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Reversible addition-fragmentation chain transfer graft polymerization of acrylonitrile onto PE/PET composite fiber initiated by γ-irradiation[*]

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Reversible addition-fragmentation chain transfer (RAFT) mediated grafting of acrylonitrile onto Polyethylene/Poly(ethylene terephthalate) (PE/PET) composite fibers was performed using γ-irradiation as the initial source at ambient temperature. Different initial concentrations of 2-cyanoprop-2-yl dithiobenzonate were used as the chain transfer agent. The kinetics of graft polymerization is in accordance with the living RAFT polymerization. The successful grafting of acrylonitrile is proved by Fourier transform infrared spectroscopy analysis. The results of monofilament tensile test show that mechanical properties of the fibers change slightly after grafting. Scanning electronic microscopy images of the fibers show that the surface of RAFT grafted fibers is smoother than that of fibers grafted conventionally.

Keywords: Radiation, Graft polymerization, Reversible addition–fragmentation chain transfer, Acrylonitrile, PE/PET composite fiber

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I. INTRODUCTION

Surface modification of polymers is an important method to obtain new materials from available polymers of desirable bulk properties like elasticity, permeability, and biocompatibility [1]. Graft polymerization [2–5] can be initiated by chemical initiators [4, 6], plasma treatment [7] and ionizing radiations [3, 8, 9]. Radiation-induced graft polymerization is advantageous to avoidance of adding chemical initiators: ionizing radiations generate free radicals on various kinds of polymers at ambient temperatures to initiate graft polymerization [10, 11]. However, traditional radiation-induced graft polymerization does not offer an organized grafting kinetics, molecular weight and surface morphology of the product are uncontrollable.

Controlled/living radical polymerization, including nitroxide-mediated polymerization (NMP) [12, 13], atom transfer radical polymerization (ATRP) [14–16] and reversible addition-fragmentation chain transfer (RAFT) [17–19] polymerization, has been developed significantly during the past two decades. NMP is not suitable for acrylonitrile (AN) because of its high reaction temperature [12] and ATRP cannot be initiated by γ-irradiation directly [16]. However, using RAFT technique to graft polymers onto available polymer matrix initiated by γ-irradiation at ambient temperature was reported [1, 20, 21]. In RAFT polymerization, thiocarbonylthio compounds are used as chain transfer agents (CTA) to mediate the polymerization, so as to establish an equilibrium under which all the propagating chains have approximately the same chain length at the same instant of time to make the polymerization controllable. This technique has been successfully applied to synthesize well-controlled brushes from polymer surfaces to obtain desirable surface properties of several materials.

Polyacrylonitrile (PAN) is a common polymeric material, and acrylonitrile is widely used in surface graft modifications of polymers because its reactive nitrile groups can be further derived to other useful groups such as amidoxime groups [22]. Polymerization of acrylonitrile via RAFT technique was studied by using 2-cyanoethyl dithiobenzoate (CED) [23], cumyl phenyldithioacetate (CPDA) [24] and 2-cyanoprop-2-yl dithiobenzonate (CPDB) [25]. In this paper, RAFT mediated graft polymerization of acrylonitrile induced by γ-irradiation is investigated. Polyethylene/Poly(ethylene terephthalate) (PE/PET) composite fibers are used as the matrix material because the inner PET core is stable under irradiation and the outer PE layer is easy to generate free radicals by γ-irradiation. ^{60}Co γ-rays are used as the initiate source and CPDB as the CTA to graft AN onto PE/PET composite fibers to synthesize PE/PET-g-PAN fibers with controllable degrees of grafting (DG) and desirable surface morphology. The kinetics of graft polymerization and characterization of chemical structure, thermal properties and mechanical properties are presented. Scanning electron microscopy (SEM) is used to check surface morphology of the grafted fibers.

II. EXPERIMENTAL

A. Materials

PE/PET composite fibers were purchased from SINOPEC Shanghai Petrochemical Company. The dimethylformamide

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(DMF), AN, CPDB and other chemical agents, all of analytical grade, were purchased from Sinopharm Chemical Reagent Co., Ltd.

