

ON THE THERMAL DECOMPOSITION OF ACRYLIC COPOLYMER/ NITRIC ACID LIQUORS

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(Received July 20, 1982; accepted October 5, 1982)

Summary

The hazards of the ASAHI process for the wet-spinning of an acrylic copolymer (90% by weight polyacrylonitrile and 10% by weight methylacrylate) by water precipitation from a nitric acid liquor have been experimentally evaluated.

The experimental program has been performed using a Sikarex-3 adiabatic calorimeter, for initial temperatures up to 50°C and acrylic copolymer concentrations from 5% to 20% by weight.

The experiments have shown that, at the highest PAN concentrations, self-heating of the liquors occurs even when starting from ambient temperature, producing about 30 mol of uncondensable gases (N₂, CO₂, N₂O and CO) per kilogram of polymer, accompanied by boiling of the nitric acid–water solution. Therefore, dangerous overheating and overpressure may occur, along with the emission of toxic gases, mainly in the storage tanks and in the piping.

A two step reaction mechanism has been tentatively proposed. During the first step, reactive intermediates are formed through a slightly exothermic reaction, without production of gaseous compounds. The second step is characterized mainly by the strongly exothermic decomposition of this intermediate, that generates the gaseous products.

Introduction

In many chemical processes the hazards associated with the thermal behaviour of reactive chemicals and mixtures require accurate stability evaluations. Knowledge of the behaviour of these processes under different operating conditions is necessary during the process development, not only to design the various equipment but also to establish safe operating conditions and control procedures. Both steady and transient plant behaviour can be effectively simulated by computer via mathematical modelling. In this approach to the problem of thermal instabilities, the rate of heat release and other thermokinetic properties of the chemicals involved appear as the main parameters to be considered.

The overall thermokinetic parameters can be rapidly evaluated by adiabatic calorimetry [1]. In particular, this technique is very useful for studying

weakly exothermic reactions, especially if the induction times are very long. In some of these cases, with the more usual techniques, such as differential scanning calorimetry (DSC), the exothermic reactions will be not detected at all, even if they can generate dangerous over-heating and over-pressure in the equipment.

This is the case in the ASAHI process [2] for the wet spinning of acrylic copolymer/nitric acid liquors by water precipitation. In this process the operating temperature is critical both for fiber quality and for plant safety, so that a value lower than 0°C is recommended. Accordingly, fortuitous liquor overheating, for example due to the failure of the cooling unit, may give rise to loss of product quality and sometimes to dangerous emissions of nitric vapours. To achieve a better understanding of these phenomena, the liquor was analyzed using a DSC calorimeter, but no exothermic reaction was detected.

In this paper some preliminary results concerning the thermal stability of the acrylic copolymer/nitric acid liquor obtained using an adiabatic calorimeter are reported. This method makes it possible to detect hazardous thermal reactions when the temperature is increased, even if these reactions are only weakly exothermic. The long induction times observed appear to be determined by the development of a two-step process, whose nature is discussed here.

Experimental apparatus and procedure

All experimental data reported here were obtained by a Sikarex III calorimeter [1] used in the adiabatic mode.

The samples (about 25 g) were prepared by dissolving at room temperature the acrylic copolymer (PAN, about 90% by weight polyacrylonitrile, 10% by weight methylacrylate) in azeotropic nitric acid–water solutions.

The Sikarex standard glass reactor was modified to allow the measurement of the flow rate of the evolved gases, using a bubble flowmeter mounted on the exit line. An on-line gaschromatograph (HP 5830A), placed downstream of a water-cooled trap, was used to analyze the uncondensable gases. The analyses were performed on a PORAPAK S column, 4 m long and 2 mm I.D., with carrier gas (helium) flow rate of 20 cm³ min⁻¹, and temperature programming from -50°C to 170°C.

The experimental adiabatic tests were performed at initial temperatures ranging from 15°C to 50°C and at PAN concentrations in the liquor ranging from 5% to 20% by weight. Most of the experimental runs were started just after the dissolution of copolymer in the nitric acid solution, but the effect of aging of the samples was also determined.

