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DEGRADATION BEHAVIOR AND KINETIC STUDY OF ABS POLYMER

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The degradation kinetics of the ABS terpolymer (acrylonitrile–butadiene–styrene) was investigated by means of thermogravimetric analysis. The samples were heated from 30 to 900°C in nitrogen atmosphere applying three different heating rates: 5, 10 and 20°C min^{-1}. The Vyazovkin model-free kinetic method was used to calculate the activation energy (E) of the degradation process as a function of conversion and temperature. Between 20 and 80% of conversion, E was calculated and the figures were : for ABS GP, E is 204.5±11.5 kJ mol^{-1} (medium value); for ABS HI, E is 239.0±9.8 kJ mol^{-1}; for ABS HH, E is 242.4±5.4 kJ mol^{-1}.

Keywords: *acrylonitrile–butadiene–styrene (ABS), model-free kinetics, thermal degradation, thermogravimetry*

Introduction

Acrylonitrile–butadiene–styrene (ABS) is an important engineering terpolymer. Due to its superior mechanical properties, chemical resistance, ease of processing and recycling ability is widely used in the industry. Those properties are directly related to the polar nature of the acrylonitrile component. Typically, ABS consists of a styrene/acrylonitrile continuous phase (SAN matrix) partially grafted to a dispersed butadiene phase, which acts as impact modifier, giving excellent mechanical properties to the polymer. ABS has various application, e.g. in architecture and construction, personal care products, toys, computer and business equipments, medical devices and in automotive interior components. ABS is also used with fiber-reinforcement to enhance the mechanical properties such as tensile strength, flexural modulus and hardness [1, 2]. Another reason to use ABS is its price that is between the lower priced commodity thermoplastics and the more expensive high performance engineering plastics [2].

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) are commonly used methods to investigate the thermal stability of polymers and composites [3]. With proper experimental procedures, information on the degradation kinetics of decomposition can be obtained. There are several reports on the thermal analysis (TG, DTA, FTIR, DSC) of ABS as well its individual components under various conditions (purging gases, heating rates, etc.) [3–15]. Degradation of ABS is a radical process where end-chain and random scission occurs. Based on different characterizing conditions the degradation of ABS took place either in one step or two steps with different kinetic parameters (degradation starting temperature, ending temperature, peak temperature, reaction order, pre-exponential factor and activation energy) by assuming different kinetic models [14].

M. Yang [3] reported that the activation energy for ABS is 175.8 kJ mol^{-1} (using Flynn–Wall approach, dynamic method, 5, 10, 20 and 40°C min^{-1} heating rates and N_2 atmosphere) by using Freeman and Carroll isothermal approach from 350 to 450°C in N_2 atmosphere, the activation energy is 134.0 kJ mol^{-1}. A similar value was found by S. Yang *et al.* [14], the activation energy was 134.4 kJ mol^{-1}, using also Freeman and Carroll approach, in an isothermal method at 370 to 560°C, while in another work [15] at 10% conversion, N_2 atmosphere and at 0.5, 1, 2, 5 and 10°C min^{-1} heating rates, an activation energy of 190.0 kJ mol^{-1} was reported by Day [15]. Under dynamic circumstances (nitrogen atmosphere and heating rates between 5–30°C min^{-1}) by assuming an autocatalytic model [16] the activation energy is varied between 140–160 kJ mol^{-1} as determinate by Balart [16].

Experimental

The degradation process of three different commercial ABS: GP, an ABS for general-purpose use; HI, an ABS high impact; and HH, an ABS high heat resistance was studied. The ABS samples were produced by addition of styrene and acrylonitrile to polybutadiene latex; the resultant is a material with polybutadiene grafted with acrylonitrile and styrene (a SAN matrix) that is essential to obtain the required properties of the desired polymer.

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The resulted substance in the form of pellets was dried in an oven at 105°C for 4 h to remove humidity; for all analysis small pieces were cut from the dried pellets.

