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Recycling of vinylidene chloride copolymer coated polypropylene film: a study of the thermal degradation of VDC copolymer

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Abstract

Thermogravimetric analysis has been used to study the dehydrochlorination of VDC copolymer. Dynamic and isothermal methods have been compared and the problem of active mass considered. Results indicate that whilst useful information can be rapidly obtained from a single dynamic analysis, consistency and accuracy are often compromised compared to isothermal studies.

Keywords: Dehydrochlorination; Chlorinated polymer; TG; Kinetic analysis

1. Introduction

Thermoplastics are among the easiest materials to recycle. On economic grounds, the industry has always reground and reused the plastics waste generated during manufacture and processing. At present, however, only a relatively low proportion of plastic post-consumer waste is recycled and this is almost entirely due to problems related to the collection and sorting of mixed waste. An additional complication occurs with products consisting of two or more plastic materials, e.g. multi-layer films and coated films.

Polyvinylidene chloride (PVDC) is a chlorine-containing polymer and at temperatures above 150°C will undergo thermal degradation. The main volatile product of this process is hydrogen chloride gas which is not only strongly acidic but highly corrosive to numerous types of metals used in processing equipment.

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The thermal degradation of PVDC is a typical chain process with distinct initiation, propagation and termination phases [1]. It has been demonstrated [2] that the initiation of the process is strongly facilitated by the presence of unsaturation in the polymer's backbone. Such unsaturation may be introduced into the polymer via its interaction with a variety of agents which might commonly be encountered during the polymerisation process or its processing.

Because of its thermal instability and associated processing problems many applications for PVDC as a barrier material cannot be exploited. As a consequence vinylidene chloride copolymers have been developed and have assumed a position of prominence in the packaging industry [3]. The comonomer acts as a "stopper" unit to the dehydrochlorination reaction [4]. The copolymers are also easier to process because the comonomer unit has the effect of reducing crystallinity and crystalline melting point. Comonomers commonly used are acrlyonitrile, acrylates or methacrylates.

In the study reported in this paper a vinylidene chloride/methyl acrylate copolymer (VDC/MA) has been subjected to both isothermal and dynamic thermogravimetry (TG) at elevated temperatures. The mechanisms and kinetics of the dehydrochlorination process have been investigated.

This work forms part of a much larger programme to develop a process for the controlled thermal degradation of VDC/MA [5] to facilitate recycling of a polypropylene film carrying this material as a coating. The process developed involves the use of additives which both catalyse the dehydrochlorination process and neutralise the hydrogen chloride liberated and afford a product which is effectively a filled PP. This work will be reported later.

2. Supporting theory

2.1. Dynamic thermogravimetry

The rate of reaction (i.e. the rate at which mass is lost) can be summarised by the general rate expression

$$-\mathrm{d}W/\mathrm{d}t = f(\text{mass}) \times f(\text{temperature})$$

where

$$f(\text{mass}) = W^n \qquad \text{and} \qquad f(\text{ temperature }) = (A/\beta)\,\mathrm{e}^{-E/RT}$$

W is the active material (mg), n is the order of the reaction, E is the activation energy (kJ mol^{-1}), R is the gas constant, T is the temperature in K, β is the rate of heating and A is the pre-exponential factor.

Alternatively, the general rate expression may be written as

$$R_t = -\mathrm{d}W/\mathrm{d}t = (A/\beta)\,\mathrm{e}^{-E/RT}W^n \qquad (1)$$

Manipulation of this equation for studies at two temperatures, β remaining constant, gives the following expression, commonly known as the Freeman and Carroll equation [6]:

$$\Delta \log R_t = n\Delta \log W - \left(\frac{E}{2.303R}\right)\Delta\left(\frac{1}{T}\right) \qquad (2)$$

Thus, a plot of Δ log R_t against Δ log W should be linear when $\Delta(1/T)$ is held constant. The slope of the resulting plot will give a value for n, whilst E can be calculated from the value of the intercept.

2.2. *Isothermal thermogravimetry*

Assuming a first order reaction, rate constants can be determined at various temperatures from the slopes of plots of $\ln[(W_\infty - W_0)/W_\infty - W_t)]$ versus time.

W_∞ is the mass of the sample at infinite time (t_∞) and is taken as that mass which would remain after the loss of 1 mole of hydrogen chloride per mole of vinylidene chloride unit in the copolymer. At temperatures used in isothermal studies [7] the second mole of HCl associated with each VDC unit was not released. W_0 is the mass at time zero (t_0), i.e. the time at which the first data point was recorded. W_t is the mass at time t during the run. By applying the Arrhenius equation and plotting ln(rate constant) versus $1/T$, the activation energy for the process can be calculated from the slope of the plot.