B. RAFT graft polymerization

The 5%–20% monomer solutions were prepared by dissolving acrylonitrile in DMF. Different amount of chain transfer agent CPDB were added to the solutions. The mixtures of acrylonitrile (AN) and CPDB were contained in glass vials. The PE/PET fibers were added to the vials, and deoxygenated by bubbling with nitrogen gas for 15 min. The samples were irradiated at room temperature in a ^{60}Co source to different doses at dose rate of 0.18 kGy/h or to 12 kGy at different dose rates of 0.12, 0.16, 0.19, 0.23 and 0.3 kGy/h. Different initial monomer concentrations and initial molar ratios between monomer and RAFT agent ($[\mathrm{AN}]_0/[\mathrm{CPDB}]_0$) were used. For comparison, a group of samples without CPDB were irradiated to complete grafting polymerization. The grafted samples were extracted by DMF to remove homopolymer, and vacuum-dried for 24 h.

C. Degree of grafting (DG)

The degree of grafting is calculated by

$$DG = [(W_{\mathrm{g}} - W_0)/W_0] \times 100\%, \qquad (1)$$

where W_{g} is the dry weight of grafted polymer, W_0 is the initial weight of PE/PET fibers.

D. Characterizations

A RAFT mediated grafting polymer was measured on a gel permeation chromatography (GPC) system to analyze the molecular weight and polydispersity index (PDI). The grafted polymers were characterized by FT-IR spectra on a Nicolet Avatar FT-IR spectrometer in the range of 3500–500 cm^{-1}. Thermogravimetric (TG) analysis was performed on a TG 209 F3 Tarsus (NETZSCH, Germany) instrument at a heating rate of 10 °C/min under nitrogen atmosphere. Morphology and diameter of the fibers were analyzed with an scanning electron microscope (SEM) instrument (FESEM, JEOL, JS-M6700F). Mechanical properties were tested on an Electronic Single Silk Strength Tester (LaiZhou Electron Instrument Co., Ltd.).

III. RESULTS AND DISCUSSIONS

A. Kinetics of graft polymerization

The relationships between DG and absorbed dose, dose rate, monomer concentration and CTA concentration were studied. The dose-DG effect of PE/PET-g-PAN is shown in Fig. 1(a), from the samples with an initial AN concentration of 15% (v/v) and $[\mathrm{AN}]_0/[\mathrm{CPDB}]_0$=800:1, irradiated to different doses at 0.18 kGy/h. The DG increased linearly with the absorbed dose. Free radicals which initiate the graft polymerization were generated by the γ-rays on surface of PE/PET fibers and in the monomer solution. The propagating chains combined to the thiocarbonyl group of RAFT agents, which in turn released the living group radicals and re-initiated polymerization. All the RAFT combining and releasing steps were reversible, when an equilibrium was established [26], the rate of free radical generation was proportional to the absorbed dose under a fixed dose rate. The DG increase was proportional to the number of free radicals, so the DG increased linearly with dose when the graft polymerization was performed in presence of the RAFT agent (CPDB). However, without CPDB in the grafting system under the same conditions as the samples in Fig. 1(a), the DG increase was not linear (Fig. 1(b)), because the equilibrium mentioned above did not exist.

