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DSC STUDY OF STABILIZATION REACTIONS IN POLY(ACRYLONITRILE–co–ITACONIC ACID) WITH PEAK-RESOLVING METHOD

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The effect of itaconic acid (IA) content and heating rate on the stabilization reactions in poly(acrylonitrile-co-itaconic acid) (P(AN-co-IA)) was investigated by differential scanning calorimetry (DSC) with peak-resolving method. Increasing IA content was effective in decreasing the initial temperature and the heat evolved, and found to enhance oxidative reactions to some extent. While, promoting heating rate resulted in a shift of the exotherm to a higher temperature and a more rapid liberation of heat. The percentage of area of the first exothermic peak increased with increasing heating rate, which would be attributed to the enhancement of the free radical cyclization reactions.

Keywords: *DSC, PAN, peak-resolving method, poly(acrylonitrile-co-itaconic acid), stabilization*

Introduction

Polyacrylonitrile (PAN) is one of the most important precursor polymers for preparing high performance carbon fiber, which is known as a versatile reinforcement material extensively applied in sport, recreational, aerospace and defense industries [1]. A small amount of suitable comonomers is necessarily incorporated into PAN so as to improve its operability and the stabilization treatment. Among the various candidates, itaconic acid (IA) is the preferably and most widely used one because of the presence of two carboxylic groups [2–5].

Among the complex techniques during the process of transforming the precursor to carbon fibers, the thermo-oxidative stabilization has attracted much attention due to its crucial effect on the properties and quality of resulting carbon fibers [6]. The stabilization treatment is conducted in an oxidizing atmosphere between 200 and 300°C forming the thermally stabilized structures so as to endure the higher temperature in carbonization. During this step, the furious exothermic behavior accompanied by the stabilization reactions, including cyclization reactions of nitrile groups, dehydrogenation and oxidative reactions, needs to be properly controlled [5].

In this work, dynamic DSC was applied to study the exothermic behavior during stabilization of poly(acrylonitrile-co-itaconic acid) (P(AN-co-IA)). The effect of itaconic acid (IA) content in the copolymer and heating rate on the exothermic reactions was investigated with the aid of a peak-resolving method.

Experimental

Polymer synthesis

The copolymerization of acrylonitrile (AN) with itaconic acid (IA) was carried out in dimethylsulfoxide (DMSO) at 60°C under nitrogen atmosphere with α,α'-azobisisobutyronitrile (AIBN) as an initiator. At the end of the reaction, the polymer dope was precipitated in deionized water. The precipitate was washed with a large amount of deionized water several times, dried at 80°C under vacuum, and then ground to a fine powder.

Measurements

The IA content in the copolymers was determined by elemental analysis carried out using a Vario EL III elemental analyzer. Intrinsic viscosity $[\eta]$ of the polymers was measured in dimethylformamide (DMF) solution using an Ubbelohde viscometer in a constant temperature water bath at 30±0.01°C. Four samples with IA content of 0, 1.69, 2.20 and 3.01%, and $[\eta]$ of 2.01, 1.41, 1.10 and 0.86, respectively, were prepared and named as P0, P1, P2 and P3 in turn.

The DSC studies were carried out using a NETZSCH STA 409PC thermal analyzer. The samples were scanned at a certain heating rate under air atmosphere (60 mL min^{-1}) in Al_2O_3 pans from ambient temperature to 450°C. The various parameters obtained from the DSC curves, including initial temperature (T_i), peak temperature (T_{peak}) and heat evolved (ΔH), were listed in corresponding tables.

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Results and discussion

The exothermic reactions occurring during the stabilization treatment are mainly classified as cyclization reactions of nitrile groups, dehydrogenation and oxidative reactions [6]. The former two reactions are responsible for formation of a condensed naphthyridine ring structure through oligomerization of –C≡N groups to –C=N– groups and conversion of C–C structure to C=C structure, respectively. The oxidative reactions generate oxygen-containing groups such as –OH and >C=O, etc. These groups promote intermolecular crosslinking and formation of the thermally stabilized structures which can endure the high temperature with less cleavage during carbonization process [7].

As shown in Fig. 1, the PAN homopolymer (P0) exhibits a sharp single exothermic peak between about 230 and 360°C. It is known that the cyclization reactions in the PAN homopolymer follow a free radical mechanism and can be initiated only at a higher temperature [8]. The single exothermic peak found would be attributed to the overlapping of the free radical cyclization reactions and other exothermic reactions at the higher temperature. This may cause a large amount of heat to be evolved at the same time. Thus, the PAN homopolymer is not beneficial for producing high performance carbon fiber.