The amounts of each component in the ABS terpolymers were determined by FTIR analysis, using a Nicolet Protege System 460 spectrometer, with DTGS (Deutered Triglycene Sulfate) detector using OMNIC ESP-5.1 software. The calibration was made from a pattern of a polystyrene film. The experiments have been done in the 4000–450 cm^{-1} range with 4 cm^{-1} resolution. Four ABS terpolymer samples were used as a pattern to determine the master curves for the acrylonitrile, butadiene and styrene contents. For acrylonitrile the absorption band at 2237 cm^{-1}, for the butadiene content the absorption at 969 cm^{-1} and for styrene the absorption band at 1493 cm^{-1} were used. 300±0.5 mg of each sample was dissolved in 10 mL of methylene dichloride to prepare a solution. The transmission spectra of the solutions were obtained using 0.5 mm wide liquid cell. In each spectrum the height of the selected peak was defined according to the Lambert–Beer law.

DSC experiments have been performed to determine the transition temperature of the samples using a TA 2910 DSC equipment by TA Instruments in N_2 atmosphere. The first heating run (scan 1) was done from ambient temperature to 300°C at a heating rate of 20°C min^{-1} followed by cooling from 300 to 25°C and then the second heating (rescan) from 25 to 300°C at a heating rate of 20°C min^{-1}.

The thermal degradation of ABS was measured by a Mettler-STGA 851 thermobalance in the 30–900°C temperature range under N_2 atmosphere (flow rate: 25 mL min^{-1}), using alumina crucible of 70 μL and heating rates of 5, 10 and 20°C min^{-1}. In each experiment ca. 20 mg initial sample masses were used. The Vyazovkin model free kinetics method was applied to determine the activation energy, conversion and isoconversion.

The model free kinetics method is based on an isoconversional computational technique that calculates the effective activation energy (E) as a function of the conversion (α) of a chemical reaction, so far $E=f(\alpha)$. A chemical reaction is measured at least in three different heating rates (β) and the respective conversion curves are calculated out of the TG measured curves. For each conversion (α), $\ln\beta/T^2$ is plotted *vs.* $1/T_\alpha$, giving rise to a straight line with slope $-E_\alpha/R$, therefore providing the activation energy as a function of conversion [17–22].

Results and discussion

The contents of the components of the ABS terpolymers obtained by FTIR experiments are summarized in Table 1.

Figures 1–3 show the DSC curves of ABS GP, HI and HH, respectively. The T_g (glass transition temperature) in the onset point is: ABS GP=105.4, ABS HI=105.2 and ABS HH=125.6°C, respectively. It has to be noted that the T_g of ABS HH is the highest which is in accordance with the content of each component in the samples: e.g. the higher amount of acrylonitrile implies higher thermal resistance, consequently higher is the T_g. The T_g of the ABS GP and ABS HI are practically identical.

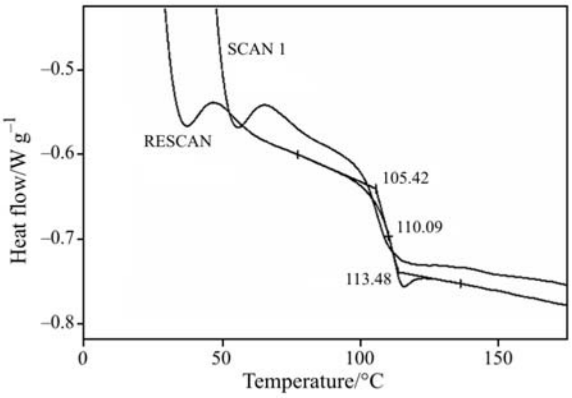

Fig. 1 DSC curve of ABS GP (onset T_g=105.4°C)

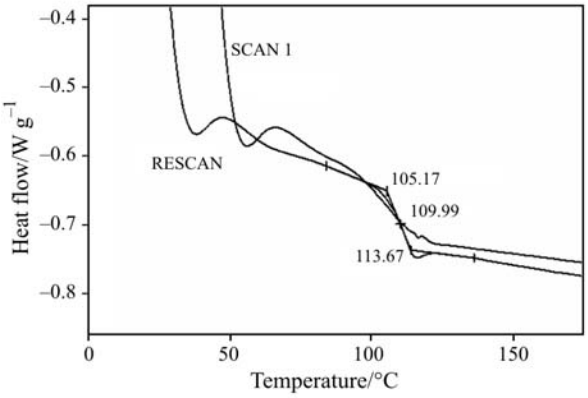

Fig. 2 DSC curve of ABS HI (onset T_g=105.2°C)

