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SYNTHESIS AND PROPERTIES OF CONTROLLABLE CROSS-LINKING POLY(ARYL ETHER KETONE)S

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Abstract

In our recent work, We have introduced thioether moieties into PAEK main chain and obtained thermoplastic material. Its properties can be controlled by adjusting content and distribution of thioether moieties in the polymer chains. It can be transformed into thermosetting material by annealing at 380°C. The novel material was combined successfully with advantages of thermoplastic material and thermosetting material. It can be processed as conveniently as pure PEEK before cross-linking and possesses high application temperature as thermosetting plastic after cross-linking.

Keyword Poly(aryl ether ketone), Controllable cross-linking, Thermosetting material

Introduction

Poly (ether ether ketone) (PEEK), as a semicrystalline high performance thermoplastics resin has been applied in many high-technology fields, such as nuclear industry and aerospace fields^(1,2). But PEEK has some disadvantages, such as low glass transition (T_g) and Comparatively low melting point (T_m) lead to low application temperature (240°C as normal). In order to increase application temperature of material. Synthesis of structurally related polymers containing more rigid chains, which have higher T_g and T_m, have been studied broadly^(3,4). However, the increasing T_g and T_m accompany the increasing processing difficulty⁽⁵⁾.

Engineer plastic can be divided into thermoplastic material and thermosetting material on the basis of processing. They have respective advantages and disadvantages. In our recent work, we have introduced thioether moieties into PEEK main chain in the molecular design, in which sulfur acts as a cross-linking point, and obtained thermoplastic material. Its properties can be controlled by adjusting content and distribution of thioether moieties. It can be transformed into thermosetting material by annealing at 380°C⁽⁶⁾. The novel material was combined successfully with advantages of thermoplastic material and thermosetting material. It can be processed as conveniently as pure PEEK before cross-linking, and processes high application temperature as thermosetting plastic after cross-linking.

Here we describe a dynamic rheological detection and thermal property and mechanical property of the controllable cross-linking poly (aryl ether ketone).

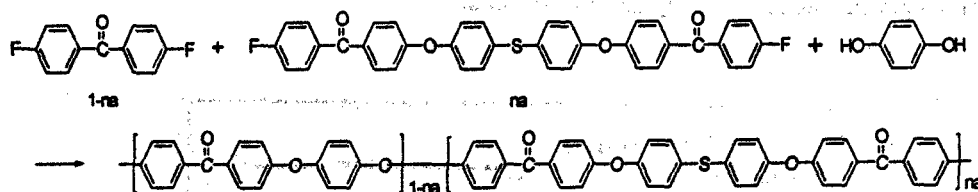
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Experimental

Materials. Powder resin, wrapped aluminum foil, was molded on a compression machine at a fixed temperature. The molded film was used for rheological measurement. The molded film quenched into water as quickly as possible to obtain an amorphous sheet. Then the sheet was annealed at different condition. It was used for DSC measurement. Powder resin was used for TGA test.

Instrumentation The ARES (Advanced Rheological Expansion System, Rheometrics, USA) was used for rheological measurements. Dupont TA-910 differential scanning calorimeter (DSC) was carried out at a heating rate of 20°C/min from 50°C to 500°C under nitrogen atmosphere, and at least 10mg of the film a sample used for DSC measurement. TGA7 High Temp Analysis. INSTRON-1121 universal material testing machine.

Synthesis Polymer was synthesized through nucleophilic substitution route by polycondensation of difluoromonomer and 4, 4'-difluorophenone with 1, 4-biphenol using diphenylsulfone as a solvent. The reaction was heated to 320°C by K₂CO₃ and Na₂CO₃ as a base for 5h. The solution was pured into water and precipitate was obtained. After the crude polymer was filtered, washed and dried, a white power resin was finally obtained. Here we selected the copolymer in which content of tripolymer(na) is 5 percent.(SPEEK-5%).



Scheme 1. Synthesis of block copolymer

Results and Discussion

Figure.1 shows dynamic time test of rheological trace for SPEEK-5% at 380°C. Kinetics of cross-linking reaction can be clearly observed at 380°C. At the beginning of cross-linking reaction, modulus and viscosity of copolymer increased fast because segmental motion moved easily. Increasing of modulus and viscosity becomes slow along with increasing of degree of cross-linking reaction. The formation of cross-linking network leads to freezing of segmental motion. Finally, rheological traces approach to platform when cross-linking reaction attained to 5 hours.

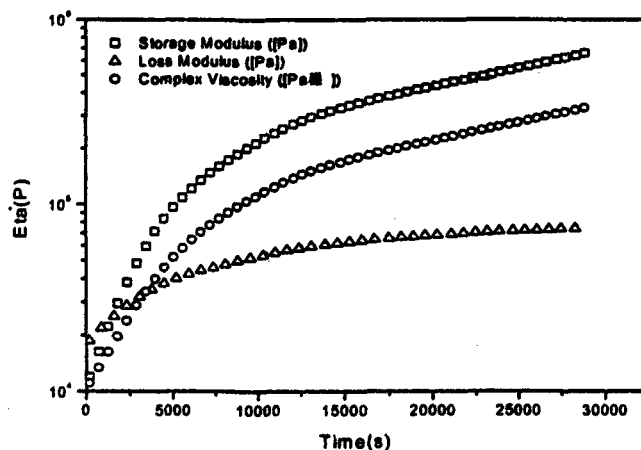


Figure.1. Rheological traces of SPEEK-5% DTime at 380°C

In Figure.2. SPEEK-5% shows different DSC traces annealed for different time at 380°C. We can see that increasing of Tg and crystalline peak and decreasing of Tm accompany with increasing of degree of cross-linking reaction. If annealing time is above 5 hours, Tg, Tm And crystalline peak of copolymer disappeared. The copolymer was transformed into thermo-setting plastic. So it possesses the advantages of thermo-setting plastic, such as high application temperature.

