Studies on the Effect of Laser Radiation on the Thermal Stability of Stabilized Poly(vinyl chloride)

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ABSTRACT: Nonisothermal studies were carried out using thermogravimetry (TG) and differential thermogravimetry (DTG) to obtain the activation energy of the decomposition for poly(vinyl chloride) (PVC), stabilized by ethyl, *N*-phenylmaleimide, and 4-carboxylate (ENPMC). Thermal gravitational analysis (TGA) indicated that the ENPMC–PVC samples decompose in two main breakdown stages. The effect of the addition of a stabilizer (ENPMC), with different concentrations, to PVC was studied. The results indicate that the addition of ENPMC with 0.01 g/1 g PVC enhances the thermal stability of pure PVC. Samples from 0.01 g ENPMC/1 g PVC were exposed to infrared laser radiation with energy fluency at levels between 0.95 and 8.53 J/cm^2. The results of the thermal experiments indicate that the onset temperature of decomposition T_0 and thermal activation energy of decomposition E_a are affected by the laser energy fluency owing to the simultaneous processes of degradation and crosslinking. The variation of transition temperatures with either the stabilizer concentration or the laser energy fluence was determined using differential thermal analysis (DTA). The results indicate that the irradiation with a laser to 7.11 J/cm^2 decreases the melting temperature of the pure PVC and this is most suitable for applications requiring the molding of this polymer at lower temperatures. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2249–2255, 2003

Key words: radiation; thermal properties; additives; poly(vinyl chloride)

INTRODUCTION

Poly(vinyl chloride) (PVC) has many desirable characteristics that has allowed it to achieve its present status as one of the most important commercial polymers. In spite of its enormous technical and economic importance, PVC still possesses many problems accompanied by changes in its physical properties. One of these problems is its poor thermal stability due to the structure defects formed during the polymerization process. Therefore, the stabilization of a PVC polymer using a variety of additives is required.[1] Organic materials as additives have the advantage of being metal free and environmentally acceptable.[2–6]

At the same time, a laser is presently being used in a variety of materials–processing applications. Its effect on polymers has progressively attained more and more interest from research due to the ever-increasing important applications of laser technology. Several studies on the effect of laser radiation on the thermal properties of polymers were performed.[7–11]

In the present study, ethyl, *N*-phenylmaleimide, and 4-carboxylate (ENPMC) was used as a stabilizer for PVC to overcome the problem of the poor thermal stability of PVC, improving its performance in different applications. In addition, laser radiation was used to obtain information concerning its effect on the thermal stability of PVC.

EXPERIMENTAL

Samples

Preparation of ENPMC

ENPMC was prepared by a two-step process as previously reported.[12] In this process, *para*-ethylaniline carboxylate (0.5 mol) in chloroform or ether was added to a cold solution of maleic anhydride (0.5 mol) in the same solvents. The resulting *N*-substituted maleamic acid obtained as a fine precipitate was treated with fused sodium acetate (0.6 mol) and acetic anhydride (10 mol) for each mole of maleamic acid at 70–80°C for 30 min. The maleimide (MI) formed was precipitated with water and crystallized from ethanol.

Preparation of PVC–MI films

One gram of PVC and definite concentrations from MI were dissolved in tetrahydrofuran and then poured

into a Petri dish with a 6-cm diameter. After about 24 h, a film of a nearly 0.25-mm thickness was formed.

Irradiation facilities

The laser tube used in the present work was an infrared laser tube of 5-W power (Model No. SSL_3; USA). The unit is capable of producing 2000 pulses per second with a pulse duration 200 ns at 904 nm. The laser beam was in the form of a circle of 1.8 cm in diameter of a Gaussian intensity profile across circles focused on the sample surface, giving pulses once in 1 s.

Experimental apparatus

The thermal behavior was investigated using a differential thermal analysis (DTA) and thermal gravitational analysis (TGA)-type Shimadzu-50. α-Al_2O_3 powder was used as a reference for the DTA measurements. Thermal experiments were carried out on all samples at a heating rate of 10°C/min with N_2 as a carrier gas at a flow rate of 30 cm^3/min.

