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Strong, and recyclable thermosets cross-linked by MWCNT/poly(aryl ether ketone) containing furan based on Diels-Alder cycloaddition

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Abstract−Multi-walled carbon nanotube (MWCNT)/poly(aryl ether ketone) networks cross-linked by Diels-Alder cycloaddition possess outstanding mechanical and rheological properties. Poly(aryl ether ketone) containing pendant furan (PAEK-Fu) was synthesized, which had excellent thermal and mechanical properties, and a series of cross-linked materials with reversible covalent cross-linked crosslinking network were synthesized through a furan/MWCNTs Diels-Alder (D-A) reaction between PAEK-Fu and MWCNTs. Thermal and mechanical properties for MWCNT/PAEK-Fu composites were studied, and after crosslinking, MWCNT/PAEK-Fu composites exhibited good flexibility and resistance against organic solvents. After heating to 180 °C, the cross-linked MWCNT/PAEK-Fu composite membranes could be dissolved in NMP. This work demonstrates that the poly(aryl ether ketone)s can be made into recyclable thermoset materials using the concept of associative dynamic bonding. Given the dramatically increasing interest in environmentally sustainable materials, this MWCNT/poly(aryl ether ketone) interaction mode provides a robust approach to high performance engineering plastics with improved performance compared with the thermoplastic counterparts.

Keywords: Poly(aryl ether ketone), Multi-walled Carbon Nanotubes, Recyclable Thermosets, Composites

INTRODUCTION

Classic thermosets, unlike thermoplastics, are commonly recognized as a chemically cross-linked polymer that has high mechanical properties, dimensional stability, and outstanding environmental resistance [1,2]. These outstanding properties in combination with their light weight make thermoset resins in fiber reinforced composites form ideal candidates for finding applications in many important and high-tech areas, such as automotive industry, adhesives, coatings, shore structures, clean energy production, solar cell encapsulations, electronic packaging, and so on [3-5]. Yet, it is rather difficult to shape, reprocess, or recycle thermosets due to their permanent polymer networks generated during curing reactions [6]. Recently, the European Commission set a target of 2030 to increase recycling of plastic packaging stating that “the only long term solution is to reduce plastic waste by recycling and reusing more” [7]. Due to the importance of polymer recycling, scientists are interested in the concept of designing materials based on exchangeable chemical bonds that will lead to a dynamic crosslinked network [8-10].

Materials can be designed to build the temporary network by incorporating bonds which can undergo reversed pathways by degradable, associative, and dissociative linkages and as such offering inherent recyclability. The D-A reversible cycloaddition could be used for healing in the chemically crosslinked polymer networks. The D-A reaction is one of the most promising reactions of intrinsic approach in which sp2 carbons are involved and C-C bonds are formed in the products. A dienophile, such as an alkene or an alkyne, combines with a diene via the D-A reaction to generate [4+2] cyclic adducts [11]. It was reported that pristine CNTs without any pre-modification can be used as dienes or dienophiles to take part in the D-A reaction [12]. The functionalization of MWCNTs with a P(St-co-FMA-co-BODIPY-MA) polymer was carried out via D-A reactions with the pendant furan groups at 100 °C for 48 h. The grafted MWCNTs were soluble in THF and high resolution transmission electron microscopy revealed a 3 nm thick layer of polymer surrounding the MWCNTs [13]. The D-A reaction between furan as diene and carbon nanotubes (CNTs) as dienophile moieties is a thermally reversible, catalyst-free reaction that has received less attention in the development of self-healing polymers [14,15]. Cracks can be healed by heating the polymer above the temperature that reconstructing D-A reaction. The applied heat causes partial polymer chain dissociation and increases the mobility of individual chain. Upon cooling, new D-A bonds are formed and the chains are cross-linked again [16]. CNTs are added into a polymer matrix that could also take part in a D-A reaction, the D-A chemical activity of the CNTs could be triggered by a D-A reactive polymer. This could provide an ideal in-situ chemical interaction to increase the compatibility between CNTs and the reactive polymer matrix [17].

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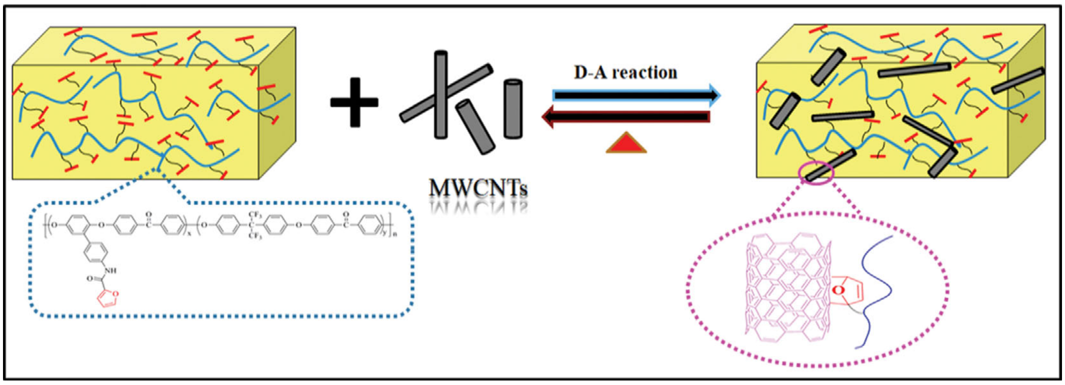


Fig. 1. Mechanism of preparing the cross-linked MWCNT/PAEK-Fu composite through D-A reaction.

Poly(ether ether ketone)(PEEK) is an outstanding thermoplastic with excellent properties, such as good corrosion resistance, excellent thermal stability and mechanical properties [18-20]. So it would have high strength and toughening effect when used to construct recyclable thermosets. MWCNTs have attracted considerable attention in the research and industrial fields due to the extraordinary mechanical, electrical, and thermal properties [21]. The excellent properties of MWCNTs make them into promising candidates for reinforcing fillers in polymer composites.