Experimental results and discussion

Figure 1 shows a typical temperature–time recording, together with the relative flow rate of the evolved gases (broken line). The plotted data refer

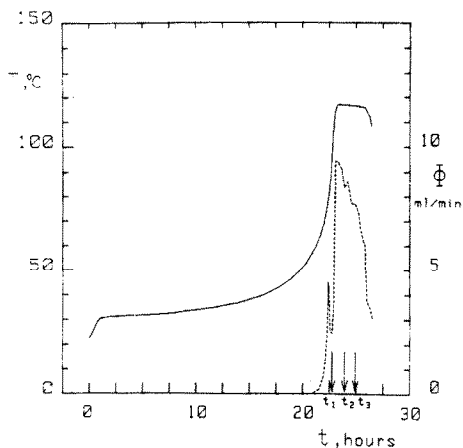


Fig. 1. Sample temperature T (continuous line) and gas flow rate Φ (broken line) as a function of time t for an 11% by weight PAN liquor and $T_0 = 30^\circ\text{C}$.

to an 11% by weight PAN liquor, at the initial temperature $T_0 = 30^\circ\text{C}$. Four different stages can be identified. In the first stage, a slight increase in temperature is observed, while no gas is evolved. Subsequently both temperature and gas flow rate increase sharply. The third stage is characterized by a maximum of the gas flow rate while the sample temperature remains nearly constant for about 150 minutes at approximately 120°C , that is, very close to the boiling point of the nitric acid—water azeotrope. In this period, noticeable amounts of an acidic liquid phase were collected in the water-cooled trap. Finally in the last stage, both temperature and gas flow rate decrease, suggesting that an endothermic process is taking place.

The composition of the uncondensable gases, measured at three different times (marked as t_1 , t_2 and t_3 in Fig. 1) is reported in Table 1. In all cases, nitrogen and carbon dioxide are by far the most important gaseous products,

TABLE 1

Composition of the evolved gases for an 11% by weight PAN liquor and $T_0 = 30^\circ\text{C}$

	Composition (% vol.) at time		
	t_1	t_2	t_3
N_2	80.0	58.9	57.7
O_2	0.5	0.3	0.7
CO_2	12.4	36.1	37.0
CO	1.1	2.1	2.1
N_2O	2.1	1.2	1.2
H_2O	3.1	1.4	1.3

whereas only small amounts of nitrous oxide and carbon monoxide were detected.

From t_1 to t_2 , the nitrogen percentage decreases from 81% to 59%, while the carbon dioxide percentage increases from 12% to 36%; correspondingly, the carbon monoxide percentage increases and the nitrous oxide percentage decreases. The composition measured at time t_3 is almost identical to that measured at time t_2 . From these data, it appears that on the whole about 1 mol nitrogen and 0.6 mol carbon dioxide were produced per mol acrylonitrile monomer initially present in the sample.

Figure 2 shows the effect of the initial temperature T_0 at constant PAN concentration (11% by weight). The measured temperature—time recordings are very similar, even if the exothermic process appears to proceed faster as the initial temperature is increased. Also the measured flow rates and compositions of the evolved gases are similar to those reported in Fig. 1 and Table 1 for $T_0 = 30^\circ\text{C}$. For initial temperatures lower than 30°C , induction times longer than 100 hours were observed.

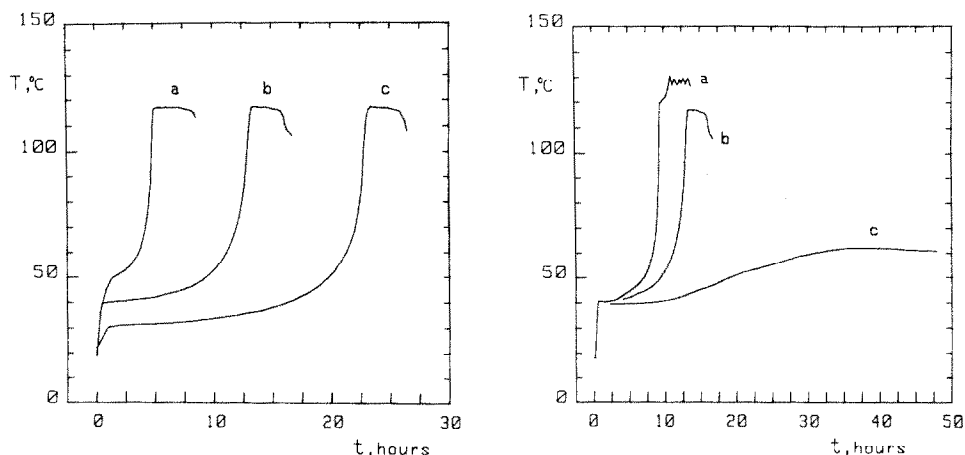


Fig. 2. Sample temperature T as a function of time t for an 11% by weight PAN liquor and different initial temperatures: (a) $T_0 = 50^\circ\text{C}$; (b) $T_0 = 40^\circ\text{C}$; (c) $T_0 = 30^\circ\text{C}$.

