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Graphene/star polymer nanocoating

Qiang Ren*, Jun Chen, Fuqiang Chu, Jian Li, Qiang Yu, Dun Wu, Jianbo Fang

Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, School of Materials Science and Engineering, Changzhou University, Changzhou, Jiangsu 213164, China

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ABSTRACT

A kind of novel nanocoating based on star polymers and graphene was developed. The hydroxyl functionalized star polymers were synthesized by Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) using core-first approach. The branching behavior, copolymer composition and glass transition temperature was characterized clearly. Graphene/star polymer coating shows lower conductive percolation threshold values relative to linear analog. Transmission electronic microscopy verified the better dispersion of graphene sheet in star polymer matrix than linear polymer matrix. Rheological tests revealed that the increase of viscosity of star polymer solution aroused by addition of graphene was much weaker compared to that of linear counterpart. Star polymer based coating exhibit very short tack-free time and superior impact resistance. All the results demonstrate that star polymer is a good candidate to fabricate graphene filled nanocoating with advantages in performance as well as processing.

1. Introduction

Graphene is an atomically thin, planar sheet composed of sp^2 carbon atoms arranged in a honeycomb structure. It exhibits exceptional mechanical, electrical and thermal conductive property [1–3]. Application of graphene in coating formulation design is a new approach to fabricate functional coating with attractive performance [4–6]. Unfortunately, incorporation of graphene into polymers would increase the viscosity of polymer in melt or solution state due to strong interaction of nano-sheet with polymer chains [7–9]. This would have to decrease the desired solid content of the coating, that is, increase the content of volatile organic compound (VOC) of solvent-born coating to keep acceptable viscosity for film forming process. So except for desired electronic and mechanical performance of cured coating film, low viscosity is another important aspect should be addressed for liquid coating.

For traditional linear polymer, molecular weight has to be decreased to achieve low viscosity goal. The functionality that provides the crosslinking ability decreases with molecular weight as well. With that, the crosslinking ability of the resin and the performance of the coating also decrease. The inherent limitation can be overcome by developing a new class of macromolecule with new topology architecture. Star polymers are the right kind of resin that can meet the requirement due to its sphere-like structure that have little intermolecular or intramolecular entanglements [10,11]. Meantime, star polymers can be prepared by facile method, including core-first [12,13] and arm-first [14,15] routes. ATRP is a robust approach to star polymers with wide range of functionality, especially for polyacrylates which can be widely used in coating industry [16,17].

Good dispersion of graphene into polymer matrix is a highly addressed question to fabricate graphene/polymer nanocomposites [18,19]. Meanwhile, star polymer can be expected to have good steric stabilization to nanoparticle in solution. Star polymer holds the promising prospect to work as coating binder to improve the dispersion and stability of graphene and address the viscosity increasing problem in coating formulation.

In this work, we devised three-arm and six-arm hydroxyl functionalized star polymers as matrix to disperse graphene for fabrication of novel graphene nanocoating. The characteristics of star polymer, excellent performance of obtained nanocoating and the underlining mechanism was investigated in detail.

2. Experimental

2.1. Materials

Butyl methacrylate (BMA, 98%) and 2-hydroxypropyl methacrylate (HPMA, 97%) were purchased from Aladdin Reagent Co., Ltd, Shanghai, China. Both of them were distilled under reduced pres-

* Corresponding author.
E-mail address: renqiang@cczu.edu.cn (Q. Ren).

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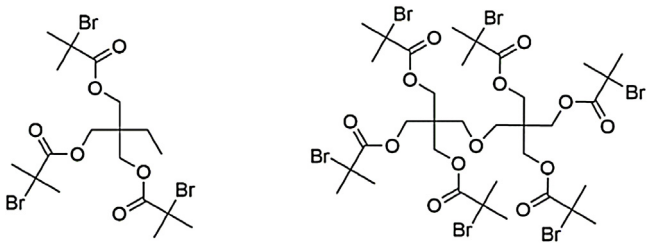

Scheme 1. Left to right, tri and hexa-functional initiators.

sure prior to use. Tris (2-dimethyl amino) ethyl amine (Me_6TREN) was purchased from Alfa Aesar. 2-bromoisobutyryl bromide (98%) was commercially obtained from SuqianYongxing Pharmaceutical Co., Ltd. (Jiangsu, China). Stannous octoate ($Sn(EH)_2$), $CuBr_2$ (99%), ethanol, toluene, ethyl acetate, *n*-butyl acetate, anisole, tetrahydrofuran (THF), methylbenzene, dimethylbenzene, were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. Isocyanate curing agent (Solid content 67.5 wt%, -NCO group content 15.6 wt%) was kindly provided by Shanghai Zhenhua Heavy Industry Changzhou Coatings Co., Ltd. Graphene (GN) powder, GNP-001, was produced and kindly provided by Jiangnan graphene research institute (Changzhou, Jiangsu, China). DISPERBYK-161, a dispersing additive for solvent-borne coatings of BYK chemical Co., Ltd., Germany, was used as received. It is a solution of a 30% high molecular weight block copolymer with pigment affinic groups in methoxypropylacetate/butylacetate (6/1 in weight).

2.2. Synthesis of multi-functional initiator

Multi-functional initiators prepared in this work are shown in Scheme 1. The synthesis procedure is based on that described in our previous work [20]. Chemical and physical parameters of trimethylolpropanetris (2-bromoisobutyrate) with yield of 62% are as follows: purity 95.8% via HPLC, T_m 65 °C. ^{1}H NMR ($CDCl_3$) ppm: 0.98 (t, 3H, CH_3CH_2–C), 1.63 (q, 2H, CH_3CH_2–C), 1.94 [s, 18H, $(CH_3)_2$– CBr], 4.19 (s, 6H, CH_2–O–C=O).