RESULTS AND DISCUSSION

Effect of concentration of ENPMC

TGA

TGA provides quantitative information on the weight-change process while differential thermogravimetry (DTG) provides the rate of weight loss (dw/dT). TGA and DTG were performed for the PVC stabilized by different concentrations of ENPMC and the pure PVC sample at a heating rate of 10°C/min in the temperature range from room temperature to 600°C. The thermograms obtained are shown in Figure 1. It is clear from the figure that the samples decompose in two weight-loss stages. Using the TGA and DTG thermograms, the values of the weight loss were calculated for all the ENPMC–PVC samples and the pure PVC sample. Figure 2 shows the variation of these weight-loss values with the temperature in a relatively high temperature range. From the figure, we see that the sample with 0.01 g ENPMC/1 g PVC has the maximum thermal stability over the whole temperature range.

The values of the onset temperature of decomposition, T_0, were calculated using TGA and DTG curves and are given in Table I. Figure 3 shows the variation of T_0 with the ENPMC concentration. The figure shows that T_0 reaches a maximum value around the 0.01 g ENPMC/1 g PVC sample, indicating that the suitable concentration of the stabilizer required for maximum thermal stability is 0.01 g/1 g PVC. This can be attributed to the displacement of labile chlorine atoms by more stable MI moieties.
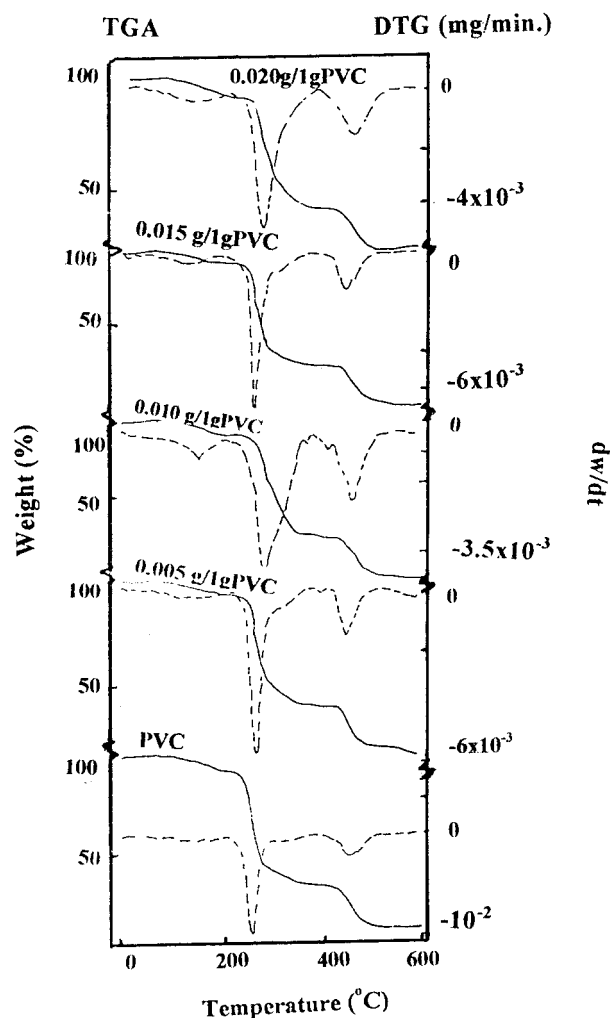

Figure 1 TGA and DTG thermograms for PVC stabilized by different ENPMC concentrations and the pure PVC sample.