In our case, the PAEK-Fu was synthesized by nucleophilic polycondensation and amidation. A series of cross-linked materials with reversible covalent cross-linked network were synthesized through a furan/MWCNTs D-A reaction between PAEK-Fu and MWCNTs. Their cross-linked effect for MWCNT/PAEK-Fu composites on the thermal and mechanical properties was researched by dynamic mechanical test, thermogravimetric analysis and mechanical test. Specifically, we were interested in the recyclable effect of the MWCNT/PAEK-Fu composites. After crosslinking, the MWCNTs/PAEK-Fu composites exhibited good flexibility and resistance against organic solvents. When the cross-linked MWCNT/PAEK-Fu composite membranes were heated to 180 °C, they could be dissolved in NMP. The cross-linked MWCNT/PAEK-Fu composite, made by MWCNTs and PAEK-Fu in-situ reaction, whose mechanism was exhibited in Fig. 1, will become environmentally sustainable materials.

EXPERIMENTAL

1. Materials

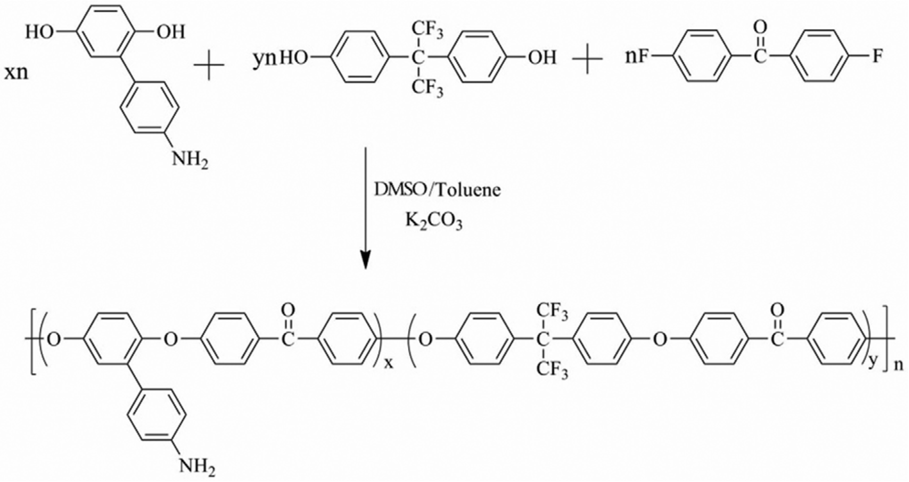
(4-Amino)phenyl-hydroquinone (4-NH_2PHQ) was synthesized in our lab through a two-step coupling-reduction reaction [22]. Hexafluorobisphenol A (6FBPA), 4,4′-Difluorobenzo-phenone (DFB), 2-Furoic acid, N,N′-Dicyclohexylcarbodiimide (DCC) and 4-Dimethylaminopyridine (DMAP), were purchased from energy chemical Co. Ltd., China. N-Methyl-2-pyrrolidone (NMP), chloroform ($CHCl_3$), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dimethylformamide (DMF), methylbenzene were purchased from Beijing Chemical Factory. All other reagents and solvents were obtained commercially and were purified by conventional methods. K_2CO_3 was dried at 120 °C for 24 h before polymerization. MWCNTs (>90%) produced by chemical vapor deposition (CVD) were purchased from Timesnano Inc. (Chengdu, China) and used as received. According to information provided by the supplier, the outside diameter of the nanotubes is about 4-6 nm, length about 0.5-2 μm, and purity more than 98 wt%.

2. Characterization

FT-IR spectra were measured on a Bruker Vector22 Fourier-transform infrared spectrometer. ^{1}H-NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz) using DMSO-d^6 or $CDCl_3$ as solvent. The morphology of MWCNT/PAEK-Fu composites was observed by SEM (HITACHI, SU8020) with quenched samples in liquid nitrogen. Mechanical test was carried out by a Shimadzu AG-I instrument at room temperature. Before the test, all samples were treated at 200 °C for 2 h. The thermal stability of the composites was tested by the TA Q50 thermogravimetric analysis under nitrogen or air atmosphere with a heating rate at 10 °C·min^{-1}. To study the mechanical capacity change of reactive materials as the temperature increased, dynamic mechanical tests (DMA) were carried out on a TA Q850 (New Castle, DE) over the temperature range from −70 °C to 150 °C at a frequency of 1 Hz and a heating rate of 5 °C/min.

3. Synthesis of Poly(aryl ether ketone)s with (4-Amino)Phenyl Side Groups (PAEK-Am)

The following is a representative procedure for the synthesis of PAEK-Am (PAEK-Am-x). The polymers were prepared by copolymerization polycondensation with dihalo- and bisphenol monomers. 2.01 g (10 mmol) 4-NH_2PHQ, 13.45 g (40 mmol) 6FBPA, 10.91 g (50 mmol) 4,4′-difluorobenzophenone, 8.29 g (60 mmol) anhydrous K_2CO_3 were added into a three-neck flask equipped with a mechanical stirrer, a Dean-Stark trap and nitrogen inlet, and then 100 mL DMSO and 23 mL toluene were charged into the reaction flask. The reaction mixture was refluxed at 140 °C for 3 h to dehydrate the system. After dehydration and removal of toluene, the reaction temperature was increased to 170 °C and held there for another 5 h. The viscous mixture was poured into 2,000 mL distilled water. The threadlike polymer was pulverized into a powder after cooling. The powder was washed with hot methanol and water several times under the atmosphere of nitrogen, and dried at 80 °C for 24 h. The grey polymer powder was obtained in a quantitative yield. This polymer was named PAEK-Am-20. Number-average molecular weight (Mn): 38.2 KDa; PDI (Mw/Mn), 2.68. To reach amino levels of 40%, the equivalents of 4-NH_2PHQ were

