

# Determination of Gelation Temperature of Poly(Vinyl Chloride) by Thermomechanical and Thermogravimetric Parameters

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Received 6 November 2003; accepted 23 August 2004

DOI 10.1002/app.21615

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Preheating between the temperatures of 200 and 280°C is done to a film-structured poly(vinyl chloride) (PVC) sample, which has a gelation temperature  $\sim$  250°C. After this preheat, the PVC's thermomechanical and thermal differences, at temperatures before and after thermal gelation, are observed. Consequently, when some thermomechanical and thermal parameters, obtained at temperatures

before and after gelation, are compared, it can be said that this is an easier method to determine the gelation temperature of a polymer. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1635–1640, 2005

**Key words:** poly(vinyl chloride); mechanical properties; thermogravimetric analysis; stress; strain

## INTRODUCTION

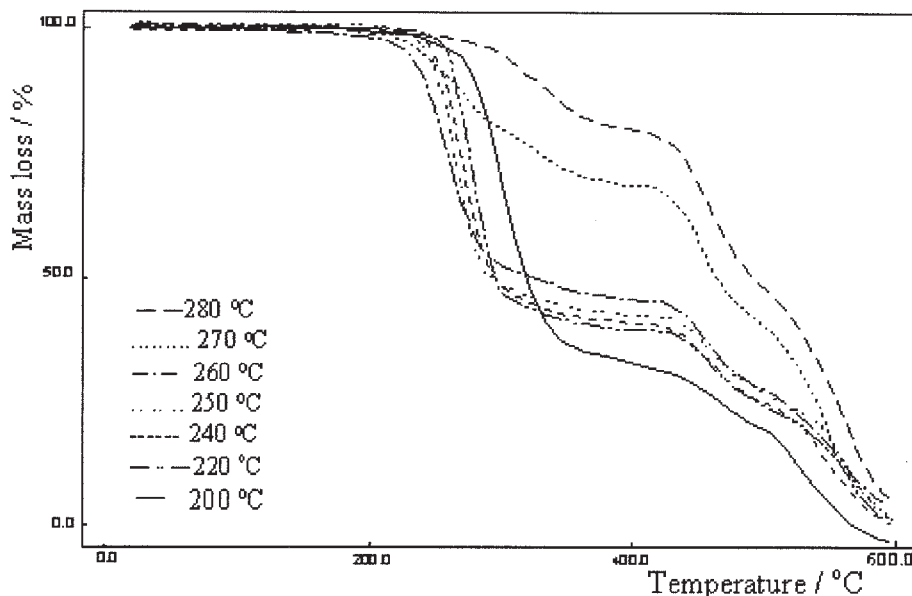
It is generally accepted that poly(vinyl chloride) (PVC) is unstable when exposed to high temperatures during its molding and applications. PVC undergoes extensive autocatalytic dehydrochlorination with the formation of conjugated double bonds.<sup>1–4</sup> This in turn leads to unacceptable dischlorination of the polymer and a drastic change in the physical and mechanical properties together with a decrease or an increase in molecular weight as a result of the breaking of a chain or crosslinking, respectively.<sup>5–8</sup> The poor stability of PVC against heat and some kinds of radiation is attributed to structural defects formed during polymerization.<sup>9</sup> The thermal degradation of PVC in the presence of HCl is generally believed to proceed by an ionic or molecular-ionic mechanism.<sup>10</sup> It is well known that atactic PVC is a low crystalline polymer and the gelation of the semidilute solution takes place under a large amount of solvent, so that the crystallization becomes more difficult.<sup>11</sup>