Activation energy of decomposition

Evaluation of the activation energy of decomposition is useful for studying the thermal stability of materials. Various thermogravimetric methods have been proposed for the measurements of activation energies. The method proposed by Horowitz and Metzger[13] was used in the present work. In this method, thermogravimetric (TG) curves obtained at a heating rate of 10°C/min are required, for which the following equation is valid:

$$\ln[(W_0 - W_f)/(W - W_f)] = E_a\theta/RT_s^2 \qquad (1)$$

where W_0 and W_f are the initial and final weights of the stage, respectively; W, the remaining weight at a given temperature T; θ, the temperature difference between T and T_s; T_s, the temperature that satisfies the equation
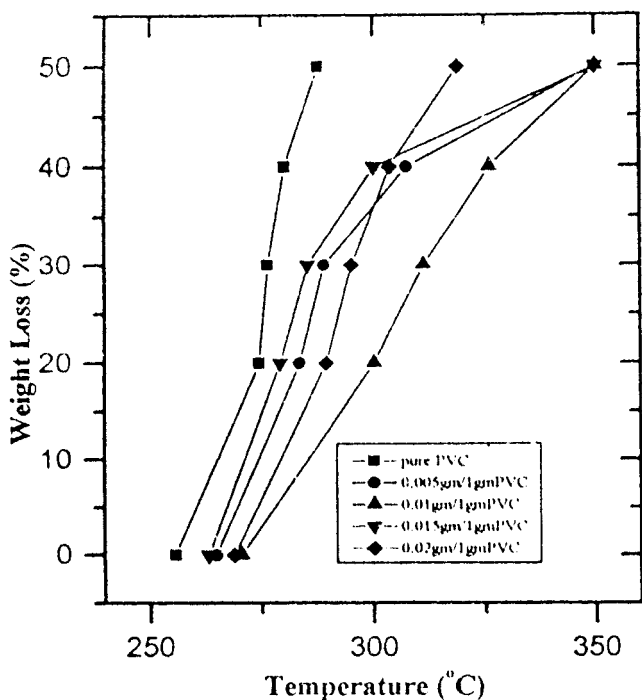
Figure 2 Variation of weight loss for PVC stabilized by different ENPMC concentrations and the pure PVC sample with the temperature.

$$[(W - W_f)/(W_0 - W_f)] = (1/e) = 0.3679 \qquad (2)$$

and R, the general gas constant. According to the above equation, a plot of $\ln[(W_0 - W_f)/(W - W_f)]$ against θ leads to a straight-line relationship in the range where the decomposed ratios are equal. Hence, the activation energy of decomposition can be evaluated from the slope of the line. Using the TGA and DTG curves, the values of the thermal activation energy of decomposition E_a were calculated for all the ENPMC–PVC samples and are given in Table I. Figure 4 shows the variation of E_a for the two stages of decomposition with the ENPMC concentration. From the figure, it is clear that, for the two stages of decomposition, E_a increases in magnitude up to a maximum

TABLE I
Values of Onset Temperature of Decomposition T_0, Activation Energy of Decomposition E_a, and Melting Temperature T_m for All the ENPMC–PVC Samples as a Function of ENPMC Concentration

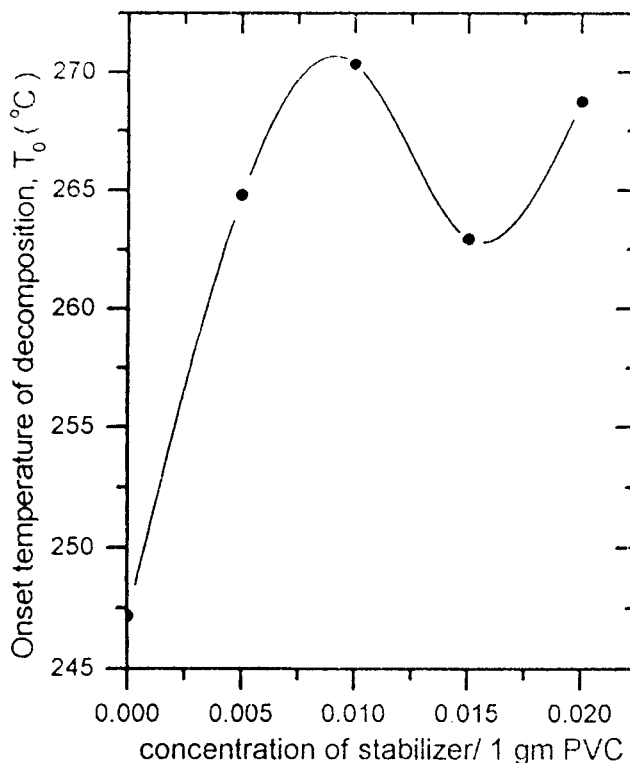| Concentration of ENPMC/1 g PVC	T_0 (°C)	E_a (eV)		T_m (°C)
		First stage	Second stage	
0.000	247.20	2.18	2.29	273.25
0.005	264.80	2.75	2.64	277.78
0.010	270.35	3.42	3.00	280.41
0.015	262.95	2.27	2.78	275.28
0.020	268.75	1.82	2.49	282.09