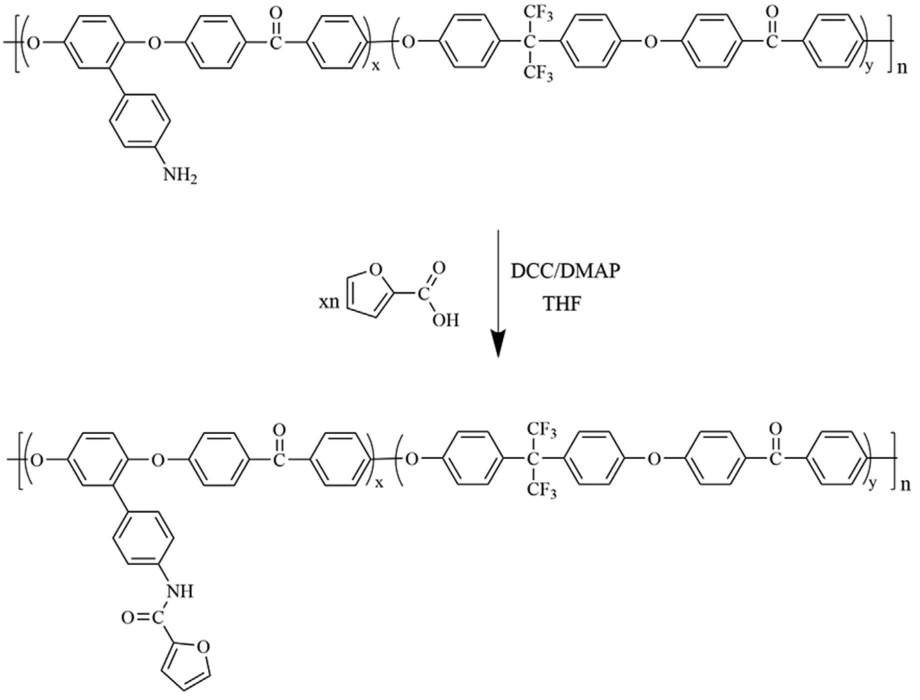


Scheme 1. Synthesis of PAEK-Am.

increased to 0.4, respectively. This polymer was named PAEK-Am-40. Number-average molecular weight (Mn): 23.6 KDa; PDI (Mw/Mn), 1.92. The mol % of amino was estimated based on the relative intensity of the o-hydrogen atom of -(C=O)- in the polymer main chain (at 7.75-7.92 ppm) and the amino groups of the (4-amino)phenyl side groups (at 6.65-6.72 ppm) (shown in Scheme 1).

4. Synthesis of Poly(aryl ether ketone)s with (4-Furan) Phenyl Side Groups (PAEK-Fu)

Scheme 2 shows a representative procedure for the synthesis of PAEK-Fu (PAEK-Fu-x). PAEK-Am-20 (4.8742 g, 0.01 mol of polymer repeating unit), 2-furoic acid (0.2241 g, 0.002 mol, 0.2 equiv), DCC (0.6190 g, 1.5 equiv based on the amount of 2-furoic acid), DMAP (0.0366 g, 0.15 equiv based on the amount of 2-furoic acid), and a magnetic stirring bar were placed into a 250 mL round-bottom flask fitted with a reflux condenser, and then THF (100 mL) was injected into the reaction system, stirred in a 50 °C oil bath for 10 h under a nitrogen atmosphere. After cooling to room temperature, the reaction solution was diluted with 100 mL THF and filtered through a short plug of silica gel to remove the catalyst. The filtrate was concentrated using a rotary evaporator and poured into methanol to precipitate the polymer. The dissolution and precipitation process was repeated one more time. The polymer was isolated as white fibers after drying in vacuum at 80 °C for 12 h (4.35 g). This polymer was named PAEK-Fu-20. To reach an Fu of 40%, the equivalents of 2-furoic acid were increased to 0.4, respectively. The mol% of the furan was estimated based on the relative inten-



Scheme 2. Synthesis of PAEK-Fu.

sity of ortho hydrogen resonances of -CO- in the polymer main chain (at 7.7-8.0 ppm) and the imide groups of the -NH-CO- (at 10.0-10.1 ppm).

5. Preparation of MWCNT/PAEK-Fu Composite Membranes

The MWCNT/PAEK-Fu-20 and MWCNT/PAEK-Fu-40 composite membranes were prepared by solution blending and sol-gel method. The 0.99 g pure PAEK-Fu-20 was dissolved in 10 mL DMAc by magnetic stirring at room temperature. Meanwhile, 0.01 g MWCNTs was added into 2 mL DMAc accompanied with stirring for 2 h. Then the solution was ultrasonicated for another 2 h. The evenly dispersed MWCNTs solution was added to the polymer solution, and the mixed solution was continued to be ultrasonic for 2 h. After filtration by copper mesh, the mixed solution was evenly poured on a pre-leveled glass plate with the size of 10 cm× 10 cm. The coated glass plate was put in a vacuum oven that preheated at 40 °C, and then kept at 60 °C for 24 h, 80 °C for 12 h, 100 °C for 2 h, and 120 °C for 2 h step-by-step under nitrogen. After natural cooling to 80 °C, the membranes were vacuumized,

