Thermal behaviour of binary and ternary copolymers containing acrylonitrile

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A B S T R A C T

Three types of acrylonitrile copolymers (acrylonitrile-styrene-butadiene copolymer (ABS[1]), acrylonitrile-styrene random copolymer (SAN[2]) and acrylonitrile-butadiene random copolymer (BAN[3]) were studied by thermogravimetry (TG/DTG[4]) and by pyrolysis in a semi-batch process at 450 °C in order to find structure–thermal behaviour relationships. The overlapped thermo-oxidative degradation processes were separated and the corresponding kinetic parameters were calculated. The TG/DTG studies have evidenced that the styrene-acrylonitrile interactions stabilize the nitrile groups reacting by chain scission rather than cyclization and destabilize the styrene units. Also, the cyclization of the acrylonitrile units in ABS is favoured by interactions with the styrene and butadiene units. The pyrolysis behaviour evidenced that the styrene-acrylonitrile interactions in SAN and ABS lead to the formation of 4-phenylbutyronitrile as the most important decomposition compound. ABS shows similar composition of the degradation oil with SAN copolymer therefore in the ABS the styrene-butadiene interactions are less important than those between styrene and acrylonitrile units.

1. Introduction

Acrylonitrile-containing copolymers are increasingly used in various fields (such as interior and exterior parts of automotives, office accessories, piping, car components, computer casings) and consequently are present in large amounts (about 3–5 wt%) in municipal plastic waste [1] [2].

Unlike other common polymers such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), the thermal degradation of the acrylonitrile-containing copolymers leads to the formation of ammonia or very toxic hydrogen cyanide in the gas fraction and nitrogen-containing compound in the oil fraction [3].

The most studied acrylonitrile-containing copolymer is acrylonitrile-butadiene-styrene (ABS). Navarro et al. successfully applied the distributed activation energy model (which assumes that the thermal decomposition of numerous components is described by a distribution of activation energies) to study the effects of dynamic experiments on the solid pyrolysis of ABS copolymer [4].

Oxidative degradation of commercial grade ABS resin powders was studied by differential scanning calorimetry (DSC). Threshold temperature of oxidation was found to be as low as 140 °C. Onset temperature of the auto-oxidation was determined to be around 193 °C. Reactive sites of ABS powders were verified to be the exothermic oxidation of unsaturated polybutadiene (PB) domains, not the poly(styrene-acrylonitrile) (SAN) matrix [5].

The morphology and composition of ABS copolymers have important implications on the degradation rate: ABS prepared by mass polymerization (polymerization of styrene-acrylonitrile mixtures in the presence of a rubber dissolved in this monomer phase) has higher degradation rate than the ABS copolymer prepared by emulsion polymerisation which was explained by the greater thermal stability of the of cross-linked "composite" networks formed during emulsion polymerization [6].

Thermal degradation of recycled SAN and ABS was comparatively studied at 300–400 °C under nitrogen atmosphere/flow. The degradation oil began to be generated over 300 °C. The oil conversion at 380 °C was 91.3 wt% yield for SAN and 70.9 wt% for ABS.

Dominant product of both degradation oils was styrene; aromatic contents obtained at 360 °C were 70 wt% for SAN and 79 wt% for ABS, decreasing with increased degradation temperature at 380 °C [7].

The degradation of ABS was also compared by thermal gravimetric analysis coupled with infrared spectrometry (TGA/FTIR) with that of polystyrene (PS), polybutadiene (PB), polyacrylonitrile (PAN), and styrene-acrylonitrile (SAN) copolymer. The grafting of butadiene to SAN stabilizes the butadiene structure, since the evolution of butadiene begins 50 °C above the homopolymer. Also the presence of the butadiene destabilizes SAN [8].

In addition to ABS there are studies concerning thermal behaviour of butadiene-acrylonitrile copolymer [9] or blends of butadiene-acrylonitrile copolymer with other polymers [10]. The major pyrolysis products are butadiene, acrylonitrile, benzene, 1,4-cycloheptadiene, 4-vinylcyclohexene, cyclopent-3-enecarbonitrile, benzonitrile, and cyclohex-3-enecarbonitrile. The butadiene, benzene, 1,4-cycloheptadiene, and 4-vinylcyclohexene are formed from the butadiene sequences. The acrylonitrile is formed from the acrylonitrile unit. The cyclopent-3-enecarbonitrile, benzonitrile, and cyclohex-3-enecarbonitrile are formed from the butadiene-acrylonitrile sequence [9].