Table 1 Contents and the FTIR data of the components of the ABS terpolymers

Sample	Acryl. abs. 2237 cm^{-1}	But. abs. 969 cm^{-1}	Sty. abs. 1493 cm^{-1}	Acryl./%	But./%	Sty./%
ABS GP	0.220	0.224	0.599	22.1	16.9	60.9
ABS HI	0.184	0.291	0.534	25.4	22.2	52.4
ABS HH	0.291	0.143	0.439	49.6	10.6	39.9

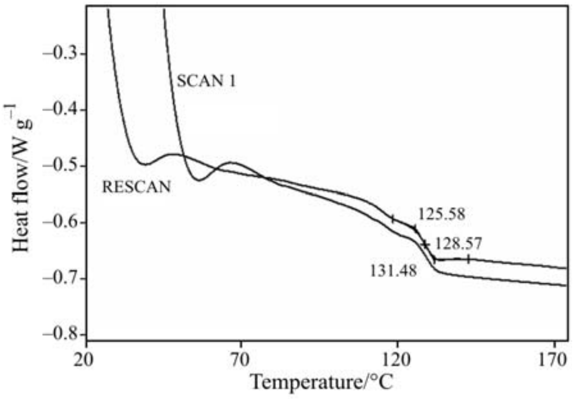

Fig. 3 DSC curve of ABS HH (onset T_g=125.6°C)

The TG and DTG curves of the three ABS at different heating rates are shown in Figs 4–6, respectively. The plots indicate that all ABS samples exhibit a one-step thermal decomposition. According to the DTG curves, there is a pronounced mass loss in the 325–475°C temperature range. Above 700°C, the residue is less than 1% for all samples. The corresponding temperatures at 5% of conversion degree for all samples were ABS GP – 370°C; ABS HI – 385°C and ABS HH – 390°C (all values were obtained from the curve applying 20°C min^{-1} heating rate). According to Jang [23] the temperature for 5% of conversion for normal ABS is 410°C (at 20°C min^{-1}) in N_2 atmosphere and above 600°C the residue was 1%.