While, the P(AN-co-IA) copolymers all show a doublet exothermic peak. This is because itaconic acid (IA) can initiate the cyclization reactions at a lower temperature through an ionic mechanism [8]. This new exothermic peak at the lower temperature is mainly corresponding to the ionic cyclization reactions. As for P1, it appears as a shoulder at about 251°C. With IA content increasing, this peak gradually becomes more and more distinct and moves to a lower temperature. As shown in Table 1, both the initial temperature (T_i) and heat evolved (ΔH) significantly decrease, which implies IA is effective to control the exothermic behavior and improve the stabilization treatment.

According to the literature [7, 9], the first exothermic peak (peak 1) at the lower temperature side is assigned to both cyclization reactions and dehydrogenation, and the second peak (peak 2) is attributed to the oxidative reactions. In this case, the effect of IA content on these exothermic reactions was investigated by a peak-resolving method. In the present work, the peak fitting module (PFM) in Origin Pro 7.5 software was applied to resolve the DSC curves. First, a baseline (see line bb' in Fig. 2) was defined, and then the exothermic peak was resolved into two substantially symmetrical constituent peaks using PFM by keeping the peak positions constant and such that the total area of the resolved peaks best approximates the area of the entire exothermic peak. The exothermic peak of P(AN-co-IA) copolymer P1 has been typically resolved as shown in Fig. 2, and the results are listed in Table 1.

As can be seen from Table 1, with IA content increasing, the percentage of area of peak 1 decreases. It seems that IA retards the extent of cyclization reactions, which may be attributed to the interruption in the sequence distribution of CN unit in the polymer chain by the IA unit [7]. While, the extent of oxidative reactions seems to be enhanced by IA as the percentage of area of peak 2 increases with IA content increasing. This is probably due to the increase in the amorphous phase caused by incorporation of the IA unit providing more passage for oxygen to diffuse into the copolymer [7].

The cyclization reactions, especially the free radical cyclization reactions, generally process very fast. While, the oxidative reactions are always stumbled by the diffusion speed of oxygen and generally act as the rate-limiting step during stabilization. Thus, it is meaningful to incorporate IA into PAN for enhancement of the oxidative reactions.

During the stabilization treatment, heating rate is one of the most important parameters. In order to study its effect on the stabilization reactions, a series of DSC curves were obtained by scanning at different

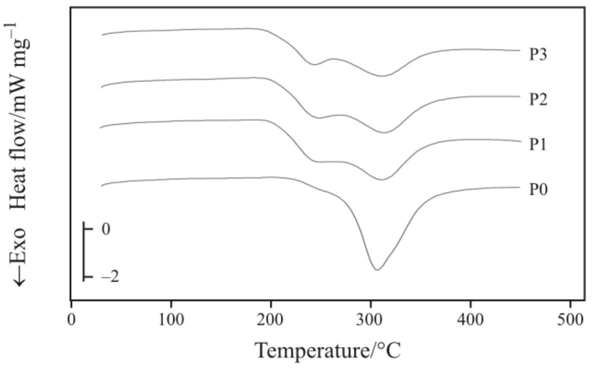

Fig. 1 DSC curves of P(AN-co-IA) with different IA contents at a heating rate of 5°C min^{-1}: P0 – 0, P1 – 1.69, P2 – 2.20 and P3 – 3.01%

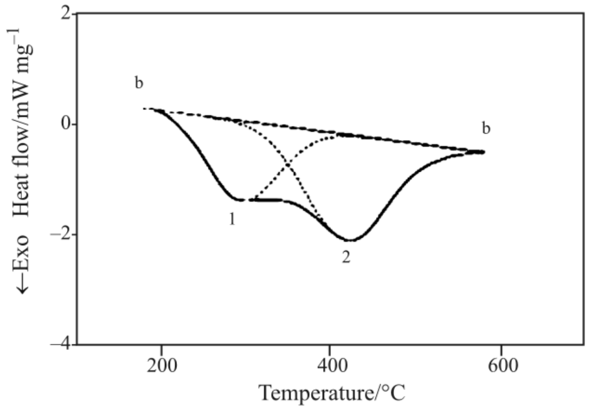

Fig. 2 Representative DSC curve (P1) treated by the peak-resolving method

Table 1 DSC data of P(AN-co-IA) with different IA contents

Code	IA content/%	T_i/°C	ΔH/J g^{-1}	T_{peak1}/°C	T_{peak2}/°C	Area %	
						Peak 1	Peak 2
P0	0	230	2213	310	–	–	–
P1	1.69	203	2207	251	311	42	58
P2	2.20	200	2136	248	313	40	60
P3	3.01	196	1637	243	310	37	63