One of the main plastic components in typical municipal waste is PVC. Thermal degradation of PVC is a more complex process than the other stable plastic wastes [i.e., polyethylene (PE), polypropylene (PP), and polystyrene (PS)]. Some mechanisms of PVC degradation are proposed in the literature, but generally the kinetic models refer to global apparent kinetics<sup>12</sup>

or to a few step mechanisms.<sup>13</sup> All the researchers agree on the presence of two main degradation steps, as clearly shown in Figure 1. Initially, dehydrochlorination forms HCl and polyene structures. The thermal dehydrochlorination reaction occurs because of the presence of various defect sites in the polymer chains. Possible defect structures in PVC chains are allylic chlorine, tertiary hydrogen and chlorine atoms, end groups such as double bonds, oxygen-containing groups, peroxide residues, head-to-head structures, and steric order of the monomer (tacticity).<sup>3</sup> When polymers are heated, a number of reactions occur simultaneously such as gas evolution, dischlorination, and breaking of chain and crosslinking. The effect of crosslinking is to increase the molecular size and to form an insoluble gel in the polymer samples. This gel formation may change the thermal and thermomechanical properties of polymers.<sup>14</sup> Crosslinking reactions between polyene molecules led to the creation of the alkyl aromatic groups, which can make the chain further condensed and grown.<sup>4</sup> The gas exits, throughout the gelation temperature, cause the elastic characteristics of PVC to increase, which makes the PVC's thermal properties unstable.

The aim of this study was to observe whether there is a change in the thermal and thermomechanical characteristics of PVC by preheating until the temperatures before and after the PVC's gelation temperature. The gelation temperature of the PVC used in this study, which has a commercial name of Breon 113, was determined as  $\sim$  250°C by a previous study.<sup>15</sup> In this study, the thermogravimetric (TGA), thermomechanical (TMA), and differential thermal analysis

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**Figure 1** TGA curves of the preheated PVC under nitrogen at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a gas flow rate of  $25\text{ cm}^3\text{ min}^{-1}$ .

(DTA) characterizations of film-structured PVC samples were determined by heating them at a temperature range between 200 and  $280^{\circ}\text{C}$ , which covers the lower and upper limits of PVC's thermal gelation temperatures. It has been concluded that the gelation, resulted from diagonal connection especially, causes important changes in the PVC's thermal, optic, and thermomechanical characteristics that makes it usable in an extensive usage area.

## EXPERIMENTAL

### Materials

The PVC sample (Breon 113), the same as used in a previous study,<sup>15</sup> was found in UK. It does not contain any stabilizer. Tetrahydrofuran (THF; 99.9%) was obtained from Merck Co. (Darmstadt, Germany) and purified by distillation (boiling point, bp:  $67^{\circ}\text{C}$ ) before use.

### Experimental technique

The polymer film was prepared by dissolving 1 g PVC in 10 mL THF. The homogeneously mixed solution was cast into a dry, clean Pyrex Petri dish of 50 mm diameter. The film, formed on complete evaporation of the solvent at room temperature, was then dried in a vacuum oven at  $50^{\circ}\text{C}$  to constant weight. All the films prepared in this way were 0.25 mm thick. First, these film samples were heated separately by cutting in a TGA furnace between 200 and  $280^{\circ}\text{C}$  for 2 h. The color was brown after the heating. Shimadzu TGA-50, TMA-50, and DTA-50

instruments were used for TGA, TMA, and DTA of the polymer samples. TGA and DTA experiments were carried out on all samples at a heating rate of  $10^{\circ}\text{C min}^{-1}$  with nitrogen as the carrier gas at a flow rate of  $25\text{ mL min}^{-1}$ . TMA experiments were carried out at a heating rate of  $10^{\circ}\text{C min}^{-1}$ , a loading rate of  $5\text{ g min}^{-1}$ , and a heating range from room temperature to  $150^{\circ}\text{C}$  in a nitrogen atmosphere. The flow experiments were carried out as loading,  $25\text{ g min}^{-1}$ , and unloading,  $-25\text{ g min}^{-1}$  to 200 g, in room temperature and a nitrogen atmosphere.