3. Experimental

Solvay PVDC WA50 (VDC/MA copolymer) emulsion was dried at 40°C under vacuum and the resulting product powdered using a high speed mixer. The coarse powder was sieved and particles below 124 mm diameter separated and used in all investigations. Thermogravimetry was performed using a TA Instruments Hi-Res TGA 2950. Nitrogen was used as a carrier gas at a flow rate of 60 ml min^{-1}.

In dynamic analyses, the copolymer powder was heated to 700°C at 20, 10, and 5 K min^{-1}. For isothermal analyses, samples were heated for 60 min at set temperatures in the range 190–220°C. Sample size varied from 15 to 35 mg.

4. Results

4.1. *Dynamic TG*

A typical trace for PVDC WA50, heated at 10°K min^{-1}, is shown in Fig. 1. In the case of PVDC WA50, VDC/MA copolymer, the mass loss recorded over the temperature range used has been assumed to be due solely to dehydrochlorination. Accordingly, as mass loss occurred, the sample mass remaining could not be considered the active material for further dehydrochlorination. Polyene sequences present in chains were assumed

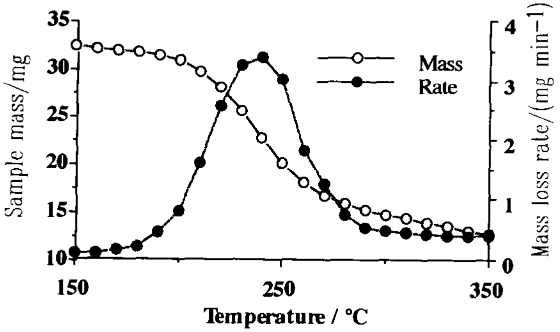

Fig. 1. PVDC WA50 heated at 10°K min^{-1}.

to take no further part in the dehydrochlorination reaction and the mass of active material was calculated from the expression

$$W = W_0 - W_T$$

where W is the mass of active material (i.e. mass of available HCl in sample), W_0 is the mass of hydrogen chloride present in the original VDC/MA copolymer, W_T is the mass loss, at temperature T, due to dehydrochlorination.

On this basis, the plots shown in Fig. 1 can be converted into those shown in Fig. 2. From Fig. 2 values for the rate of reaction and mass of active material were taken at reciprocal temperature intervals of 2×10^{-5} K^{-1} and substituted into Eq. (2) to produce the data presented in Fig. 3.

From Fig. 3, the activation energy for the dehydrochlorination process was calculated to be 136 kJ mol^{-1}. Activation energies for dehydrochlorination at heating rates of 20°K min^{-1}, 10°K min^{-1} and 5°K min^{-1} are presented in Table 1.

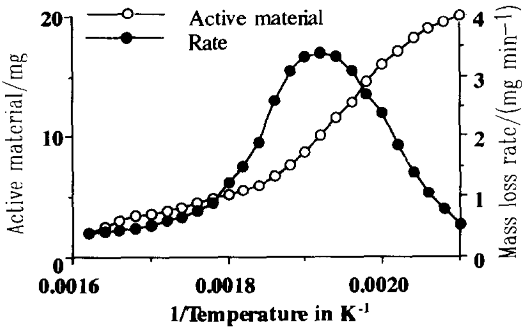

Fig. 2. Plots of mass of active material and rate of reaction against reciprocal temperature for PVDC WA50 heated at 10°K min^{-1}.

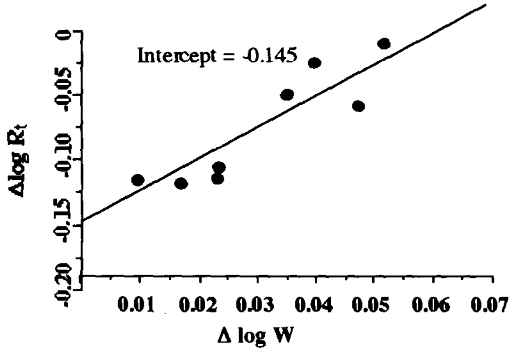

Fig. 3. Plot of Δ log W against Δ log R_t for PVDC WA50 heated at 10°K min^{-1} ($1/T = 2.0 \times 10^{-5}$ K^{-1}).

4.2. Isothermal thermogravimetry

Fig. 4 shows a typical isothermal mass versus time plot for PVDC WA50 heated at 190°C. By obtaining equivalent curves at a series of temperatures, namely 190°C, 200°C, 210°C and 220°C, plots of $[(W_\infty - W_0)/(W_\infty - W_t)]$ versus time can be obtained and are shown in Fig. 5.

Rate constants calculated from the slope of these lines are presented in Table 2, data from which was used to produce the Arrhenius plot shown in Fig. 6. From the slope of Fig. 6 an activation energy for the dehydrochlorination process of 118 kJ mol^{-1} was calculated.