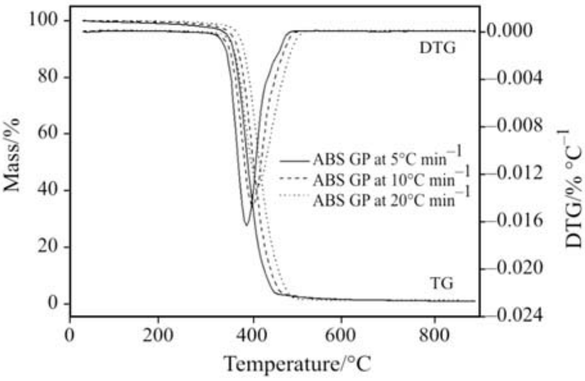

Fig. 4 TG and DTG curves of ABS GP at different heating rates

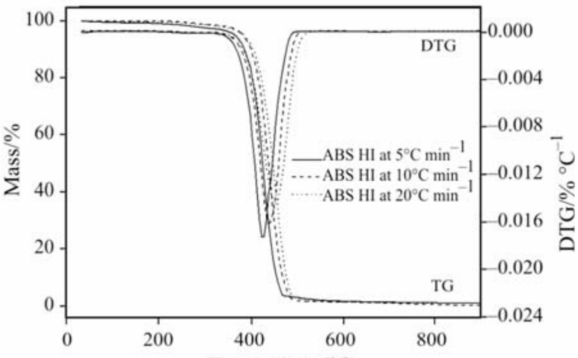

Fig. 5 TG and DTG curves of ABS HI at different heating rates

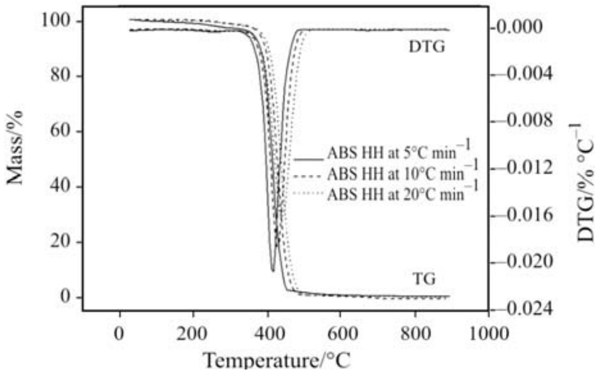

Fig. 6 TG and DTG curves of ABS HH at different heating rates

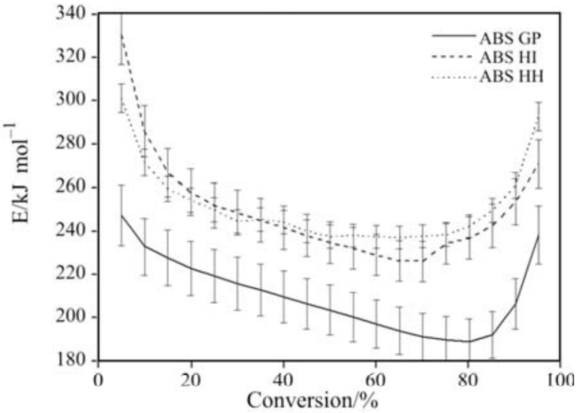

Fig. 7 Activation energy (E) of ABS using the model-free kinetics

The activation energy (E) for the thermal degradation process of ABS, predicted by the model free kinetics theory is shown in Fig. 7. At 10% of conversion the corresponding activation energies for ABS GP, ABS HI and ABS HH are 233.2, 286.0 and 271.6 kJ mol^{-1}, respectively. Between 20 and 80% of conversion the activation energies E are: for ABS GP, E is 204.5±11.5 kJ mol^{-1} (medium value); for ABS HI, E is 239.0±9.8 kJ mol^{-1} and for ABS HH, E is 242.4±5.4 kJ mol^{-1}.

It must be noted on the graph of Fig. 7, that the activation energy for ABS HI at 10% of conversion is 6% higher than that for ABS HH. This may due to the fact that SAN is directly bonded to butadiene units, so the liberation of butadiene should be more difficult; also, as it can be seen in the FTIR analysis, the butadiene content in this sample is higher than the others. After 30% of conversion the E for ABS HH is higher than ABS HI, which becomes evident when the medium values at 80% of conversion are compared. This is in agreement with the fact that the ABS HH has more acrylonitrile content, as it was de-

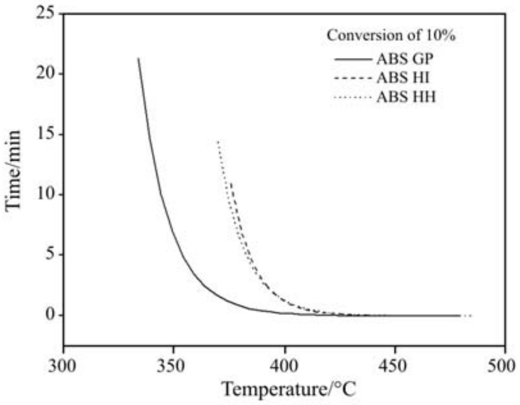

Fig. 8 Time *vs*. temperature plot at 10% conversion (isoconversion process)

termined by the FTIR analysis, implying in more thermal resistance.

The temperature of the degradation process for all ABS predicted by model free data providing an estimation of the time required to the degradation reaction (the isoconversion process). Figure 8 exhibits the time *vs*. temperature plot at 10% conversion for all ABS. It can be observed that for e.g. at 5 min the ABS GP must be kept at 355°C to achieve this conversion; while ABS HI has to kept at 385°C and ABS HH has to be treated at 383°C.

Conclusions

The model free kinetics method applied in this research showed higher activation energy values compared to the values reported in the literature. One reason for that could be the fact that ABS terpolymer is produced worldwide by a great number of producers and from a great variety of process, procedures and different supply of raw materials. From the FTIR experiments it can be seen that the composition of the co-monomers in ABS formulation may vary remarkable in the commercial samples. Values of the activation energy show that ABS HH is a little more thermally resistant than ABS HI and much more than ABS GP due to its highest acrylonitrile content. Despite of the low acrylonitrile content but high butadiene content, ABS HI also exhibits high activation energy, which is comparable to the ABS HH. This is probably due to the fact that the SAN matrix is directly bonded to butadiene units that make difficult the liberation of butadiene during the degradation reaction.

Acknowledgements

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