## RESULTS AND DISCUSSION

TG curves of preheated PVC are shown in Figure 1. Thermal parameters are summarized in Table I. The thermal parameters in Table I are the initial reaction temperature ( $T_i$ ), half-time temperature ( $T_h$ ), maximum rate temperature ( $T_m$ ), and maximum rate ( $R_m$ ). According to the TGA curves in Figure 1,

**TABLE I**  
Values of  $T_i$ ,  $T_h$ ,  $T_m$ , and  $R_m$  of heated PVC

Temperature ( $^{\circ}\text{C}$ )	$T_i$ ( $^{\circ}\text{C}$ )	$T_h$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$R_m \times 10^{+2}$ ( $\text{mg min}^{-1}$ )
200	262	287	278	3.1
220	263	288	278	3.0
240	244	287	273	2.7
250	235	291	269	3.0
260	228	326	258	1.6
270	231	470	282	0.6
280	285	495	318	0.4

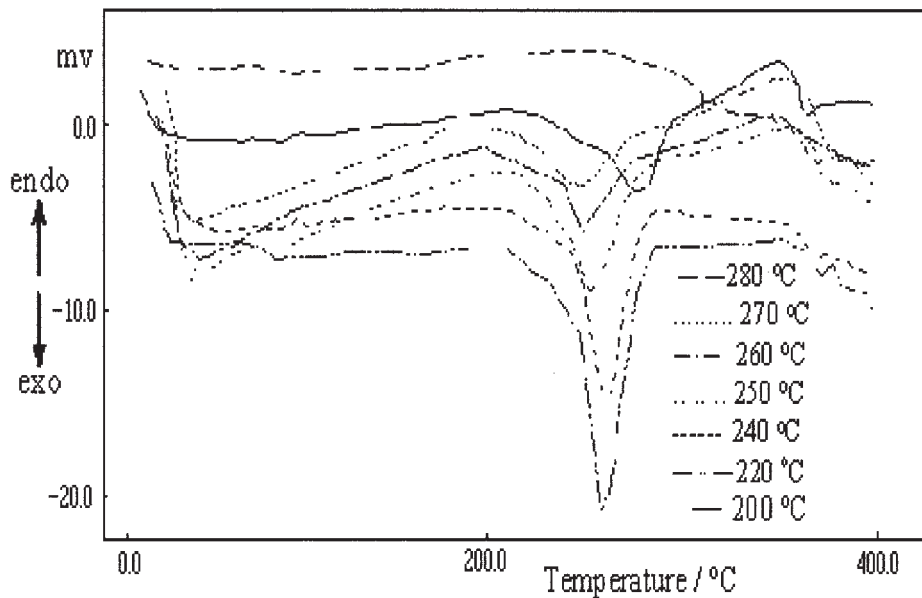


Figure 2 DTA curves of the preheated PVC under nitrogen at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a gas flow rate of  $25\text{ cm}^3\text{ min}^{-1}$ .

