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THERMAL BEHAVIOR OF POLYACRYLONITRILE POLYMERS SYNTHESIZED UNDER DIFFERENT CONDITIONS AND COMONOMER COMPOSITIONS

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Polyacrylonitrile (PAN) polymers are used as precursors for carbon fiber production. This process requires an oxidative stabilization step, which can be studied by differential scanning calorimetry (DSC). In this sense, thermal behavior of PAN based terpolymers by different polymerization processes, compositions and itaconic acid concentrations in the reaction media were investigated. The obtained results showed that the addition of itaconic acid and methyl acrylate as comonomers resulted a lower heat flow during the process comparing to the PAN homopolymer. It suggested that these comonomers aid the oxidative stabilization stage for all studied process. The redox system polymerization at 40°C resulted in a lower heat flow. Itaconic acid decreases slightly initial and peak temperatures of the terpolymer and heat flow until concentration of 3y. The cyclization temperature decreases when MA is incorporated into the terpolymer compared to the MMA terpolymer and increases when MAA is the acidic monomer. Among terpolymers the AN/MA/AA polymer showed the best thermal behavior for carbon fiber producing.

Keywords: *DSC, PAN terpolymers, thermal behavior*

Introduction

Polyacrylonitrile (PAN) is used as a precursor of carbon fiber for different purposes such as body parts of cars and airplanes [1]. Its properties can be improved by incorporation of suitable comonomers to the PAN homopolymer during polymerization, which can be tracked by thermal analysis [2–5]. Acidic comonomers increase its hydrophilicity and reduce the cyclization temperature during the heat treatment [6]. Neutral comonomers like methyl acrylate (MA) and methyl methacrylate (MMA) increase solubility, drawability and spinnability [7]. Furthermore, with increasing comonomer concentration in the PAN the crystallinity and the crystallite size [8] decrease. Due to their physical and mechanical characteristics including low temperature stabilization, extremely oriented molecular structure, light mass, inert biological and chemical properties, furthermore high corrosion resistance, the 90% of the produced carbon fibers are based on the use of polyacrylonitrile [9].

PAN based composition also plays an important role in the initial oxidative stabilization stage during carbon fiber production [10]. This is the longest and most critical step due to the necessary control of the considerable amount of evolved heat, which accompanies the degradation reactions of PAN. Because of the exotherm effect it requires rigorous control in order to obtain good quality carbon fibers from PAN precursors. This oxidative stabilization stage can be studied by differential scanning calorimetry (DSC). Depending on the comonomer composition, the molecular mass of the precursor polymer and the polymerization process, the DSC curves of PAN precursors exhibit an exothermic peak between 200–400°C. The initial temperature of the exothermic reaction should be as low as it is possible, since the evolved heat during the exothermic process may lead to low carbon yield and, consequently, to a fragile carbon fiber. Lower initial temperatures also result reduced entropic relaxation of molecules, which translate into improved tensile properties of the resulting carbon fiber [11].

Herein the thermal behavior of PAN based terpolymer using different polymerization processes, comonomers and itaconic acid concentrations investigated by differential scanning calorimetry is reported.

Experimental

Polymer synthesis

Polymerization reactions were carried out in a four-necker reactor fitted to a condenser, glass stirrer, ni-

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trogen inlet tube and a probe equipped with thermocouple. The experiments were performed in water suspension using a redox system or persulfate salts as initiators in different concentrations and reaction temperatures. The monomer mixture was slowly added to the reaction medium. The reaction was carried out for 3 h. At the end of the reaction, the polymer was filtered and washed with distilled water then dried at 50°C for 24 h.

The acrylonitrile (AN) content was determined by elemental analysis. In order to determine the acid value, potentiometric titrations were carried out in a Mettler-Toledo DL50 potentiometer. Samples were dissolved in dimethyl sulfoxide and titrating using a 0.1 mol L^{-1} KOH standard alcoholic solution.

Thermoanalytical investigations

DSC measurements were carried out on a Perkin-Elmer DSC-7 module. Polymer samples were previously grounded and homogenized using a 0.074 mm sieve. Powder sample masses were in the range of 4 mg and were heated from 50 to 400°C under dynamic nitrogen atmosphere (100 mL min^{-1}) at heating rate of 20°C min^{-1} in aluminum sealed pans. The initial peak temperature (T_{ip}), the peak temperature (T_p) and the heat flow (ΔH) associated to the oxidative stabilization stage were determined from the DSC curves.

Results and discussion

PAN precursors exhibit a sharp exothermic peak between about 240 and 350°C as is shown in Fig. 1. This peak corresponds to dehydrogenation, oxidation, cross-linking and mainly cyclization reactions. The last two reactions are responsible for the nitrile group oligomerization and represent the most important step in the conversion of PAN precursors to carbon fibers. The heat flow and the initial and peak temperatures associated to this process should be as low as possible in order to produce carbon fiber with good mechanical properties.

Initially, the thermal behavior of PAN homopolymer and terpolymers obtained in suspension using different concentrations of an initiator and a redox system at different temperatures were investigated.