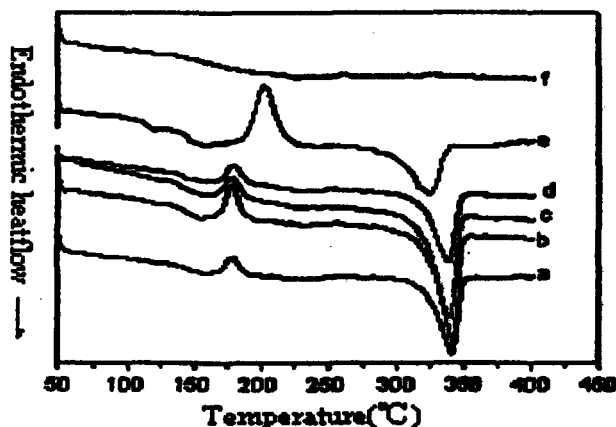


Figure.2. DSC trace of SPEEK-5% with different annealing time at 380°C.

a:5min b:20min c:30min d:1 hour e:2 hours f:5 hours

Figure 3 shows. a 5% weight loss of copolymer in air atmosphere at 546°C and 563°C before cross-linking and after cross-linking, respectively. Based on Figure3, the thermal stability and thermal oxidize stability of controllable cross-linking PEEK were excellent compared to pure PEEK, especially for copolymer after cross-linking. From Figure 4, we can see that SPEEK-5% has not weight loss in nitrogen atmosphere and has very small weight loss in air atmosphere. These datum illustrated cross-linking copolymer possesses outstanding thermal stability and thermal oxidize stability.

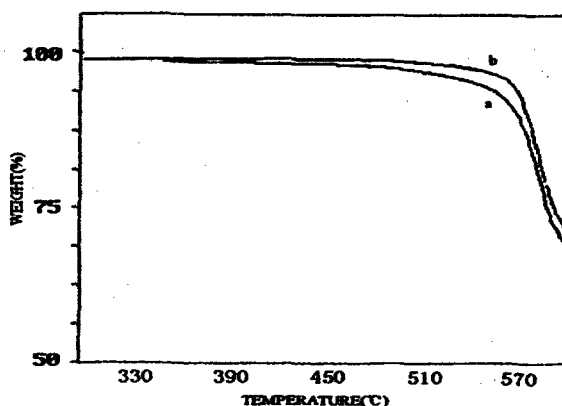


Figure.3. TGA thermogravimetric curves for SPEEK-5%r in air atmosphere.

a: before cross-linking b: after cross-linking (annealing 5 hours at 380°C)

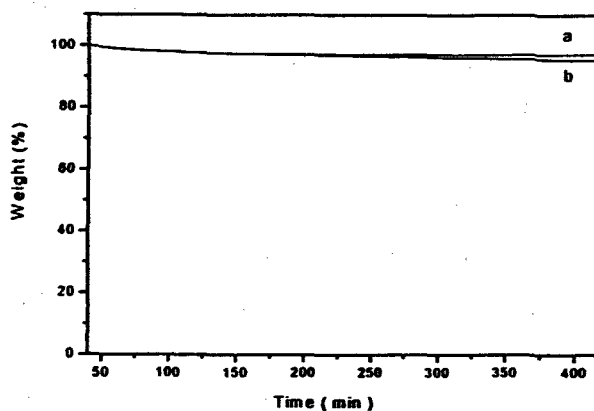


Figure.4. thermogravimetric curves for SPEEK-5% in different gas atmosphere at 380°C.

a: nitrogen atmosphere b: air atmosphere

Table.1. Stretching and bonding data of SPEEK-5%

polymer	elongation (%)	strength of stretch /MPa	modulus of stretch /GPa	strength of bending /MPa	modulus of bending /GPa
Sample before cross-linking	85	72.8	1.45	115	2.52
Sample after cross-linking	20	104	2.29	136	2.84

Table 1 shows that elongation of sample decreased from 85% to 20% when sample completely cross-linked. While the other characters, such as strength of stretch, modulus of stretch and so on, showed obviously increasment. From above, we found that samples before cross-linking and after cross-linking possessed excellent mechanical property.

Conclusions

We have introduced thioether moieties into PEEK main chain, in which sulfur acts as a cross-linking point. We obtained thermoplastic material. Its properties can be controlled by adjusting content and distribution of thioether moieties. It can be transformed into thermosetting material by annealing at 380°C. The novel material was combined successfully with advantages of thermoplastic material and thermosetting material. It can be processed as conveniently as pure PEEK before cross-linking, and processes high application temperature as thermosetting plastic after cross-linking. The cost of the novel material has not been increased compared to pure PEEK. Happening of cross-linking reaction didn't accompany with happening of degradation reaction and releasing of micromolecular. The novel material possesses excellent thermal stability and thermal oxidize stability and mechanical property.

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