Figure 3 Variation of onset temperature of decomposition T_0 with ENPMC concentration.

value around 0.01 g ENPMC/1 g PVC and then decreases with an increasing ENPMC concentration.

DTA

Thermal characterization gives a good idea of the changes taking place in polymers. DTA was performed in the temperature range from room temperature to 400°C at a heating rate of 10°C/min on all the ENPMC–PVC samples and the pure PVC sample. Figure 5 shows DTA thermograms for the PVC stabilized by different ENPMC concentrations and the pure PVC sample. All the thermograms were characterized by the appearance of one endothermic peak at the melting temperature T_m. The values of these melting temperatures are given in Table I. The change of these melting temperatures can be explained in terms of the thermal degradation where prolonged heating causes a random breaking of bonds and the formation of stable molecules with a lower molecular weight and sometimes the detachment of low molecular products because of reactions of side groups without any appreciable change in the initial molecular weight.[14]

In conclusion, the study of the effect of the concentration of the added ENPMC stabilizer to PVC shows that the sample with a 0.01 g ENPMC/1 g PVC concentration has the maximum thermal stability. This sample was
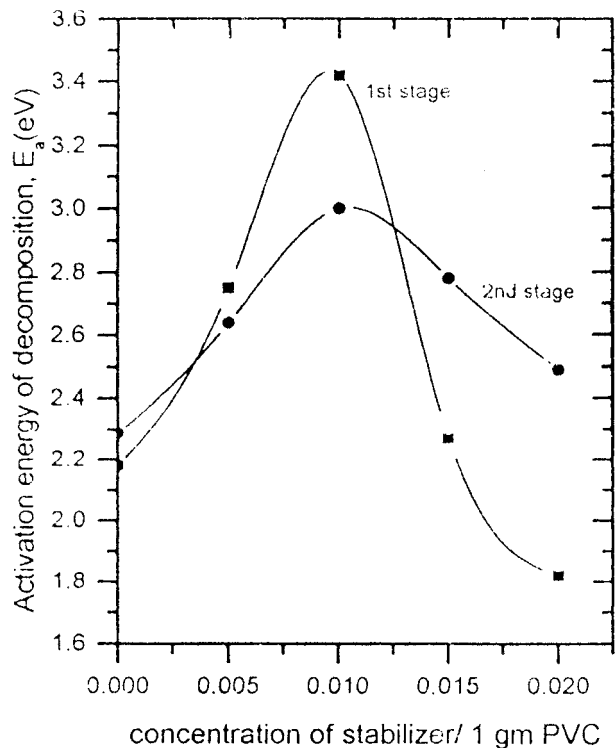
Figure 4 Variation of thermal activation energy of decomposition E_a, for the two stages of decomposition, with ENPMC concentration.

chosen to be a subject for further study to investigate the effect of infrared laser radiation on its properties.

Effect of infrared laser radiation on properties of the 0.01 g ENPMC/1 g PVC sample

TGA

The effect of laser radiation on samples of 0.01 g ENPMC/1 g PVC and 0.25-mm thickness was investigated. TGA and DTA was performed for all irradiated and nonirradiated ENPMC–PVC samples in the temperature range from room temperature to 600°C, at a heating rate of 10°C/min. The TGA and DTG thermograms obtained are shown in Figure 6. Using these TGA and DTG thermograms, the values of the weight loss were calculated for all irradiated and nonirradiated 0.01 g ENPMC/1 g PVC samples. Figure 7 shows the variation of these weight-loss values with the temperature, in a relatively high temperature range. From the figure, we see that the thermal stability of the 0.01 g ENPMC/1 g PVC sample is reduced by the action of the laser.