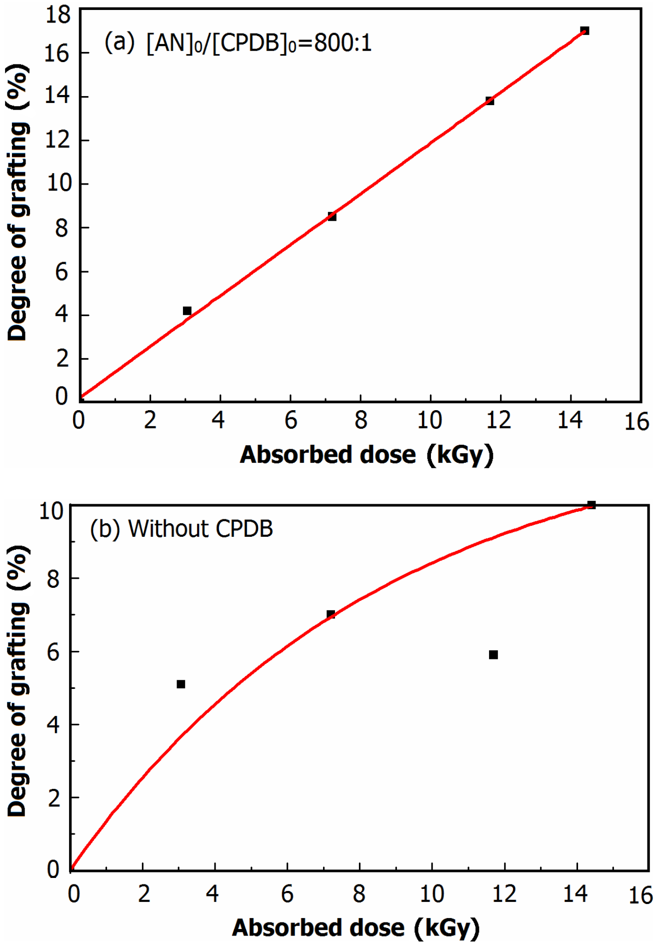


Fig. 1. (Color online) DG of PE/PET-g-PAN versus absorbed dose at $[\mathrm{AN}]_0/[\mathrm{CPDB}]_0$=800:1 (a) and without CPDB (b), at dose rate of 0.18 kGy/h and initial AN concentration of 15%(v/v).

Fig. 2(a) shows the effect of dose rate on grafting rate from the 12 kGy-irradiated samples with an initial AN concentra-

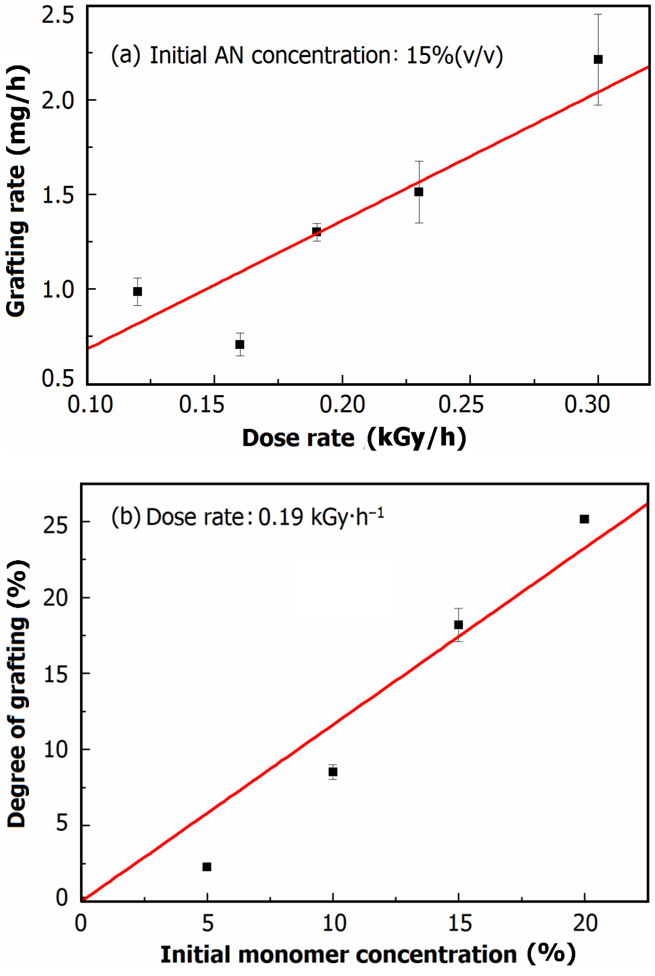


Fig. 2. (Color online) Grafting rate versus dose rate (a) and initial monomer concentration (b), at absorbed dose=12 kGy and $[AN]_0/[CPDB]_0$=800:1.

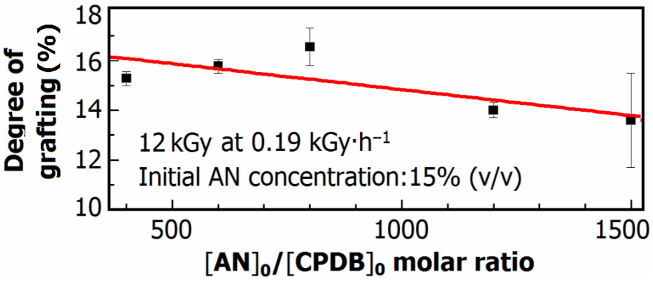
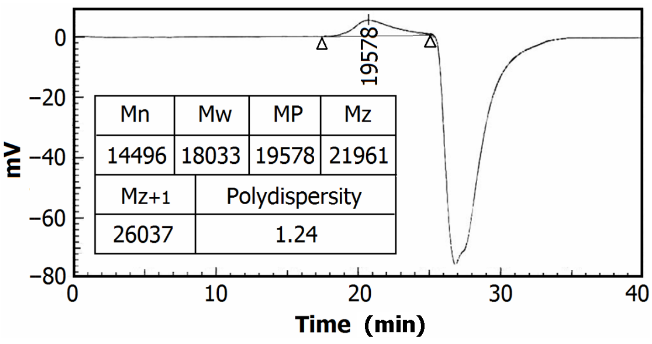