In this work acrylonitrile containing copolymers were studied by thermogravimetric analysis and by pyrolysis in a laboratory scale installation using semi-batch process at 450 °C. The products were collected and analysed by different gas chromatographic methods. The main objective of this work was to study how the thermal behaviour and product distribution is affected by the degradation conditions and the composition of the copolymers and to determine the nature of the N-containing compounds in the degradation oil. Polystyrene (PS) and polyacrylonitrile (PAN) homopolymers were also analysed for comparative purposes.

2. Experimental

2.1. Materials

The studied copolymers were presented in Table 1.

2.2. Analysis methods

(A) The **IR spectra**. The FT-IR spectra of the copolymers were recorded with an FT-IR Nicolet Protégé 460 instrument, using KBr tablets with average concentration of 5 mg sample/500 mg KBr at a Resolution 2 cm^{-1}.

(B) The **NMR spectra** were obtained by cross-polarization magic angle spinning solid state NMR spectroscopy (^{13}C NMR: Varian Unity INOVA 300 MHz). The calibration of the NMR spectrometer was performed using tetramethylsilane and hexamethylbenzene as primary and secondary references respectively.

(C) The **thermo-oxidative behaviour** of the copolymers was studied with a Paulik Paulik Erdey type Derivatograph, MOM-Budapest, in air flow of 30 cm^3/min, heating rate of 12 °C/min, sample mass of 50 mg.

(D) **Thermal degradation** of styrene copolymers (about 8 g) was performed at 450 °C in a glass reactor by semi-batch operation; the experimental set-up is shown in Fig. 1. The reactor has an internal diameter of 30 mm and a total length of 350 mm. An amount of 8 g of polymer was degraded in each experiment, using the following temperature program: room temperature → 400 °C (heating rate 10 °C/min) → 450 °C (heating rate 1 °C/min; hold 160 min). The top 70 mm of the reactor protrudes out of the furnace so a part of the heavy decomposition products condensed and returned to the reactor for further decomposition. The volatile degradation compounds escaping the reactor were condensed in a condenser and collected in a graduated cylinder that allowed for the determination of the accumulation rate. Gaseous products were passed through a flask with water and collected in a Teflon bag. The reactor was flushed with nitrogen (N$_2$) at a flow rate of 20 mL/min starting 10 min before heating the furnace, in order to evacuate the air and possible adsorbed water. The N$_2$ flow was stopped when the temperature in the furnace reached 150 °C.

The gaseous products were analysed with a gas chromatograph provided with a thermal conductivity detector instrument (TCD: YANACO G180), column PORAPAK QS, 2.5 m, isothermal condition (100 °C).

The quantitative analysis of the degradation compounds in pyrolysis oils was performed with a gas chromatograph equipped with a flame ionised detector (FID: YANACO G6800), column packed with 100% methyl silicone, 50 m × 0.25 mm × 0.25 μm, temperature program: 40 °C (hold 15min) → 280 °C ($\beta = 5$ °C/min; hold 37 min).

The identification of the main compounds in the degradation oils was performed with a GC/MS − (mass selective detector) (MSD: HP 5973), column HP-1, crosslinked methyl siloxane, 25 m × 0.32 mm × 0.17 μm temperature program: 40 °C (hold 2 min) → 190 °C (heating rate 3 °C/min) → 300 °C (heating rate 10 °C/min).

The changes in the composition of the degradation oils were evidenced using C−NP-grams (C stands for carbon and NP from normal paraffin). These curves were obtained by plotting the weight percent of the products in the degradation oil versus the carbon number of the normal paraffin having equivalent boiling points [11].

3. Results and discussion

3.1. FT-IR results

The IR spectra of the studied copolymers (Fig. 2) contain many common absorption bands of the components. However, certain

Table 1
The studied copolymers.

	Observations	Average composition (from ^{13}C NMR results)		
		Acrylonitrile units (%)	Butadiene units (%)	Styrene units (%)
ABS (acrylonitrile-styrene-butadiene copolymer), Mw=172,000 Da	Aldrich Chemical Company	49	24	26
SAN (acrylonitrile-styrene random copolymer)	CAROM Onesti Romania	33	–	67
BAN (acrylonitrile-butadiene random copolymer	CAROM Onesti Romania	27	73	–
PS (polystyrene)	Asahi Chemical Industries	–	–	100
PAN (polyacrylonitrile)	Aldrich Chemical Company	100	–	–