The values of the onset temperature of decomposition T_0 were calculated using TGA and DTG curves and are given in Table II as a function of the laser energy fluence. Figure 8 shows the variation of T_0 with the laser energy fluence. The figure shows that T_0 decreases until a minimum value around the 4.27 J/cm^2 irradiated sample, indicating a decrease in the
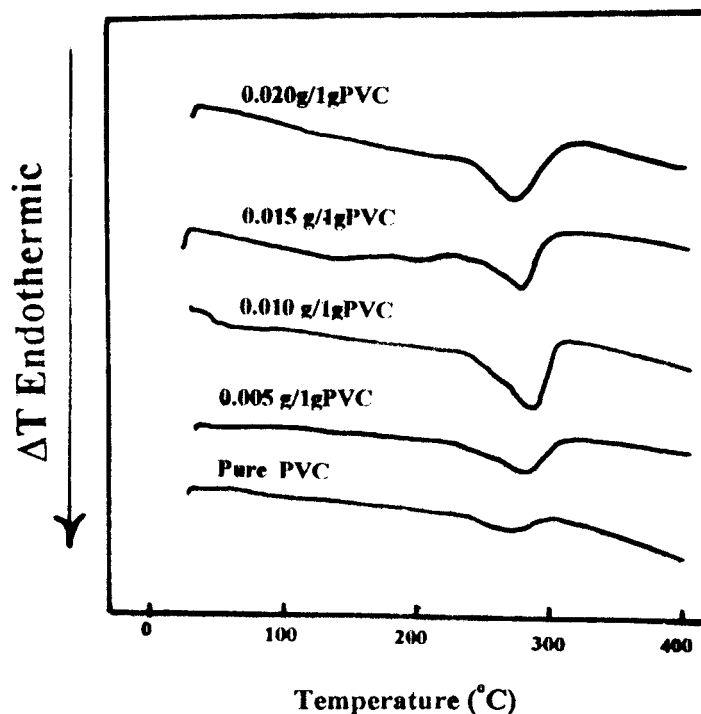

Figure 5 DTA thermograms measured in the temperature range from room temperature to 400°C for PVC stabilized by different ENPMC concentrations and the pure PVC sample.
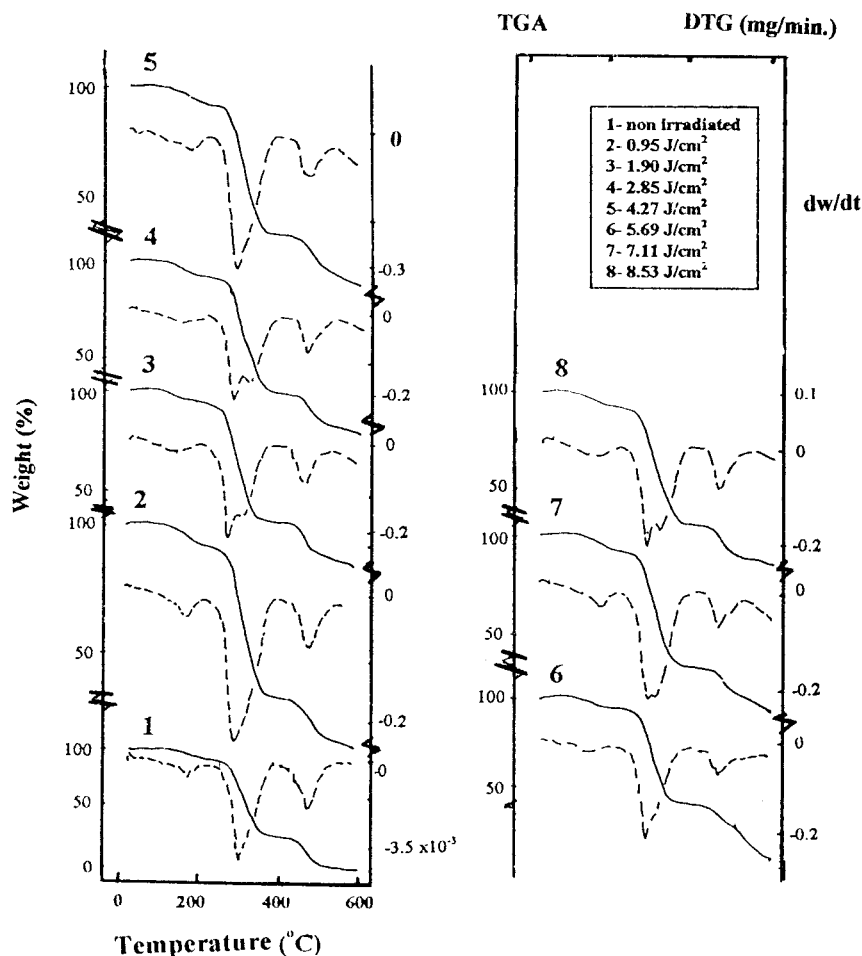
Figure 6 TGA and DTG thermograms for all irradiated and nonirradiated 0.01 g ENPMC/1 g PVC samples.