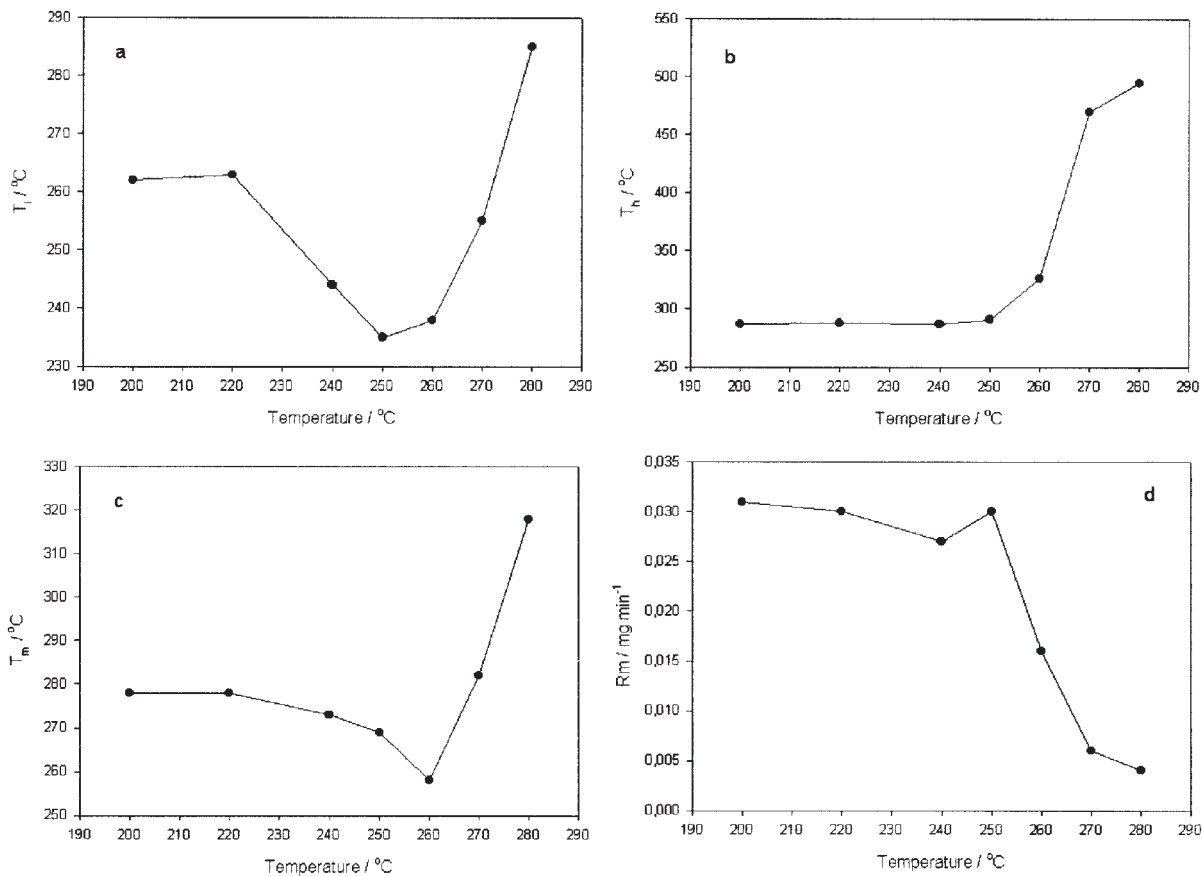
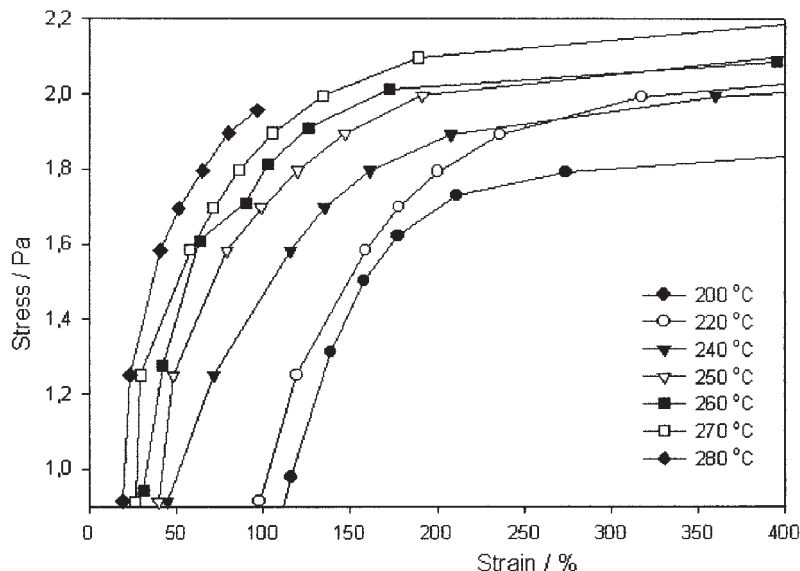


Figure 3 The curves of the preheated temperatures opposite to thermal analysis parameters obtained from curves of TG.