Fig. 3. (Color online) DG of PE/PET-g-PAN versus the molar ratio between monomer and RAFT agent.

tion of 15% (v/v) and $[AN]_0/[CPDB]_0$=800:1. As the rate of free radical generation is proportional to the dose, the grafting rate, i.e., the amount of increased weight of PE/PET-g-PAN per hour, increased in a linear relationship with the dose rate. Fig. 2(b) shows also a linear relationship between the initial monomer concentration and *DG*, from the samples with $[AN]_0/[CPDB]_0$=800:1, irradiated to 12 kGy at 0.19 kGy/h.

The effect of RAFT agent concentration on *DG* was also studied, with different initial molar ratios of $[AN]_0/[CPDB]_0$ from 400:1 to 1500:1. As shown in Fig. 3, the *DG* changed slightly. The radiation chemical yields (G-value) of PE [27] and acrylonitrile [5] are 4 and 2.4–5.6 radicals per 100 eV, respectively. With AN concentration of 15%(v/v), assuming that the weight of substrate polymer is 1g, it can be estimated that the number of free radicals generated by AN monomer and the substrate polymer is about 1.8×10^{16}. The minimum initial molar ratio between RAFT agent and monomer is 1:1500, so the number of CPDB molecules is about 2.8×10^{19}, being far more than the number of free radicals. Therefore, when the free radicals are generated, they will combine with the RAFT agents immediately to establish the equilibrium, and the grafting rates are about the same in this molar ratio range.



Mn	Mw	MP	Mz
14496	18033	19578	21961

Mz+1	Polydispersity
26037	1.24

Fig. 4. GPC image of the homopolymer formed in solution of the PE/PET-g-PAN fibers, at *DG*=4.2%, dose rate=0.18 kGy/h, initial AN concentration =15%(v/v) , and $[AN]_0/[CPDB]_0$=800:1.

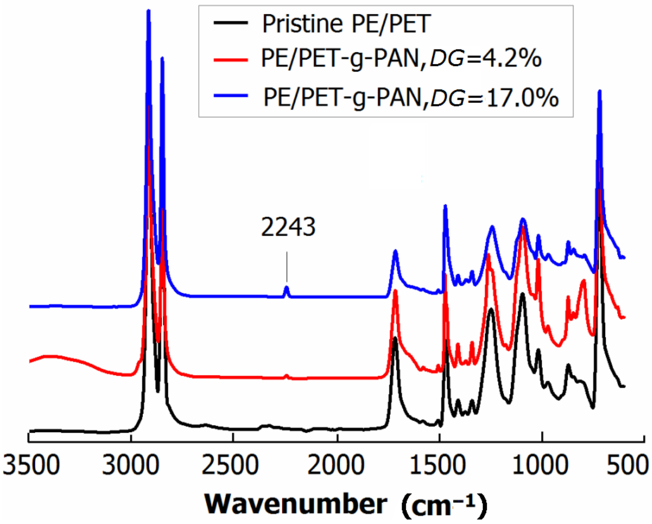


Fig. 5. (Color online) FT-IR spectra of pristine PE/PET composite fibers, PE/PET-g-PAN fibers with *DG* = 4.2% and 17.0%.

The kinetics results are in accordance with typical living polymerization and the degree of grafting can be controlled by changing experimental conditions.