thermal stability of the polymer samples due to the degradation mechanism and the detachment of the stabilizer moieties due to steric hindrance. Above 4.27 and to 8.53 J/cm², T_0 showed an increase due to the crosslinking process and the consumption of the stabilizer into the polymeric chains, annihilating all structural defects.

Activation energy of decomposition

The values of the thermal activation energy of decomposition E_a were calculated for all irradiated and non-irradiated 0.01 g ENPMC/1 g PVC samples using TGA and DTG curves and are given in Table II. Figure 9 shows the variation of E_a, for the two stages of decomposition, with the laser energy fluence. The figure shows that, for the first stage of decomposition, E_a increases in magnitude to a maximum value around 5.69 J/cm² and then decreases on increasing the laser energy fluence to 8.53 J/cm². For the second stage of decomposition, E_a showed an increase to a maximum value around 2.85 J/cm², followed by a decrease with an increasing laser energy fluence to 5.69 J/cm².

Above 5.69 and to 8.53 J/cm², it increases again. The energy range in which E_a increases can be explained in terms of a crosslinking phenomenon that results in the formation of three-dimensional networks, while the energy range in which E_a decreases can be explained in terms of a degradation mechanism as a result of random rupturing of the bonds.[15]

DTA

DTA was performed on all irradiated and nonirradiated 0.01 g ENPMC/1 g PVC samples in the temperature range from room temperature to 400°C at a heating rate of 10°C min. Figure 10 shows DTA thermograms for all irradiated and nonirradiated ENPMC–PVC samples. All the thermograms