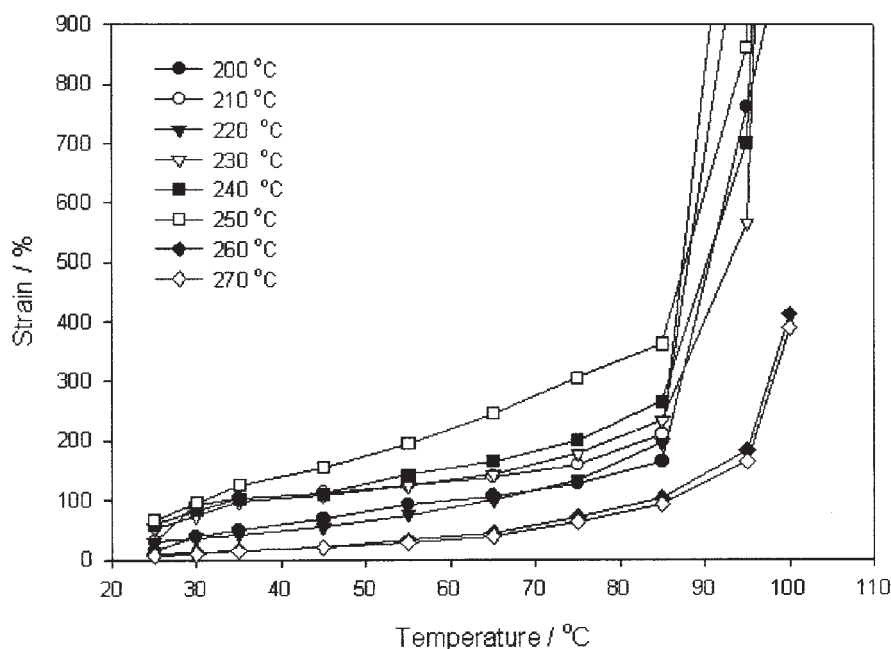


**Figure 4** Stress-strain curves of the preheated PVC under nitrogen at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a gas flow rate of  $25\text{ cm}^3\text{ min}^{-1}$ .

apparent differences are observed before and after  $250^{\circ}\text{C}$ , which is the gelation temperature, at the preheated PVC. These differences are also seen in the thermal analysis parameters, which are given in Table I. The DTA curves in Figure 2 show an apparent increase in the degradation energy of PVC with an increase of preheating temperature. Figure 2 also represents the maximum degradation energy of PVC at  $280^{\circ}\text{C}$ .

Using the information taken from Table I, Figure 3 shows more precisely the differences that occurred before and after gelation. From these curved peaks at  $250^{\circ}\text{C}$ , the gelation temperature is easily seen. According to this information, with the help of parameters obtained from TG curves, the gelation temperature can be easily found.

For thermomechanical analyses of all PVC samples, which are preheated between  $200$  and  $270^{\circ}\text{C}$ , the



**Figure 5** Strain-temperature curves of the preheated PVC under nitrogen at a heating rate of  $10^{\circ}\text{C min}^{-1}$  and a gas flow rate of  $25\text{ cm}^3\text{ min}^{-1}$ .