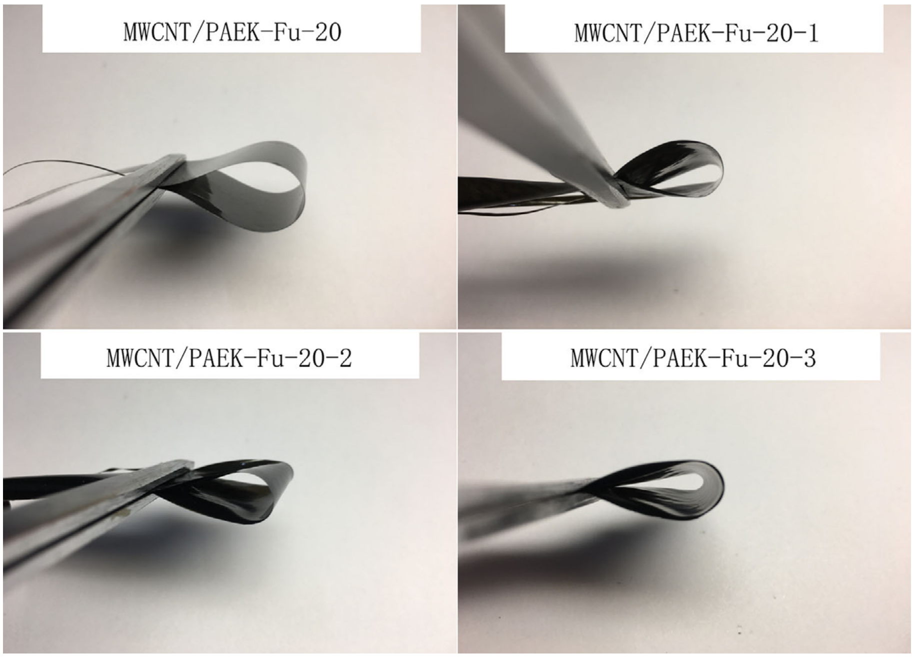


Fig. 2. Photographs of the MWCNT/PAEK-Fu-20, MWCNT/PAEK-Fu-20-1, MWCNT/PAEK-Fu-20-2 and MWCNT/PAEK-Fu-20-3.

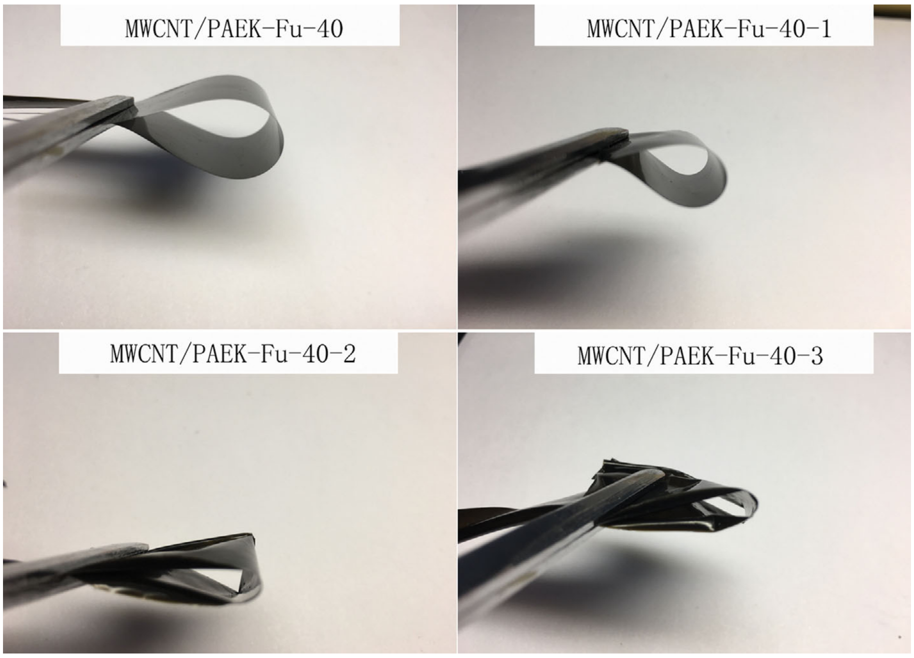


Fig. 3. Photographs of the MWCNT/PAEK-Fu-40, MWCNT/PAEK-Fu-40-1, MWCNT/PAEK-Fu-40-2 and MWCNT/PAEK-Fu-40-3.

followed by heating at 80 °C, 100 °C and 120 °C for 2 h, respectively. Then the MWCNT/PAEK-Fu-20 could be obtained. The MWCNT/PAEK-Fu-40 composite membranes were prepared by the same method, in which PAEK-Fu-20 was replaced by PAEK-Fu-40.

6. Preparation of Cross-linking MWCNT/PAEK-Fu Composite Membranes

To optimize the curing condition, the composite membranes were cured by different temperatures. They were, respectively, treated at 150 °C for 2 h, 170 °C for 2 h and 200 °C for 2 h to enhance thermal activation of the cross-linking reaction between MWCNTs and furan. The thickness of membranes was in the range of 70-100 μm. The heating composite membranes were named MWCNT/PAEK-Fu-20-1, MWCNT/PAEK-Fu-20-2, MWCNT/PAEK-Fu-20-3, respectively. Their photographs are shown in Fig. 2. The MWCNT/PAEK-Fu-40 composite membranes were heated by the same method. The heating composite membranes were named MWCNT/PAEK-Fu-40-1, MWCNT/PAEK-Fu-40-2, MWCNT/PAEK-Fu-40-3, respectively. Their photographs are shown in Fig. 3.

7. Dissolution of MWCNT/PAEK-Fu Composite Membranes

0.1 g MWCNT/PAEK-Fu-20-3 and 1 mL NMP were placed into a 5 mL sample bottle with vigorous stirring at room temperature for 10 days. The solution was then heated to 180 °C for 2 h and ultrasonic for 10 min. The membranes could be obtained. The MWCNT/PAEK-Fu-40-3 membranes were prepared in the same way, in which PAEK-Fu-20-3 was replaced by PAEK-Fu-40-3.

