvent, and do not impair the tensile properties of their blends with a structural epoxy resin. TB3b permits SWNT loading as high as 2 wt.% (which is an unusually high degree of loading for this mixing method) with improved tensile properties. The tensile strength, modulus, and elongation at

break of SWNTs (2 wt.%)/TB3b/EP increase by 40%, 34%, and 26% compared to the neat epoxy resin. This is the first report of a dispersing agent for SWNTs in a low boiling point organic solvent (THF) resulting in a significant increase in the tensile properties of SWNT-filled epoxy composite films compared to the base structural epoxy resin. The alkene groups introduced on the end blocks of TB2 were easily post-modified to epoxy groups (in TB3) to achieve chemical bonding with epoxy matrix. Further, the interfacial shear strength between SWNT/TB3b/epoxy and carbon fiber, determined by single fiber pull-out tests, increased for both as-received unsized and CNT-grafted carbon fibers with SWNTs (1 wt.%)/TB3b/EP resin system when compared to the neat epoxy matrix. These data provide the first evidence for a synergistic enhancement in interfacial properties when combining fuzzy carbon fibers with a SWNT-reinforced epoxy resin using our new PMACEP-PI-PMACEP triblock as the nanotube dispersing agent. This block copolymer synthesis method can also be employed with other poly(ester carbonate)s and with functionalities other than epoxy to permit more general applications of polyimide-derived block copolymeric dispersing agents in nanomaterials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support was provided by a Singapore Ministry of Education Tier 3 grant (MOE2013-T3-1-002) and a Singapore Ministry of Health Industry Alignment Fund (NMRC/MOHIAFCAT2/003/2014) and an A*Star Specialty Chemical grant (SERC A1786a0032). We also thank Penghui Zhang and Yang Wu for technical assistance with the electron microscopy.

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