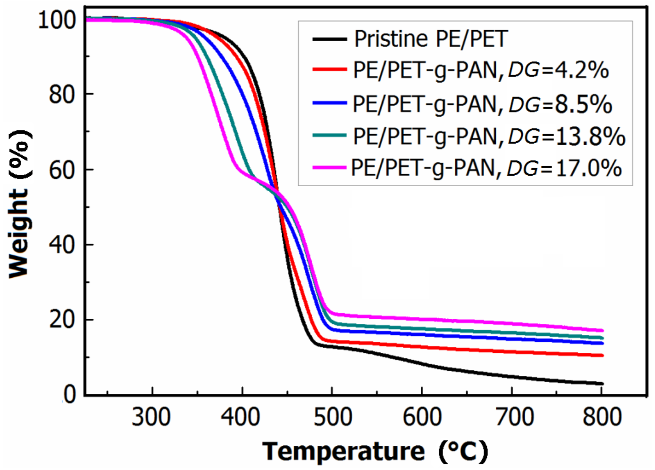


Fig. 6. (Color online) TGA spectra of pristine PE/PET composite fibers, PE/PET-g-PAN at different DGs.

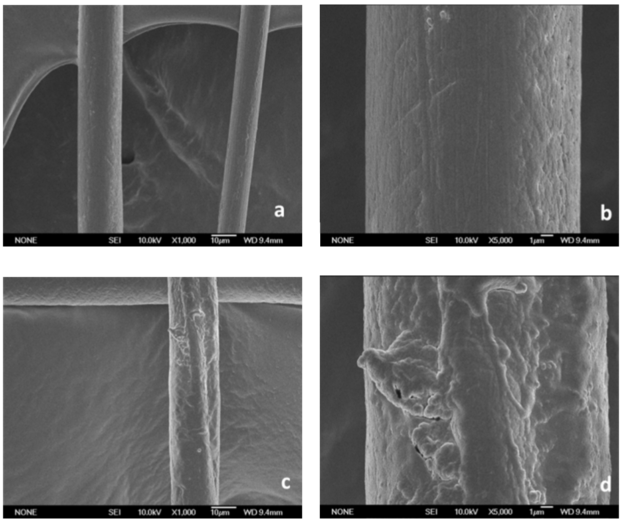


Fig. 7. SEM images of RAFT mediated PE/PET-g-PAN fibers with a *DG* of 10.0% at low (a) and high (b) magnification, and conventional grafted PE/PET-g-PAN fibers with a *DG* of 10.3% at low (c) and high (d) magnification.

B. Characterization of the PE/PET-g-PAN fibers

1. GPC results

Since the molecular weight of grafting polymer in the composite fiber is difficult to analysis, the homopolymer in solution of the sample of *DG*=4.2% (Fig. 1(a)) was measured by GPC. As shown in Fig. 4, the polydispersity index of the homopolymer is 1.24, which is in agreement with the results of conventional RAFT polymerization.

2. FT-IR spectra

Figure 5 shows FT-IR spectra of the pristine PE/PET composite fiber and PE/PET-g-PAN fibers of *DG* = 4.2% and 17%. The absorption bands at 2919 cm^{-1} and 2851 cm^{-1} are attributed to the asymmetric and symmetric stretching of -CH_2- groups, respectively [28]. The bending deformation of -CH_2- groups is demonstrated by the absorption band at 1463 cm^{-1} [28]. The absorption bands at 1720, 1100 and 720 cm^{-1} representing the stretching vibrations of ester groups and the para-substitution of benzene ring represented by the band at 870 cm^{-1} are attributed to the PET fibers contained in the original composite fibers [29]. The PAN graft chains is confirmed by the nitrile groups in acrylonitrile,and is represented by the new peak at 2243 cm^{-1} in the spectra of grafted fibers [9]. The spectra also show that the PE/PET-g-PAN of *DG*=17% has a larger peak than that of *DG*=4.2%. The FT-IR results indicate that acrylonitrile is grafted onto PE/PET composite fibers successfully.

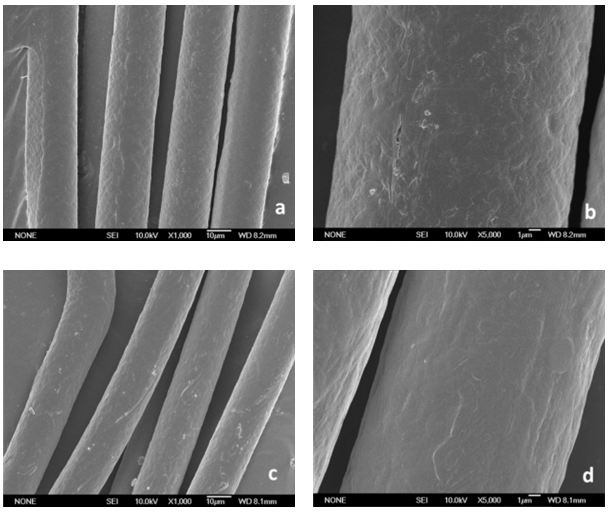


Fig. 8. SEM images of RAFT mediated PE/PET-g-PAN fibers with *DG* of 17.0% at low (a) and high (b) magnification, and pristine PE/PET composite fibers at low (c) and high (d) magnification.