RESULTS AND DISCUSSION

1. Structural Characterization and Properties of PAEK-Fu

All the polymers were well characterized by standard spectroscopic methods, from which satisfactory analysis data corresponding to their molecular structures were obtained. The structures of the synthesized polymers were confirmed by ^{1}H-NMR spectra. Fig. 4 showed the ^{1}H-NMR spectra of PAEK-Am-20 and PAEK-Am-40. We selected the ^{1}H-NMR resonance of the carbonyl group's ortho hydrogen as a reference. The mol% of attached amino group per PAEK repeating unit was calculated by comparing the resonances intensities of the carbonyl group's ortho hydrogen in the polymer backbone (at 7.76-7.91 ppm) with the amino group's ortho hydrogen (at 6.86-6.95 ppm). Fig. 5 showed the ^{1}H-NMR spectra of PAEK-Fu-20 and PAEK-Fu-40. The chemical shifted from δ= 7.9 to 8.2 were assigned to furan protons. Thus, the mol% of attached furan group per PAEK repeating unit was calculated by the carbonyl group's ortho hydrogen as a reference [23,24].

Fig. 6 shows the UV-Vis spectra of PAEK-Fu-20 and PAEK-Fu-

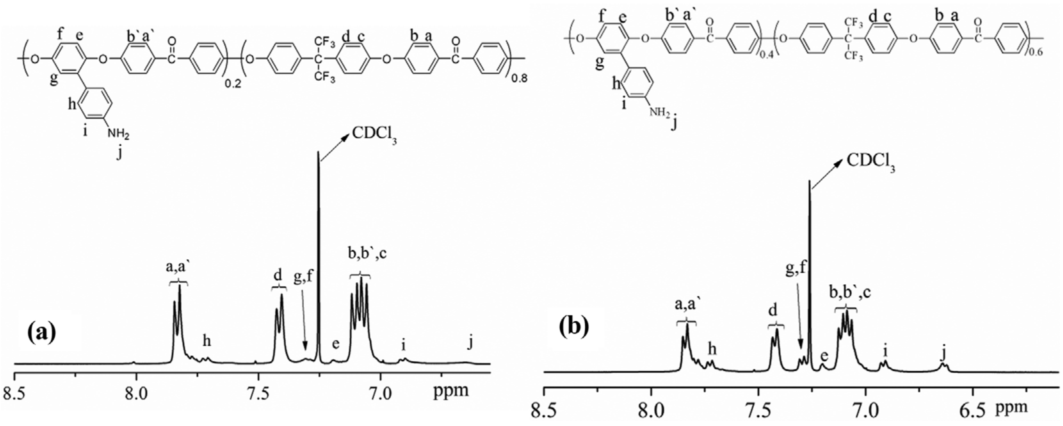


Fig. 4. The ^{1}H-NMR spectra of (a) PAEK-Am-20 and (b) PAEK-Am-40.

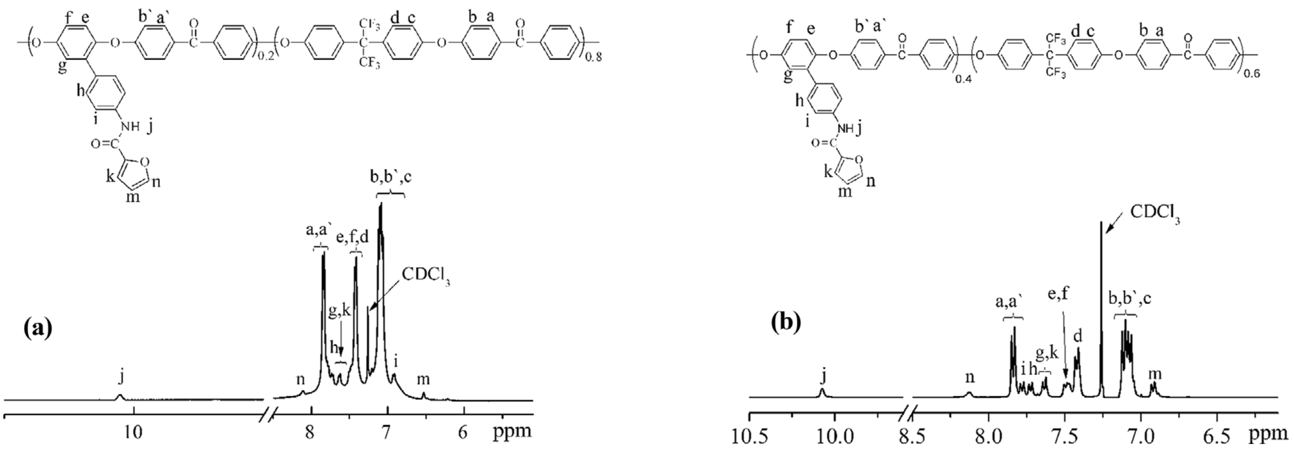


Fig. 5. The ^{1}H-NMR spectra of (a) PAEK-Fu-20 and (b) PAEK-Fu-40.

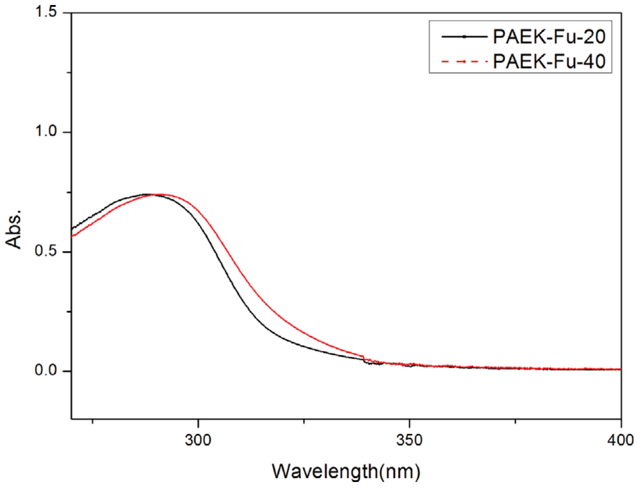


Fig. 6. UV-Vis spectra of PAEK-Fu-20 and PAEK-Fu-40 in $CHCl_3$ solution.