Fig. 3. Sample temperature T as a function of time t for $T_0 = 40^\circ\text{C}$ and different PAN concentrations: (a) 20% by weight; (b) 11% by weight; (c) 5% by weight.

The PAN percentage in the liquor has a more dominant effect on the temperature—time patterns, as compared to the effect of the initial temperature. In Fig. 3 the temperature—time recordings for three different PAN concentrations and for the same initial temperature ($T_0 = 40^\circ\text{C}$), are reported. At the lowest PAN concentration (5% by weight, curve c), only a very small temperature increase was recorded without any gas evolution. This corresponds to the first stage of the recording of the run performed

at 11% by weight PAN concentration (curve b). In this case, the final stage of temperature decrease is also evident. At the highest PAN concentration (20% by weight, curve a), the shape of the temperature—time curve is very different, as far as the last two stages are concerned. Indeed, the duration of the nearly isothermal stage is very short (only a few minutes); then, self-heating starts again and is stopped only by the calorimeter controller, when the temperature reaches the preset allowable maximum of 130°C.

Figure 4 shows the effect of aging the liquor before the calorimetric test.

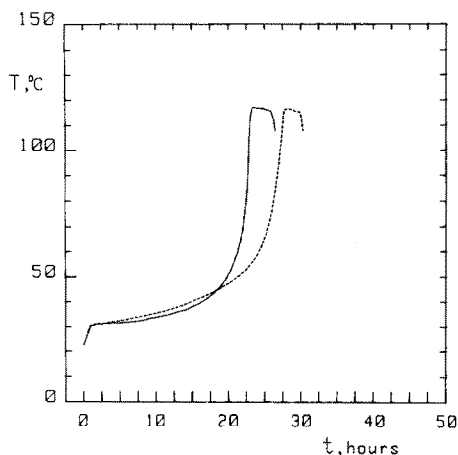


Fig. 4. Sample temperature T as a function of time t for an 11% by weight liquor and $T_0 = 30^\circ\text{C}$. Continuous line: standard sample; broken line: sample aged for about 100 hours at room temperature.

The data reported there refer to a sample aged for about 100 hours at room temperature (broken line). The initial reaction rate is slightly higher for the aged sample but, later, the temperature of the non-aged sample increases more rapidly, so that the two curves intersect each other. The overall result is that the aged sample is noticeably less reactive than the non-aged one.

As a whole, the experimental results indicate a two-step exothermic process: the first (slightly exothermic) reaction produces reactive intermediates which in the second step decompose exothermically with production of gases. This reaction scheme can explain the first two stages observed in the temperature—time recordings.

The last two stages experimentally observed can be explained by also taking into account the endothermic boiling of the nitric acid—water solution. For the intermediate PAN concentration, this boiling occurs at the same time as the exothermic reaction, so that an isothermal behaviour is observed. The decrease of temperature observed in the subsequent stage could indicate that the exothermic reaction has ended, while some vaporization still occurs. On the contrary, for the highest PAN concentration,

in the last stage the exothermic reaction is still taking place after the boiling has ended.

It appears that the amount of reactive intermediates formed in the first step depends only on the PAN concentration and that their decomposition does not involve the nitric acid. In fact, not only was a very small temperature increase detected at the lowest PAN concentration, but also, at the highest PAN concentration, the exothermic decomposition of the intermediates continued after the isothermal boiling.

The duration of this stage decreases on increasing the PAN concentration because the heat release rate of the exothermic decomposition increases, and because smaller amounts of nitric acid are available. The enhanced reactivity at the highest PAN concentration is also confirmed by the higher concentration of carbon dioxide in the evolved gases.

On the basis of these results, the chemical nature of both steps of the decomposition process of the liquor can be tentatively suggested.