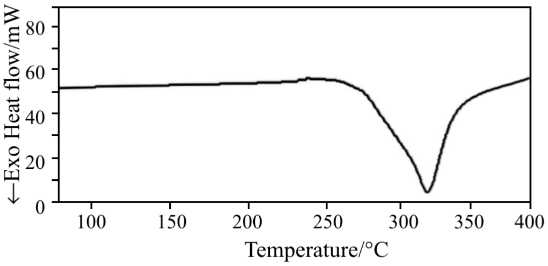

Fig. 1 Representative DSC curve of a PAN terpolymer

Table 1 Representative DSC data of the homopolymer and terpolymers obtained from different polymerization process

Sample	T_{pol}*/°C	T_{ip}/°C	T_p/°C	$-\Delta H$/J g^{-1}
Homopolymer	67	242	312	4200
persulfate – 0.75%	67	236	304	2229
persulfate – 1.50%	67	241	309	2008
persulfate – 3.00%	67	240	306	1984
Redox	40	248	306	1843
Redox	50	242	296	2009
Redox	60	241	306	1865

T_{pol} – temperature of polymerization, T_{ip} – initial peak temperature, T_p – peak temperature, ΔH – heat effect

According to the data in Table 1, the oxidative stabilization step of PAN homopolymer exhibits the highest heat flow effect. In order to decrease the evolved heat and the initial and peak temperatures, syntheses were carried out with addition of itaconic acid and methyl acrylate as comonomers. This lead to a considerable decrease in the heat effect but the initial and peak temperatures remained practically constant. When the polymerization was carried out using 0.75% of persulfate the initial and peak temperature slightly shifted to lower values compared to PAN homopolymer. On the other hand, redox system polymerizations resulted somewhat lower heat effects compared to the case of persulfates. The highest initial peak temperature was observed for the terpolymer obtained at 40°C, denoting the effect of polymerization temperature on the thermal behavior of the product.

In order to study effect of comonomers on the thermal behavior of terpolymers, the polymerizations were carried out using different neutral and acid comonomers (Table 2).

The AN/MA/IA terpolymer cyclizes at lower temperature as well as the peak temperature (T_p) somewhat shifted to lower temperature compared to (AN/MMA/IA). Moreover, the cyclization temperature increases when the methyl methacrylic acid (MAA) was incorporated into the terpolymer.

Table 2 DSC data for terpolymers with different compositions

Sample	T_{ip}/°C	T_p/°C	$-\Delta H$/J g^{-1}
AN/MMA/IA	225	313	2466
AN/MA/AA	220	312	1907
AN/MA/IA	220	309	2012
AN/MA/MAA	227	313	1818

AN – acrylonitrile, MA – methyl acrylate,
MMA – methyl methacrylate, IA – itaconic acid,
AA – acrylic acid, MAA – methyl methacrylic acid.

It is noteworthy that despite of the identical AN/(IA, MAA, AA)/(MA, MMA) molar ratio during the polymerization process, a relative variation in the terpolymer composition was observed. Among the studied acidic comonomers, itaconic acid (IA) was less incorporated into the polymer. The less reactivity of itaconic acid compared to the others is due to its hydrophilic properties and its bulky size, which contributes to sterical hindrance. On the other hand, when acrylic acid (AA) or methyl methacrylic acid (MAA) was the comonomer, the amount of the incorporated acid content to the polymer increased by 2.5 times. In all situations the amount of carboxylic group in the polymer remained constant.

Another set of experiments were carried out with different concentrations of itaconic acid using 0.75% of persulfate as initiator at 67°C. The obtained results are shown in Table 3.

Table 3 shows that the increase in the itaconic acid concentration causes a decrease of the initial peak and peak temperatures up to 3y concentration. However, increasing further the concentration of IA up to 7y, the initial peak temperature increases to 227°C. Moreover, in all studied synthesis the acid comonomer decreases the obtained heat effect of terpolymer, which is the highest at 2y and 3y itaconic acid concentrations.

Table 3 DSC data for homopolymer and terpolymers obtained from different itaconic acid concentration in the polymerization reaction media

Sample	T_{ip}/°C	T_p/°C	$-\Delta H$/J g^{-1}
Homopolymer	242	312	4200
Terpolymer y	237	313	2014
Terpolymer 2y	234	308	2077
Terpolymer 3y	215	307	2747
Terpolymer 7y	227	309	2250

T_{ip} – initial peak temperature, T_p – peak temperature, ΔH – heat flow, y – itaconic acid factor percentage (proprietary information).

Conclusions

Addition of comonomers to the polyacrylonitrile terpolymer is essential to obtain PAN precursors with adequate thermal behavior in order to produce carbon fibers with good mechanical properties.

The polymerization process and the terpolymer composition are fundamental to control the heat flow and the initial and peak temperatures during the oxidative stabilization process.

The acid comonomer plays an important role in the thermal behavior of the terpolymer. Among terpolymers, the one that acrylic acid (AA) is incorporated into the polymer (AN/MA/AA), exhibited one of the best thermal properties compared to other terpolymers: low cyclization temperature together with low heat effect. It was also observed that the itaconic acid, which incorporated into the terpolymer decreases the heat effect of the PAN terpolymer and the initial and peak temperatures, leading to a formation of carbon fiber with better mechanical properties. However, this effect is observed only up to 3y acid comonomer concentrations. In case of 7y itaconic acid concentration the initial and peak temperatures were higher than it was measured for 3y IA concentration suggesting that less itaconic acid is incorporated into the terpolymer.

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