40. Each polymer had an obvious characteristic absorption peak in range of 295-300 nm, which corresponded to the π-π* electron transition of the conjugate double bond of furan group in the polymer. This was the characteristic absorption peak of furan group. With the increase of the content of furan group in the side chain of the polymer, the characteristic absorption peak appeared red shift. The results indicated that poly(aryl ether ketones) with different furan contents were successfully obtained.

2. Micromorphologies and Mechanical Properties of MWCNT/PAEK-Fu Composite Membranes

The mechanical properties of MWCNT/PAEK-Fu composite membranes are shown in Fig. 7 and listed in Table 1. More enhancement of tensile strength, tensile modulus can be seen in heat-treated MWCNT/PAEK-Fu composite membranes owing to cross-linking reaction between PAEK-Fu and MWCNTs. With the increase of heat treatment temperature, the Young modulus and tensile strength of MWCNT/PAEK-Fu-20 composite membranes gradually increased and the elongation at break decreased. The MWCNT/PAEK-Fu-40 composite membranes had a similar result. However, the elongation at break of the MWCNT/PAEK-Fu-40 composite membranes increased and then decreased. This may be because the molecular weight of PAEK-Fu-40 was relatively small. The improvement of mechanical properties indicated that D-A reaction took place. The tensile strength of all the MWCNT/PAEK-Fu composite membranes was obviously higher than that of the

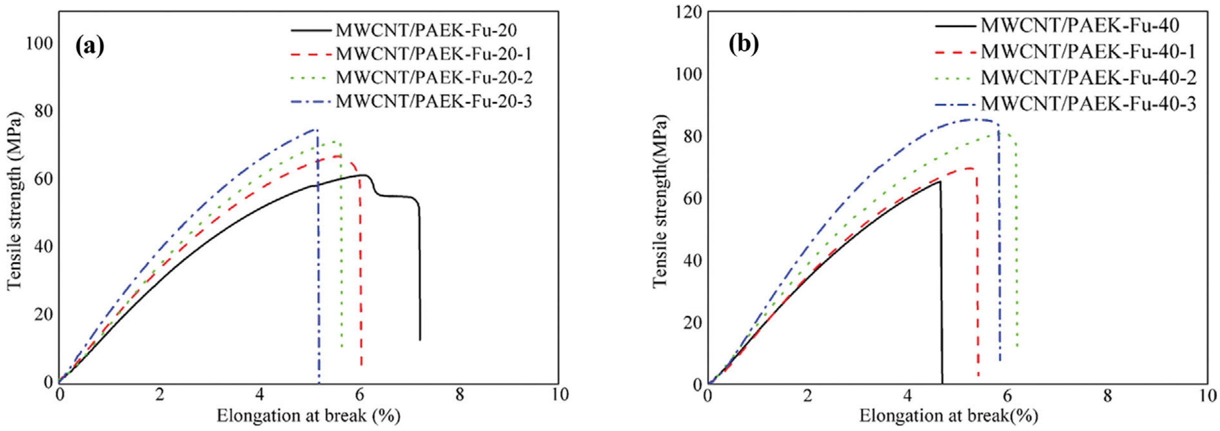


Fig. 7. Tensile curve of (a) the MWCNT/PAEK-Fu-20 and (b) the MWCNT/PAEK-Fu-40 composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively.

Table 1. The mechanical properties of the MWCNT/PAEK-Fu-20 and the MWCNT/PAEK-Fu-40 composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively, and other similar materials in the literature

Name	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
MWCNT/PAEK-Fu-20	1,615	61.7	7.2
MWCNT/PAEK-Fu-20-1	1,668	66.6	6.1
MWCNT/PAEK-Fu-20-2	1,743	70.8	5.7
MWCNT/PAEK-Fu-20-3	1,832	75.3	5.2
MWCNT/PAEK-Fu-40	1,622	63.1	4.7
MWCNT/PAEK-Fu-40-1	1,689	69.0	5.5
MWCNT/PAEK-Fu-40-2	1,831	80.0	6.2
MWCNT/PAEK-Fu-40-3	1,970	84.0	5.8
SBS-20Fu-2.5CNTs hybrids films [16]	-	18.5	800
bismalemide-MWCNT/DA-epoxy nanocomposite [25]	2,871	11.2	0.49
PGFA/BMI-1:2 [26]	-	1.72	125

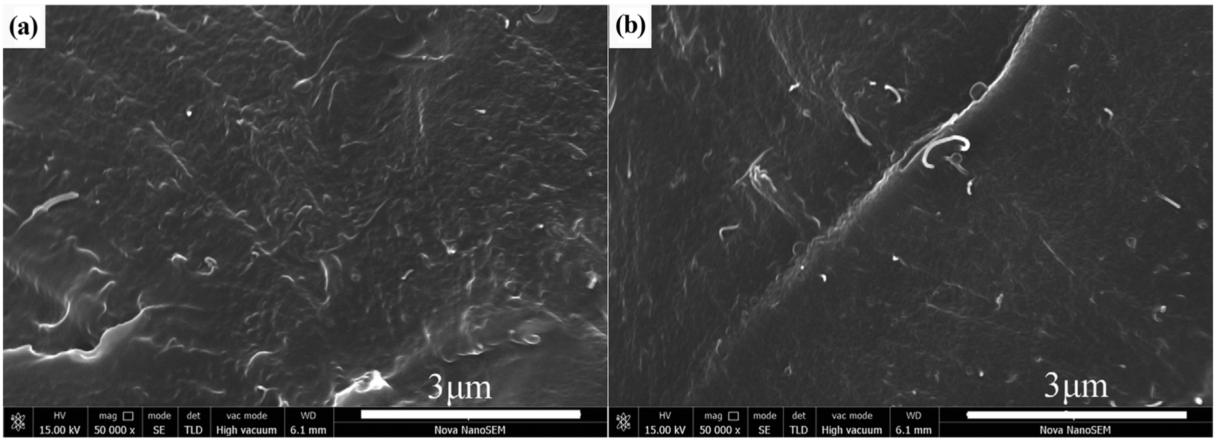


Fig. 8. SEM images of (a) the MWCNT/PAEK-Fu-20 and (b) the MWCNT/PAEK-Fu-40 composite membranes.