were characterized by the appearance of one endothermic peak at the melting temperature. The values of these melting temperatures are given in Table II. The values indicate that the melting temperature decreases with an increasing laser energy fluence to 8.53 J/cm². This suggests that infrared laser radiation could be a suitable technique for preparing stabilized PVC that is re-
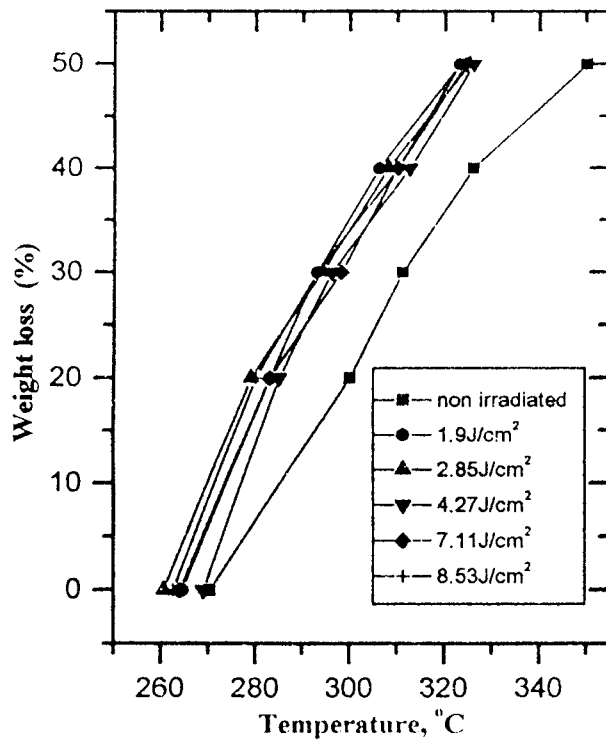
Figure 7 Variation of weight loss for all irradiated and nonirradiated 0.01 g ENPMC/1 g PVC samples with the temperature.
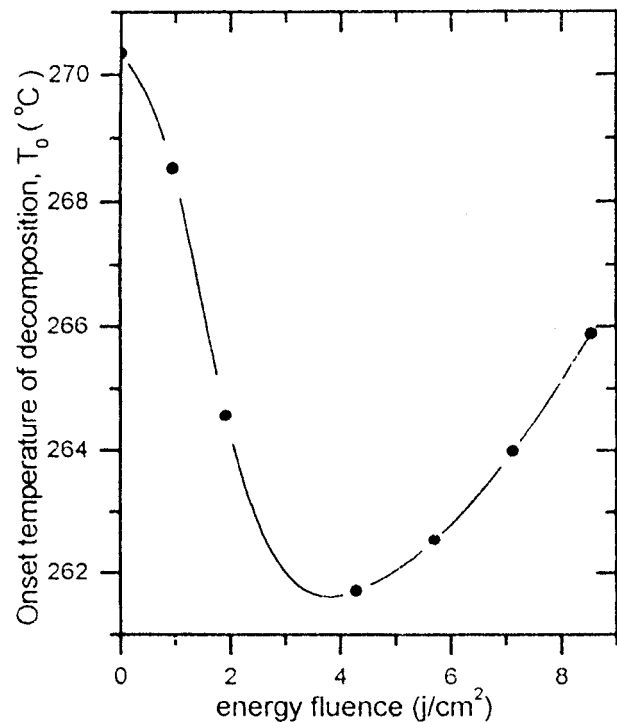

Figure 8 Variation of onset temperature of decomposition T_0 with laser energy fluencies.

quired for applications that require molding at lower temperatures.

CONCLUSIONS

From the above study, one can draw the conclusion that the addition of ENPMC to PVC with a concentration of 0.01 g/1 g PVC improves the thermal stability of pure PVC and thus prolongs the service lifetime of articles made from this polymer. The results of DTA indicate that the sample of a 0.01 g ENPMC/1 g PVC

TABLE II
Values of Onset Temperature of Decomposition
T_0, **Activation Energy of Decomposition** E_a, **and Melting Temperature** T_m **for All Irradiated and Nonirradiated 0.01 g ENPMC/1 g PVC Samples as a Function of Laser Energy Fluence**

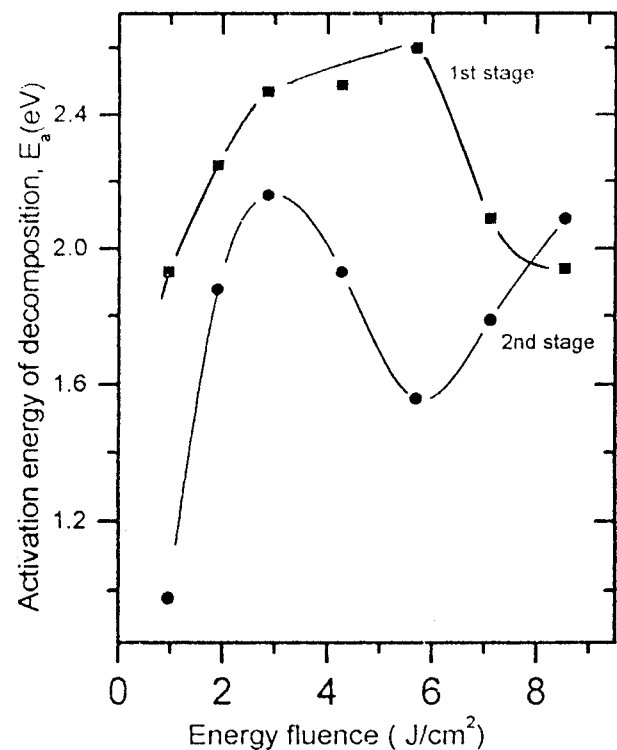| Laser energy fluence (J/cm^2)	T_0 (°C)	E_a (eV) First stage	Second stage	T_m (°C)
Nonexposed	270.35	3.42	3.00	280.41
0.95	268.53	1.93	0.98	263.18
1.90	264.58	2.25	1.88	248.07
2.85	260.56	2.47	2.16	249.50
4.27	261.71	2.49	1.93	248.18
5.69	262.55	2.60	1.56	251.40
7.11	264.00	2.09	1.79	251.22
8.53	265.89	1.94	2.09	261.31