Table 2 DSC data of P1 at different heating rates

Code	Heating rate/°C min^{-1}	T_i/°C	ΔH/J g^{-1}	T_{peak1}/°C	T_{peak2}/°C	Area %	
						Peak 1	Peak 2
1	5	203	2207	251	311	42	58
2	10	206	2099	261	323	48	52
3	15	216	1842	267	333	52	48
4	20	221	1942	271	344	54	46

heating rates. Figure 3 shows the DSC curves of P(AN-co-IA) copolymer P1 recorded at heating rates of 5, 10, 15 and 20°C min^{-1}, and the corresponding data are listed in Table 2.

As can be seen from Fig. 3, with heating rate increasing, the exotherm wholly shifts to a higher temperature, which is probably due to the delay of heat transfer. As shown in Table 2, both the initial temperature (T_i) and peak temperature (T_{peak}) increase greatly. While, the heat evolved (ΔH) firstly decreases with the increase of heating rate from 5 to 15°C min^{-1}, and then increases to some extent with further increasing the heating rate up to 20°C min^{-1}.

With increasing the heating rate, the exothermic peaks tend to become sharp and strong. However, apparently, the first exothermic peak (peak 1) increases more rapidly than the second one (peak 2). At the heating rate of 5 and 10°C min^{-1}, peak 1 just appears as a weak shoulder beside peak 2. While at 15°C min^{-1}, it turns to be nearly equally high to peak 2, and when the heating rate increases to 20°C min^{-1}, peak 1 becomes much higher than peak 2. The peak-resolving method was similarly used to treat these DSC exothermic peaks. The results show that the percentage of area of peak 1 increases with the heating rate increasing.

As mentioned above, the oxidative reactions are mainly controlled by the diffusing rate of oxygen, thus, they are more affected by the transport of mass than that of heat. While the cyclization reactions are greatly influenced by temperature, especially the free radical cyclization reactions only can be initiated at a higher temperature. With heating rate increasing, the high-temperature free radical cyclization reactions seem to be enhanced, which makes a great expansion of heat at a short time. This may mainly account for that peak 1 becomes sharper than peak 2 with increasing heating rate.

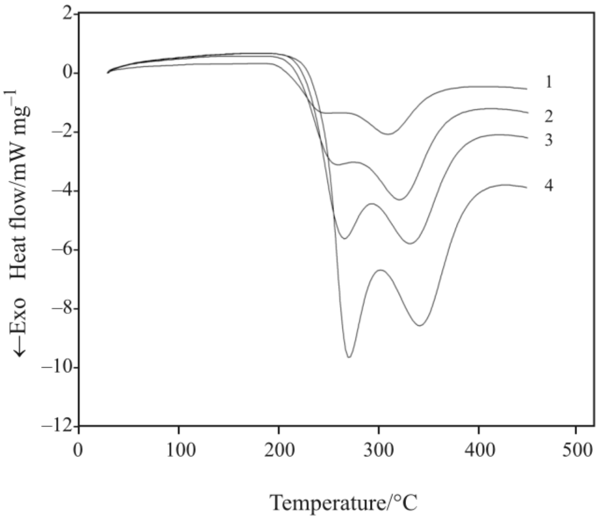

Fig. 3 DSC curves of P1 at different heating rates: 1 – 5, 2 – 10, 3 – 15 and 4 – 20°C min^{-1}

The furious exothermic behavior should be avoided during the stabilization treatment. Thus, in order to produce carbon fiber with good mechanical properties, it is suitable to carry out the stabilization treatment at a lower heating rate.

Conclusions

Incorporation of IA into PAN is an effective way to control the furious exothermic behavior of the stabilization reactions with a significant decrease of the initial temperature and the heat evolved. Increasing IA content is found to decrease the extent of cyclization reactions and enhance the extent of oxidative reactions. While, promoting heating rate resulted in a shift of the extherm to a higher temperature and a more rapid liberation of heat. The percentage of area of the first exothermic peak increased with increasing heating rate, which would be attributed to the enhancement of the free radical cyclization reactions. This is not beneficial for producing high performance carbon fiber. Thus, the stabilization treatment of PAN should be carried out at a lower heating rate with a certain amount of IA incorporated into the PAN precursor as comonomer.

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