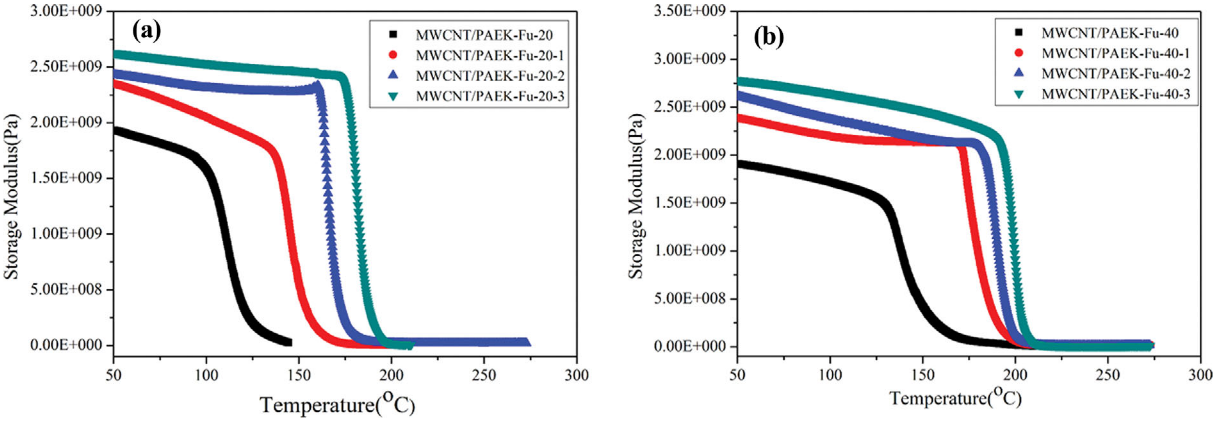


Fig. 9. Storage modulus of (a) the MWCNT/PAEK-Fu-20 and (b) the MWCNT/PAEK-Fu-40 composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively.

Table 2. The storage modulus at 80 °C and the temperature at the tanδ maximum value of the MWCNT/PAEK-Fu-20 and the MWCNT/PAEK-Fu-40 composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively

Name	Storage modulus at 80 °C (MPa)	The temperature at the tanδ maximum value (°C)
MWCNT/PAEK-Fu-20	1.84×10^3	121.6
MWCNT/PAEK-Fu-20-1	2.19×10^3	162.6
MWCNT/PAEK-Fu-20-2	2.36×10^3	177.5
MWCNT/PAEK-Fu-20-3	2.57×10^3	194.8
MWCNT/PAEK-Fu-40	1.81×10^3	202.5
MWCNT/PAEK-Fu-40-1	2.27×10^3	203.4
MWCNT/PAEK-Fu-40-2	2.46×10^3	206.1
MWCNT/PAEK-Fu-40-3	2.71×10^3	210.6

previous composites prepared by D-A reaction, as shown in Table 1.

Fig. 8 shows the SEM images of fracture surface of the MWCNT/PAEK-Fu-20 and the MWCNT/PAEK-Fu-40 composite membranes. Individual white ends of nanotubes could be found in both of Fig. 8(a) and 8(b), demonstrating that MWCNTs had good dispersion in the PAEK-Fu matrix.

3. DMA Properties of the Composite Membranes

Fig. 9 shows the storage modulus of the MWCNT/PAEK-Fu composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively. The storage modulus of the MWCNT/PAEK-Fu-20 and MWCNT/PAEK-Fu-40 composite membranes increased with the increase of the heat-treated temperature. To see the data clearly, the data were summarized in Table 2. It can be seen that the MWCNT/PAEK-Fu-40 composite membranes show better storage modulus than MWCNT/PAEK-Fu-20 composite membranes. This is attributed to the higher crosslinking density

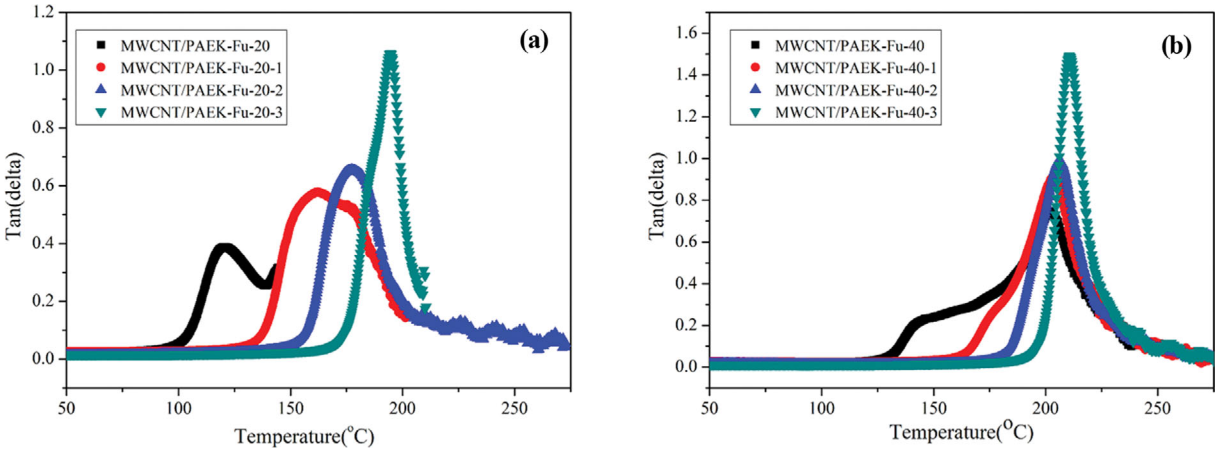


Fig. 10. Tanδ of (a) the MWCNT/PAEK-Fu-20 and (b) the MWCNT/PAEK-Fu-40 composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h, respectively.

between the MWCNTs and PAEK-Fu in MWCNT/PAEK-Fu-40 composite membranes. The other influence is reflected on the temperature at the tanδ maximum value, which is shown in Fig. 10. The MWCNT/PAEK-Fu-20 composite membranes' temperature at the tanδ maximum value increased with the increase of the heat-treated temperature, so did the MWCNT/PAEK-Fu-40 composite membranes. Moreover, the MWCNT/PAEK-Fu-40 composite membranes showed higher temperature at the tanδ maximum value than MWCNT/PAEK-Fu-20 composite membranes.