Figure 9 Variation of thermal activation energy of decomposition E_a, for the two stages of decomposition, with laser energy fluencies.
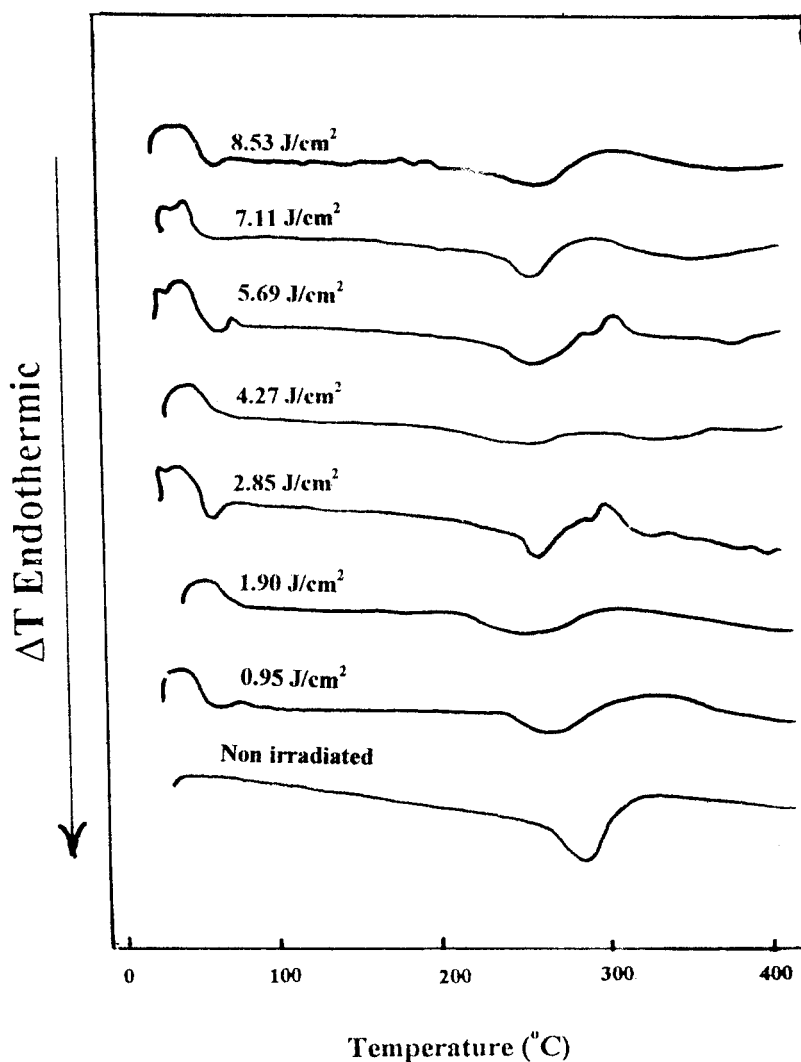
Figure 10 DTA thermograms measured in the temperature range from room temperature to 400°C for all irradiated and nonirradiated 0.01 g ENPMC/1 g PVC samples.

concentration has the highest melting temperature T_m, while exposing it to infrared laser pulses leads to a decrease in its T_m value, and this is most suitable for applications requiring the molding of this polymer at lower temperatures.

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