3. TGA analysis

Thermal stability of pristine PE/PET fiber and grafted fibers was studied by TGA measurements. Fig. 6 shows that the PE/PET fiber started degrading at 336 °C, which is in accordance with the degradation temperature of PE. The residue should be attributed to PET core of the fibers because PE gives no residue at 700 °C [29, 30]. From TG curves of the grafted fibers, it can be seen that there are two degradation stages of the grafted fibers. The degradation stage at lower temperature is attributed to the weak bonds formed on the pristine polymer by graft polymerization. The second degradation stage is due to the grafted PAN chains [31]. Its starting temperature decreases with increasing *DG*. It can be observed that the residue increased from 10.5% at DG=4.2% to 17.1% at DG=17.0%, which is due to carbonization of PAN grafted chains.

4. Scanning electron microscopy

Surface morphology of the RAFT mediated grafted PE/PET-g-PAN fibers (DG=10.0%) was compared with a PE/PET-g-PAN sample prepared via conventional grafted polymerization (without CPDB) with a similar DG (10.3%). SEM images of the samples are shown in Fig. 7. Surface of the RAFT mediated PE/PET-g-PAN fibers was smoother than the other sample. This is because the RAFT mediated polymerization is controllable through the formation of intermediate radicals and the polymerization rate is steady, hence the simultaneous growth of the grafted chains and the same length at the same instant of time.

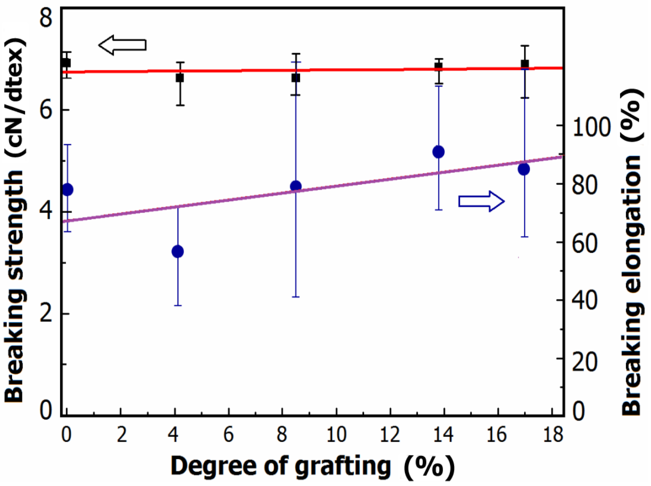


Fig. 9. (Color online) Breaking strength and breaking elongation of single fiber with different DGs.

Figure 8 shows SEM images of the pristine PE/PET fibers and the RAFT mediated grafted fibers of DG=17.0%. The diameters of the pristine and grafted fiber are 17.27 µm and 19.72 µm, respectively. It can be seen that the fibers with DG of 17% still has a smooth surface. As mentioned above, the RAFT mediated graft polymerization was controlled by RAFT agent and the grafting rate was slow, so the grafted chains propagated moderately without accumulating at one place.

5. Mechanical Properties

Mechanical properties of PE/PET-g-PAN fibers, which are expected to be maintained to maximal extent, are shown in Fig. 9. It can be seen that the breaking strength and breaking elongation of single silk change slightly compared to the pristine PE/PET fibers. This is because that mechanical properties of the composite fibers are mostly attributed to the PET inner core and PET is very stable under radiation [32].

IV. CONCLUSION

Acrylonitrile has been successfully grafted onto PE/PET composite fibers via RAFT-agent-mediated free-radical polymerization initiated by γ-irradiation. The kinetics of graft polymerization indicates that the degree of grafting can be controlled by experimental conditions, such as absorbed dose and initial monomer concentration. The successful grafting of PAN chains is proved by FT-TR measurements. Thermogravimetric analysis indicates that the degradation temperature of PAN graft chains is lower than the pristine PE/PET chains and the residue increases with DG. SEM images show that the RAFT controlled grafted fibers have a smooth surface. The single silk strength test experiment shows that the grafting of PAN has little effect on mechanical properties of the fibers.