5. Discussion

In the analysis of TG data the definition of active mass is critical. For example, when studying the degradation kinetics of polysytrene and polyethylene, Freeman assumed that both of these polymers degrade in such a manner that all the sample remaining, at a temperature T, could be considered to be active. For the dehydrochlorination of the VDC/MA copolymer studied in this paper, active mass has been assumed to be the hy-

Table 1

Activation energies calculated for the dehydrochlorination of PVDC WA50 using the Freeman and Carroll method

Heating rate/(K min^{-1})	Activation energy/(kJ mol^{-1})
20.0	115
10.0	136
5.0	122

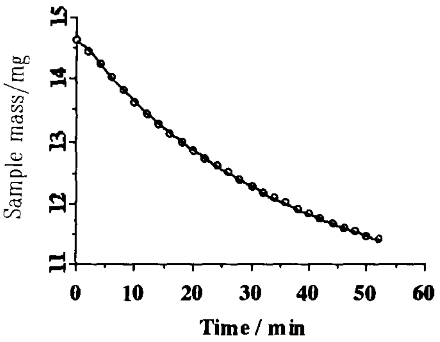

Fig. 4. Plot for PVDC WA50 heated isothermally at 190°C.

drogen chloride content of the polymer at a particular time and that any material mass loss was solely due to dehydrochlorination.

For complete dehydrochlorination to be achieved two molecules of hydrogen chloride per VDC repeat unit must be lost and in dynamic TG studies this usually means that a temperature of 700°C must be reached. However, other reactions are known to be involved in complete dehydrochlorination of PVDC, for example Diels-Alder condensation and aromatisation reactions. Additionally, where methyl acrylate units are present as comonomer they will also start to decompose at temperatures in excess of 300°C releasing carbon dioxide and methanol [8]. Degradation kinetics then can become very complicated and the use of the Freeman and Carroll equation to analyse such a situation becomes questionable.

In the work reported in this paper, the Freeman and Carroll equation has only be used to assess the dehydrochlorination of VDC/MA copolymer in the 20–60% decomposition range as both the initial and final stages of the degradation reaction were considered to be complicated by variations in the initial structures of polymer chains and, in the latter stages of the process, by the complexity of the degradation reactions and products.

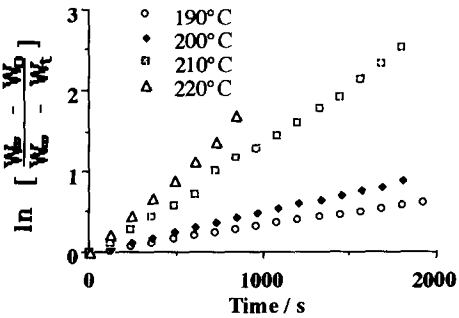

Fig. 5. Plots of $\ln[(W_\infty - W_0(/(W_\infty - W_t)]$ versus time for PVDC WA50 heated at 190°C, 200°C, 210°C and 220°C.

Table 2
Kinetic data calculated for PVDC WA50 heated isothermally at 190°C, 200°C, 210°C and 220°C

Temperature/°C	10^3/Temperature K^{-1}	10^4 × Rate constant (s^{-1})	ln[Rate constant/(s^{-1})]
190	2.16	3.20	–8.05
200	2.11	5.10	–7.52
210	2.07	13.00	–6.64
220	2.03	19.00	–6.26

The activation energy of VDC/MA dehydrochlorination does not appear to be a function of heating rate and an average activation energy of approximately 124 kJ mol^{-1} has been deduced. Bohme et al. [9] has quoted a value of 140 kJ mol^{-1} for the dehydrochlorination of PVDC in the temperature range 160–190°C. Both these values are similar to the 118 kJ mol^{-1} activation energy obtained using isothermal TGA. The isothermal method resulted in data plots showing significantly less scatter than those produced from dynamic data and although it is the more time-consuming technique it represents the more reliable approach.

6. Conclusion

The studies indicate the dehydrochlorination of VDC/MA copolymer has an activation energy of around 124 kJ mol^{-1}. The work has also shown that, at the temperatures required for the reprocessing of VDC copolymer coated polypropylene laminates (i.e. approximately 250°C), the VDC based coating will dehydrochlorinate, to say approximately 1 molecule of HCl per repeat unit. Therefore the incorporation of additives to neutralise the evolved hydrogen chloride will be necessary to protect both processing equipment and the environment.

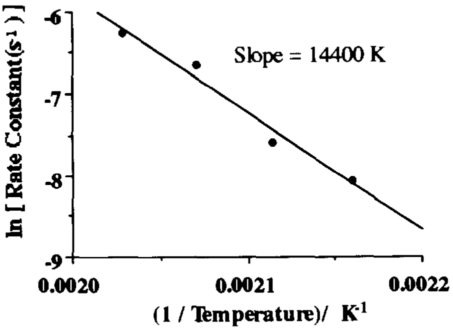

Fig. 6. Arrhenius plot for PVDC WA50 heated isothermally at temperatures between 190°C and 220°C.

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