It has been reported that the nitration of the C—H bond of nitrile compounds fails to be effective under acidic conditions [3]. Therefore, the observed reactivity of the liquor in the first step should be attributed to the nitrile groups, which are hydrolyzed in these conditions.

On the other hand, it is known that nitric acid gives electrophilic reactions, as shown by its behaviour in aromatic nitration [4]. Therefore, an electrophilic attack of NO_2^+ on the nitrile groups of the polymeric chain, through their non-bonding electron pair, is also possible.

The second step of the proposed mechanism should be an highly exothermic decomposition of the intermediates, mainly to nitrogen, carbon dioxide and water.

The results of a simplified mathematical analysis of the experimental data agree with the above discussed two-step reaction mechanism. According to Townsend and Tou [5], if a single reaction occurs, the following relationship holds:

$$\ln \left[\frac{\Delta T_F^{n-1} dT}{(T_F - T)^n dt} \right] = \ln(K_0 Y_{RO}^{n-1}) - E/(RT) \quad (1)$$

In this equation T is the instantaneous temperature, T_F the maximum temperature, $\Delta T_F = T_F - T_0$ the adiabatic temperature rise, n the reaction order, t the time, K_0 the pre-exponential kinetic factor, E the overall activation energy, R the gas constant and Y_{RO} the initial polymer concentration. Thus, a plot of $\ln(z) = \ln[(\Delta T_F^{n-1} dT)/(T_F - T)^n dt]$ versus $1/T$ must be a straight line for a single reaction.

In Figs. 5–7 the values of $\ln(z)$ are reported as a function of $1/T$ for the test performed at 11% by weight PAN concentration and at an initial temperature of 30°C. The three plots are relative to three different assumed reaction orders (respectively $n = 0, 1$ and 2). For all three reaction orders the slope

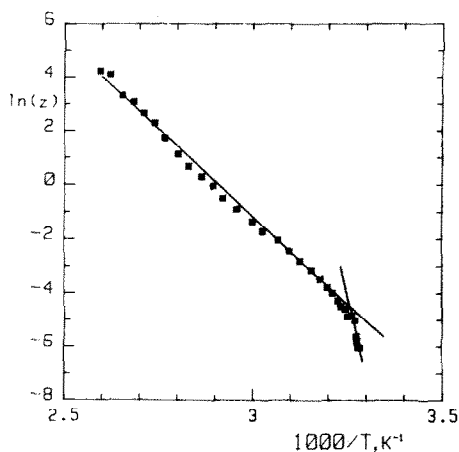
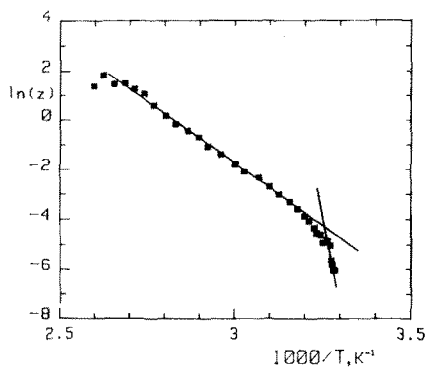
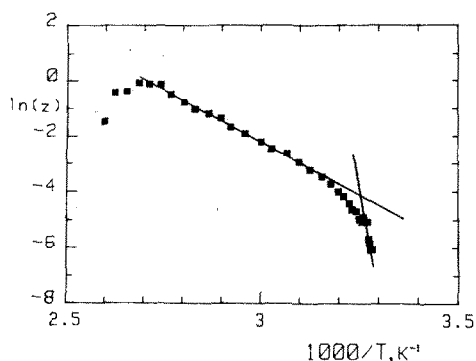


Fig. 5. $\ln(z)$ as a function of $1000/T$, assuming a zero order reaction for an 11% by weight PAN liquor at $T_0 = 30^\circ\text{C}$.

Fig. 6. $\ln(z)$ as a function of $1000/T$, assuming a first order reaction for an 11% by weight PAN liquor at $T_0 = 30^\circ\text{C}$.

Fig. 7. $\ln(z)$ as a function of $1000/T$, assuming a second order reaction for an 11% by weight PAN liquor at $T_0 = 30^\circ\text{C}$.

of the straight line drawn through the experimental data changes sharply at a temperature of about 34°C . This is the temperature, reached after a rather long reaction period (about 10 hours), where the first bubbling was observed. The correspondence with the proposed two-step reaction mechanism appears to be significant. The lower values of $\ln(z)$ computed for the highest temperatures can be attributed to the incipient boiling of the nitric acid.