4. Thermal Properties

The thermal stability of the polymers is vital to their applications. To examine the thermal durability of these polymers, several thermogravimetric (TGA) experiments were performed under N_2 atmosphere. As shown in Fig. 11, the degradation of heat-treated MWCNT/PAEK-Fu composite membranes was slower than that of untreated membranes. This was also because that the heat-treated composite membranes had high crosslinking density. The MWCNT/PAEK-Fu composite membranes untreated and treated under 150 °C, 170 °C, 200 °C had the ratio of loss of mass in two processes. TGA curves of MWCNT/PAEK-Fu-20 composite membranes were shown in Fig. 11(a). The first stage from 150 to 280 °C was due to the loss of the unevaporated solvent and the furan. The second stage was from 450 to 600 °C, accompanied by decomposition of polymer main chain. Fig. 11(b) shows TGA curves of MWCNT/PAEK-Fu-40 composite membranes. The first stage from 150 to 280 °C is due to the loss of the polymers' side chain. The second stage is from

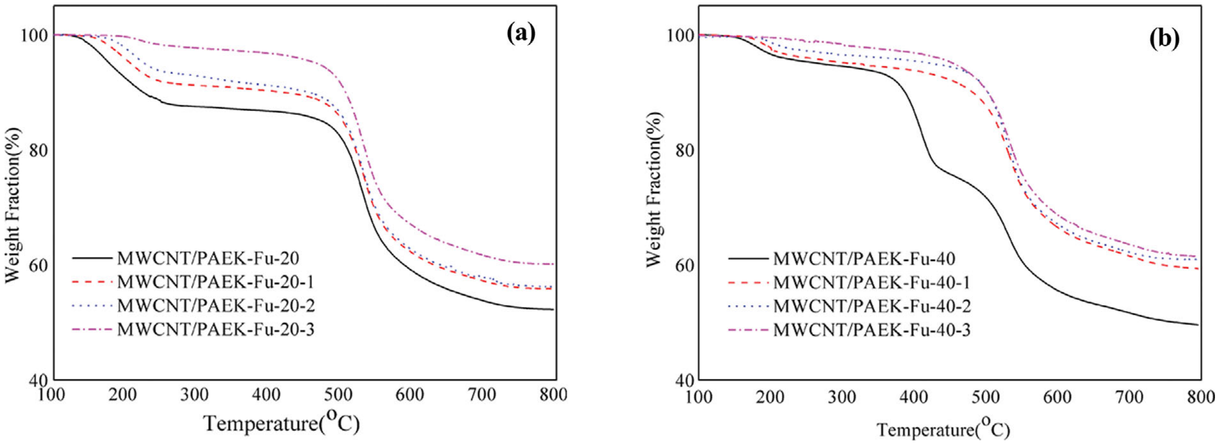


Fig. 11. The TGA curves of the MWCNT/PAEK-Fu composite membranes untreated and treated under 150 °C, 170 °C, 200 °C for 2 h.

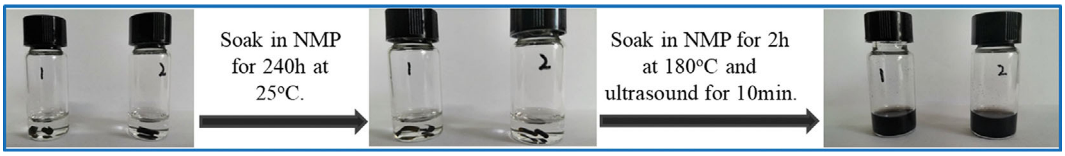


Fig. 12. The dissolution of the MWCNT/PAEK-Fu composite membranes treated under 200 °C.

450 to 600 °C, accompanied by decomposition of polymer main chain. After heat treatment, the MWCNT/PAEK-Fu-40 composite membranes exhibited better thermal stability.

5. Dissolution

Fig. 12 exhibits the dissolution of the MWCNT/PAEK-Fu composite membranes treated under 200 °C. As shown in Fig. 12, after soaking in NMP for ten days, the MWCNT/PAEK-Fu-20-3 (Fig. 12(1)) and MWCNT/PAEK-Fu-40-3 (Fig. 12(2)) composite membranes did not dissolve. When the membranes suffered from heating at 180 °C for 2 h and then ultrasound for 10 min, the membranes dissolved. The results indicated that the MWCNT/PAEK-Fu composite membranes could be recycled.

CONCLUSIONS

PAEK-Fu polymers with various content of furan were synthesized through a classic condensation polymerization method and characterized using ^{1}H-NMR, UV and GPC techniques. A series of cross-linked materials with reversible covalent crosslinking network were synthesized through a furan/MWCNTs DA reaction. The MWCNTs were evenly dispersed in the membranes. After heat treatment, the MWCNT/PAEK-Fu composite membranes showed better mechanical properties, thermostability and solvent resistance. However, after heating to 180 °C, the MWCNT/PAEK-Fu composite membranes could be dissolved in NMP, so the MWCNT/PAEK-Fu composite membranes may be recycled and repaired again.

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