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[1] Barsbay M, Güven O, Davis T P, *et al*. RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via gamma-radiation. Polymer, 2009, **50**: 973–982. DOI: 10.1016/j.polymer.2008.12.027
[2] Bhattacharya A and Misra B N. Grafting: a versatile means to modify polymers: techniques, factors and applications. Prog Polym Sci, 2004, **29**: 767–814. DOI: 10.1016/j.progpolymsci.2004.05.002
[3] Nasef M M. Gamma radiation-induced graft copolymerization of styrene onto poly(ethylene terephthalate) films. J Appl Polym Sci, 2000, **77**: 1003–1012. DOI: 10.1002/1097-4628(20000801)77:5¡1003::AID-APP7¿3.0.CO;2-K
[4] Yuan J, Chen L, Jiang X F, *et al*. Chemical graft polymerization of sulfobetaine monomer on polyurethane surface for reduction in platelet adhesion. Colloids and Surfaces B: Biointerfaces, 2004, **39**: 87–94. DOI: 10.1016/j.colsurfb.2004.08.019
[5] Hassanpour S. Radiation grafting of styrene and acrylonitrile to cellulose and polyethylene. Radiat Phys Chem, 1999, **55**: 41–45. DOI: 10.1016/S0969-806X(98)00310-7
[6] Liu P, Tian J, Liu W M, *et al*. Surface Graft Polymerization of Styrene onto Nano-Sized Silica with a One-Pot Method. Polym J,2003, **35**: 379–383. DOI: 10.1295/polymj.35.379
[7] Wenzel A, Yanagishita H, Kitamoto D, *et al*. Effects of preparation condition of photoinduced graft filling-polymerized membranes on pervaporation performance. Journal of Membrane Science, 2000, **179**: 69–77. DOI: 10.1016/S0376-7388(00)00502-0
[8] Zhang Y H, Huang Y D, Liu L, *et al*. Effects of γ-ray radiation grafting on aramid fibers and its composites. Appl Surf Sci, 2008, **254**: 3153–3161. DOI: 10.1016/j.apsusc.2007.10.081
[9] Liu H Z, Yu M, Deng B, *et al*. Pre-irradiation induced emulsion graft polymerization of acrylonitrile onto polyethylene nonwoven fabric. Radiat Phys Chem, 2012, **81**: 93–96. DOI:

10.1016/j.radphyschem.2011.09.013

[10] Sokker H H, Badawy S M, Zayed E M, *et al.* Radiation-induced grafting of glycidyl methacrylate onto cotton fabric waste and its modification for anchoring hazardous wastes from their solutions. J Hazard Mater, 2009, **168**: 137–144. DOI: 10.1016/j.jhazmat.2009.02.039

[11] Kabanov V Y, Kudryavtsev V N, Degtyareva T V, *et al.* Modification of polyethylene and poly (vinyltrimethylsilane) by radiation-induced graft polymerization. Nucl Instrum Meth B, 1997, **131**: 291–294. DOI: 10.1016/S0168-583X(97)00393-5

[12] Enright T E, Cunningham M F and Keoshkerian B. Nitroxide-mediated polymerization of styrene in a continuous tubular reactor. Macromol Rapid Commun, 2005, **26**: 221–225. DOI: 10.1002/marc.200400531

[13] Bartholome C, Beyou E, Bourgeat–Lami E, *et al.* Viscoelastic properties and morphological characterization of silica/polystyrene nanocomposites synthesized by nitroxide-mediated polymerization. Polymer, 2005, **46**: 9965–9973. DOI: 10.1016/j.polymer.2005.07.057

[14] Coessens V, Pintauer T and Matyjaszewski K. Functional polymers by atom transfer radical polymerization. Prog Polym Sci, 2001, **26**: 337–377. DOI: 10.1016/S0079-6700(01)00003-X

[15] Patten T E, Xia J H, Abernathy T, *et al.* Polymers with very low polydispersities from atom transfer radical polymerization. Science, 1996, **272**: 866–868. DOI: 10.1126/science.272.5263.866