Chemical and physical parameters of dipentaerythritol hexa (2-bromoisobutyrate) with yield of 65% are as follows: purity 85% via HPLC, T_m 150 °C. ^{1}H NMR ($CDCl_3$) ppm: 1.91 (s, 36H, $(CH_3)_2$–CBr), 3.6 [s, 4H, (C–CH_2–O)], 4.32 [s, 12H, (C–CH_2–O–C=O)].

2.3. Synthesis of star and linear poly (BMA-co-HPMA) by ARGET ATRP

Hexa-arm star poly (BMA-*co*-HPMA) was prepared as follows. $CuBr_2$ was dispersed in anhydrous ethanol to form a stock dispersion solution with 0.35 wt% concentration. A 50 mL three neck flask with a magnetic stirring bar was charged with 5.743 g of the stock solution which contained 0.0638 g of $CuBr_2$ (0.01 mmol), 0.0230 g of Me_6TREN (0.1 mmol), 0.0405 g of stannous octoate (0.1 mmol), 6 mL of toluene (40% of monomer by volume) and 2 mL of anisole. The mixed solution was then purged with argon flow for 15 min to deplete air. Dipentaerythritol hexa (2-bromoisobutyrate) (2.2270 g, 1.9 mmol) was dissolved in BMA (12.5 mL, 79 mmol) and HPMA (2.8 mL, 21 mmol) (purged with argon for 15 min before use) were added to the flask with an argon-washed syringe. The flask was then immersed in a preset oil bath at 70 °C. Samples were taken by syringe periodically and analyzed by gas chromatography to determine the monomer conversion using anisole as internal standard. When monomer conversion exceeded 90%, the flask was taken out of oil bath and exposed to air to stop the reaction. After that, the solution was diluted with 150 mL ethyl acetate and passed through a neutral alumina column to remove the small amount of catalyst. Rotary evaporation was used to remove the majority of the solvent, and then the product was poured onto a PTFE dish to form a thin film, dried in air for 72 h, and then under vacuum at 80 °C to a constant weight, resulting a colorless transparent polymer sample.

Tri-arm and linear star poly (BMA-*co*-HPMA) were prepared following the above procedure but using trimethylolpropanetris (2-bromoisobutyrate), 2-bromoisobutyryl bromides as the initiator, respectively.

2.4. Coating sample preparation

Firstly, star polymer solution with 60% solid content (15 g) and DISPERBYK-161 (0.15 g) was mixed homogeneously in ball mill. Then, graphene (1 g) was added slowly under stirring. After that, the ball mill was running at 500 rpm for 2 h to prepare millbase. Next, millbase (5 g) was mixed with additional 60% solid content star polymer solution (7.5 g) by mechanical stirring (1000 rpm, 15 min) to obtain coating component with 4% graphene (denoted as 4% graphene/star). Finally, coating film was obtained by curing of star polymer/graphene using isocyanate curing agent with —NCO/-OH mole ratio of 1.02/1.

To prepare substrate for coating, tinplate sheet was polished by using 400 grit sand papers, then cleaned by ultrasonic degreasing with acetone and dried. Coating film was casted onto tinplate sheets by using 20 μm wire bar. The whole process is shown in Scheme 2.

2.5. Characterization and testing methods

High performance liquid chromatography (HPLC) was carried out on a Waters Millennium 2010 HPLC with a C-18 column as the stationary phase and acetonitrile as the mobile phase to determine purity of initiator. Monomer conversion was determined by gas chromatography (GC) on a GC-1690 of Kexiao Instrument Co., Ltd, Hangzhou, China, using anisole as an internal standard. Molecular weights and molecular weight distributions were obtained using a triple detection size exclusion chromatography (TD-SEC) system at 25 °C. The system is composed of a Waters 1515 isocratic HPLC pump with three 5 μm Waters styragel column (guard 0.5 HR, 4 HR and 1 HR), a Waters 717 PLUS auto sampler, a Waters2414 differential refractive index detector (k = 880 nm), a Wyatt multi-angle laser light scattering (MALLS) detector DAWN HELEOS II (k = 658 nm) a Wyatt ViscoStar viscometer detector and a Waters Breeze gel permeation data manager. The eluent was HPLC grade THF with flow rate of 1.0 mL/min. Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy were carried out on a Bruker ARX-300 type NMR spectrometer at room temperature in $CDCl_3$. The melting point of initiator and glass transition temperature (T_g) of polymers was determined on a PE Pyris 1 differential scanning calorimeter under N_2 atmosphere at a heating rate of 20 °C/min. Rotational rheological tests were performed on Physical MCR 301 rheometer at 25 °Cwith shear rates from 0.01–1000 s^{-1}. Particle size distribution measurement is performed on a BT-9300S particle analyser of Baite Instrument Co. Ltd, Dandong, Liaoning province, China. Transmission Electron Microscopy was performed using JEM −2100 instrument. A diluted droplet of each millbase of various graphene/polymer composition was deposited on a carbon grid to get the sample to detect the dispersion state of graphene in solution. Cured graphene/6-arm star coating film was wrapped in epoxy resin and cured to get a block sample. The sample was cut to 100 nm thick sections using Leica ULTRACUT UC6 with a glass knife to get an ultrathin film containing graphene/6-arm star polymer for TEM testing. The properties of coating film was determined after 7 days. Electrical surface resistivity of coating film on tinplate was determined using high resistance instrument of Agilent 4339 B according to ASTM D257-07. Pencil hardness was determined according to ASTM D-3363. Adhesion was determined by the cross-hatch tape test described in ASTM D-3359. Impact tests were