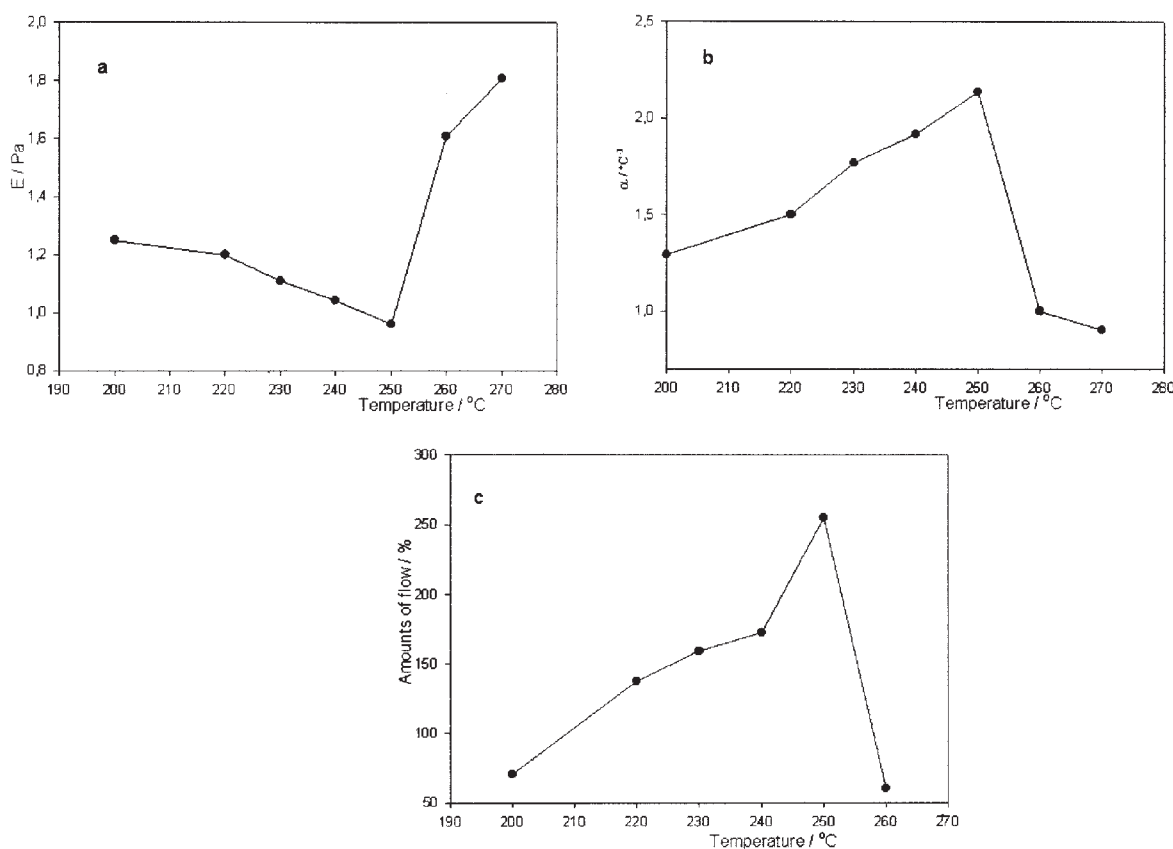
**TABLE II**  
**Values of  $E$ ,  $\alpha$ , and Amount of Flow of Heated PVC**

Temperature (°C)	$E$ (Pa)	$\alpha$ (°C <sup>-1</sup> )	Amount of flow (%)
200	1.25	1.29	70.25
220	1.20	1.50	137.45
230	1.11	1.77	158.86
240	1.04	1.92	172.40
250	0.96	2.14	255.10
260	1.61	1.00	60.15
270	1.81	0.90	—

stress-strain curves are obtained and thermomechanical parameters of them are determined. Because the PVC sample at 280°C has a brittle structure, the stress-strain curve could not be obtained. Moreover, to determine the flow amounts (quantity) of the PVC samples at the preheated temperatures, experiments of loading and unloading with temperature increases are conducted. Each sample's elastic moduli values ( $E$ ) are calculated from the slope of the linear parts of the stress-strain curves. By obtaining the temperature-strain curves, the coefficients of thermal expansion ( $\alpha$ ) were determined from linear parts of these curves. TMA curves can be seen in Figures 4 and 5; TMA parameters can be seen in Table II. There was no flow

at 270 and 280°C. The values before and after gelation, as shown in Table II, are graphed versus preheating temperatures in Figure 6. It is clearly seen from Figure 6 that 250°C is the gelation temperature for PVC. This result, obtained from the TMA curves, is in accordance with the results obtained from TG curves.

As a consequence of the crosslinking formation occurring after gelation temperature, a harder structure at the thermomechanical characteristics and thermal determination was observed. As a result, it can be said that the gelation temperature of a polymer can be easily found from the parameters obtained from thermal and thermomechanical curves of a preheated polymer. In this study, the gelation temperature of the PVC was found to be 250°C by observing some significant changes in the thermomechanical and thermogravimetric parameters occurring in pre- and postgelation temperatures. The same gelation temperature was already determined in our previous work by employing a different method.<sup>15</sup> The gelation temperature is a considerable parameter that must be recognized during the processes of polymers. Therefore, we claim that the method used in this study to get the gelation temperature of any polymer is much easier and reliable than those of other methods because this method has been based mainly on the crosslinking



**Figure 6** The curves of the preheated temperature opposite to TMA parameters.

and the relevant thermomechanical changes induced by gelation.

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