[16] Matyjaszewski K and Xia J H. Atom transfer radical polymerization. Chem Rev, 2001, **101**: 2921–2990. DOI: 10.1021/cr940534g

[17] Millard P–E, Barner L, Reinhardt J, *et al.* Synthesis of water-soluble homo-and block-copolymers by RAFT polymerization under γ-irradiation in aqueous media. Polymer, 2010, **51**: 4319–4328. DOI: 10.1016/j.polymer.2010.07.017

[18] Moad G, Chong Y K, Postma A, *et al.* Advances in RAFT polymerization: the synthesis of polymers with defined end-groups. Polymer, 2005, **46**: 8458–8468. DOI: 10.1016/j.polymer.2004.12.061

[19] Hong C Y, You Y Z and Pan C Y. Synthesis of water-soluble multiwalled carbon nanotubes with grafted temperature-responsive shells by surface RAFT polymerization. Chem Mater, 2005, **17**: 2247–2254. DOI: 10.1021/cm048054l

[20] Huang Y K, Liu Q, Zhou X D, *et al.* Synthesis of silica particles grafted with well-defined living polymeric chains by combination of RAFT polymerization and coupling reaction. Macromolecules, 2009, **42**: 5509–5517. DOI: 10.1021/ma900604v

[21] Barsbay M, Güven O, Stenzel M H, *et al.* Verification of controlled grafting of styrene from cellulose via radiation-induced RAFT polymerization. Macromolecules, 2007, **40**: 7140–7147. DOI: 10.1021/ma070825u

[22] Liu X Y, Liu H Z, Ma H J, *et al.* Adsorption of the uranyl ions on an amidoxime-based polyethylene nonwoven fabric prepared by preirradiation-induced emulsion graft polymerization. Ind Eng Chem Res, 2012, **51**: 15089-15095. DOI: 10.1021/ie301965g

[23] Tang C B, Kowalewski T and Matyjaszewski K. RAFT polymerization of acrylonitrile and preparation of block copolymers using 2-cyanoethyl dithiobenzoate as the transfer agent. Macromolecules, 2003, **36**: 8587-8589. DOI: 10.1021/ma034942

[24] Liu X H, Zhang G B, Lu X F, *et al.* Dibenzyltrithiocarbonate mediated reversible addition–fragmentation chain transfer polymerization of acrylonitrile. J Polym Sci Pol Chem, 2006, **44**: 490-498. DOI: 10.1002/pola.21169

[25] An Q F, Qian J W, Yu L Y, *et al.* Study on kinetics of controlled/living radical polymerization of acrylonitrile by RAFT technique. J Polym Sci Pol Chem, 2005, **43**: 1973-1977. DOI: 10.1002/pola.20622

[26] Barner L, Quinn J F, Barner-Kowollik C, *et al.* Reversible addition-fragmentation chain transfer polymerization initiated with γ-radiation at ambient temperature: an overview. Eur Polym J, 2003, **39**: 449–459. DOI: 10.1016/S0014-3057(02)00247-1

[27] Perera M C S and Hill D J T. Radiation chemical yields: G values. Polymer handbook. New York (USA): Wiley-Interscience, 1999, 482.

[28] Gulmine J V, Janissek P R, Heise H M, *et al.* Polyethylene characterization by FTIR. Polym Test,2002, **21**: 557–563. DOI: 10.1016/S0142-9418(01)00124-6

[29] Khayet M, Nasef M M and Mengual J I. Radiation grafted poly(ethylene terephthalate)-*graft*-polystyrene pervaporation membranes for organic/organic separation. J Membrane Sci, 2005, **263**: 77–95. DOI: 10.1016/j.memsci.2005.04.006

[30] Gupta B and Anjum N. Development of membranes by radiation grafting of acrylamide into polyethylene films: Characterization and thermal investigations. J Appl Polym Sci, 2001, **82**: 2629–2635. DOI: 10.1002/app.2115

[31] Hajir Bahrami S, Bajaj P and Sen K. Thermal behavior of acrylonitrile carboxylic acid copolymers. J Appl Polym Sci, 2003, **88**: 685–698. DOI: 10.1002/app.11637

[32] Grassie N and Scott G. Degradation in special environments, Polymer degradation and stabilisation. Cambridge(UK): Cambridge University Press, 1988, 211.