An exhaustive kinetic analysis cannot be performed at the moment, nor a definitive mechanism proposed, because of the proven complexity of the reaction path. However, the present data may be used for a first estimate of

the hazards related to the process. Since a continuous self-heating rather than a sharp "ignition" was observed, the data are conveniently presented as delay times Δt necessary to reach a fixed increase of temperature ΔT . The values of Δt for $\Delta T = 10, 20$ and 50°C are plotted in Fig. 8 as a function of the initial temperature T_0 , for constant PAN concentration (11% by weight), and in Fig. 9 as a function of the PAN concentration for constant initial temperature ($T_0 = 40^\circ\text{C}$). An almost linear relationship holds between Δt and T_0 (Fig. 8) whereas Δt is a highly non-linear function of the PAN concentration (Fig. 9).

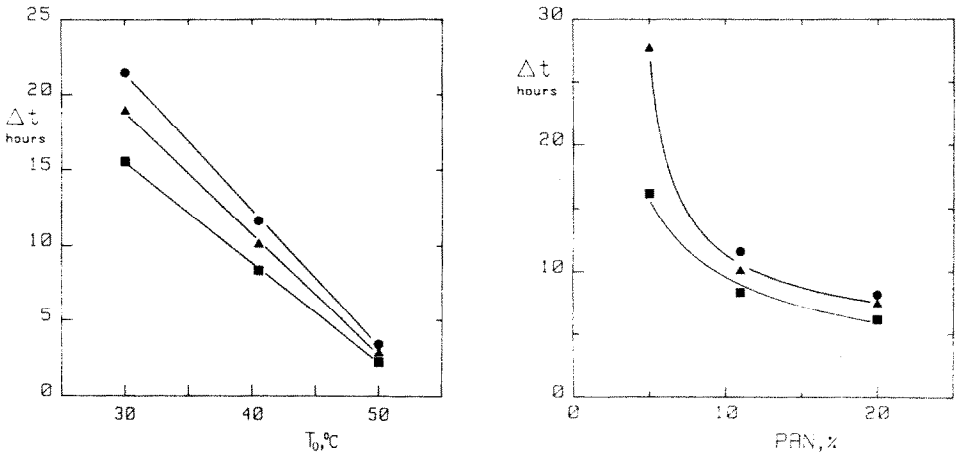


Fig. 8. Delay times Δt necessary to reach fixed increases of temperature, ΔT , as a function of the initial temperature T_0 , for an 11% by weight PAN liquor; \blacksquare : $\Delta T = 10^\circ\text{C}$; \blacktriangle : $\Delta T = 20^\circ\text{C}$; \bullet : $\Delta T = 50^\circ\text{C}$.

Fig. 9. Delay times Δt necessary to reach fixed increases of temperature, ΔT , as a function of PAN concentration for $T_0 = 40^\circ\text{C}$; \blacksquare : $\Delta T = 10^\circ\text{C}$; \blacktriangle : $\Delta T = 20^\circ\text{C}$; \bullet : $\Delta T = 50^\circ\text{C}$.

Conclusions

The thermal instability of polyacrylonitrile/nitric acid liquors was proved to be due to a two-step process. The first reaction, which is only slightly exothermic and does not produce gaseous products, involves an interaction between the polymer and nitric acid. The second step, which is highly exothermic and produces gaseous products, appears to be due to the decomposition of the reactive intermediates, which is probably not affected by the presence of nitric acid.

The delay times necessary to reach a prefixed increase of temperature were measured as a function both of the PAN concentration and of the initial temperature, and may be used in the safety analysis for the ASAHI wet-spinning process. Moreover, in evaluating the hazards related to this process, the production of gaseous products must be taken into account. Indeed, not

only relatively slow but noticeable increase of pressure may occur, but also the emission of dangerous nitric vapours.

New experimental runs and the analysis of the composition of both the condensable products and of the residual liquor at different reaction stages are necessary to achieve a better understanding of the reaction mechanism and to support a kinetic analysis of the experimental data to determine the kinetic parameters.

Acknowledgments

This work was carried out with the contribution of Progetto Finalizzato "Chimica Fine e Secondaria" by Consiglio Nazionale delle Ricerche.

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