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Thermogravimetric analysis of heat treated CR-39 polymer

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ABSTRACT

Thermogravimetric analysis (TGA) of virgin and heat treated CR-39 samples has been carried out, starting from room temperature to a maximum upto 600 °C, at a linear rate of heating of 6 °C per minute. The change in degradation activation energy, frequency factor, entropy of activation, enthalpy of activation, free energy of decomposition and rate coefficient have been studied as a consequence of heat treatment. The results indicate the enhancement in thermal stability of CR- 39 polymer as an effect of heat treatment.

Keywords: CR-39, TGA, Heat treatment, Activation energy.

INTRODUCTION

The polymers, now a day, have become promising materials in various scientific and technological applications. This is due to the fact that in addition to their excellent inherent characteristics [1], their properties can be customized for appropriate use by various treatments e.g. chemical doping, gamma irradiation, ion implantation [2-4] etc. In addition, heat treatment is also a promising mean [5] in this direction. It is well known that heat treatment of polymeric materials changes their morphology at temperatures higher than their glass transition temperature (T_g) which may lead to alter their electrical, optical and thermal properties [6-10] etc.

Among polymers, CR–39 (monomer composition: $C_{12}H_{18}O_7$) is a high grade amorphous optically transparent plastic widely used as nuclear track detector [11-12] besides many other applications in optical devices etc. In continuation to our earlier studies related to the effect of heat treatment on optical properties of CR-39 [10],in the present work, the thermal properties of virgin and heat treated samples of CR–39 (at temperatures 140, 160 and 180 °C) are studied through Thermogravimetric Analysis (TGA). The changes in various parameters related to the thermal stability of this polymer like activation energy, frequency factor, entropy of activation, free energy of decomposition and rate coefficient have been deduced and analyzed as a consequence of heat treatment.

EXPERIMENTAL SECTION

The procured sheets of CR-39 (TASTRAK, Bristol, England) were cut (1cm x 1cm) and subjected to heat treatment in air for one hour, at temperatures 140, 160 and 180 °C, within an accuracy of ± 1°C, in a specially designed oven. All these samples along with the virgin sample were subjected to the Thermo Gravimetric Analysis (TGA) using PerkinElmer Diamond TG/DTA instrument in the temperature range ~30 to 600 °C at a heating rate of 6 °C per minute.

RESULTS AND DISCUSSION

3.1. Thermogravimetric analysis

Thermal degradation is a very important process which enables us to know the influence of the polymer structure on the thermal stability, the optimum temperature of operation and the activation energies associated with the degradation processes [5, 13]. Thermogravimetric analysis (TGA) has been proved to be relatively fast and accurate method for the determination of the kinetic parameters of degradation processes.

In order to determine various kinetic parameters related to the thermal degradation for virgin and heat treated samples of CR-39 polymer, TGA thermograms for these samples have been recorded and are presented in Figure1.

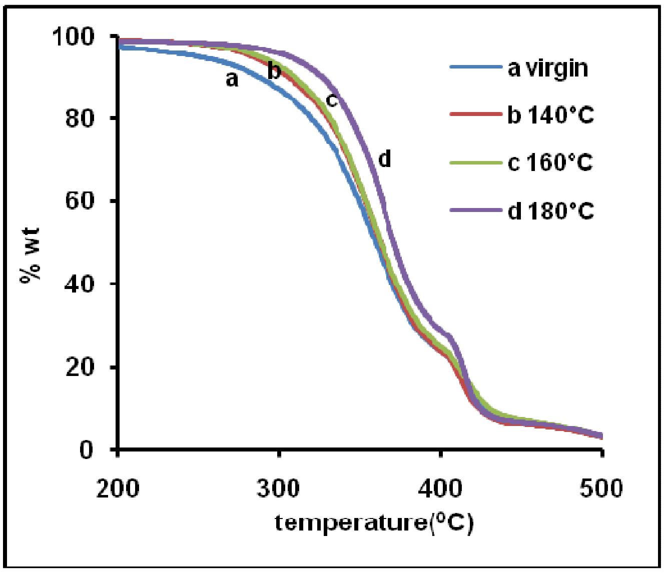

Fig 1. TGA plots for virgin and heat treated samples of CR-39 polymer

The corresponding DTG thermograms as deduced from TGA thermograms have been presented in Figure 2.

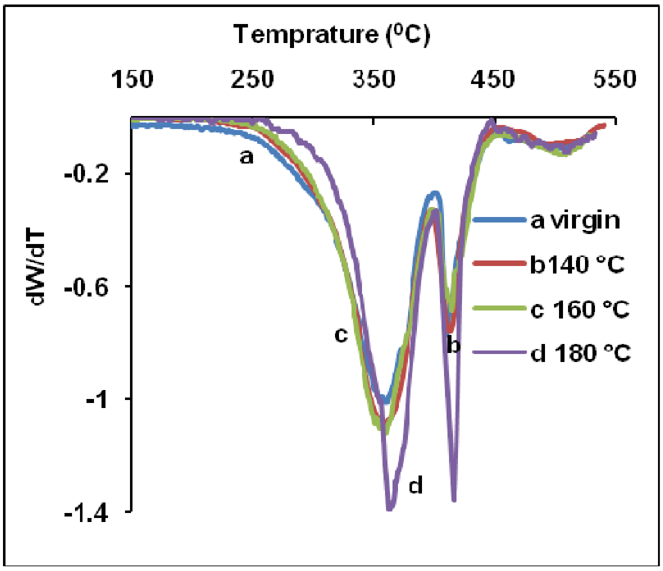

Figure 2. DTG plots for virgin and heat treated samples of CR-39 polymer

It is clear from Figure 1 that degradation process for CR-39 polymer proceeds in three steps which is again supported by the presence of three peaks in DTG thermograms (figure 2).

Several methods have been used to evaluate various kinetic parameters of degradation reaction. Most commonly used methods for this purpose are the differential method of Freeman and Carroll, integral method of Coats and Redfern, the approximation method of Horowitz and Metzger [14-22] etc. The kinetic parameters calculated using any of these methods reveals no significant difference [20-22] and hence any of these methods can be employed equivalently. In the present study, we have employed Horowitz –Metzger method.

3.1.1. Determination of activation energy

The activation energies of virgin and heat treated samples of CR-39 corresponding to the major degradation process (1st step) have been deduced using the expression [18]

$$\ln\ln\left(\frac{W_o}{W}\right)=\frac{E_a\theta}{RT_s^2}$$

where W_0 is the initial weight, W is the remaining weight at temperature T, E_a is the activation energy, R is gas constant and $\theta = T-T_s$ with T_s as the reference temperature corresponding to $W/W_0 = 1/e$.

The activation energies E_a can be calculated from the slope of the linear fitted line between ln (ln (W_0 / W)) and θ, illustrated in Figure 3, for virgin and thermally heated samples at temperatures 140, 160 and 180 °C.

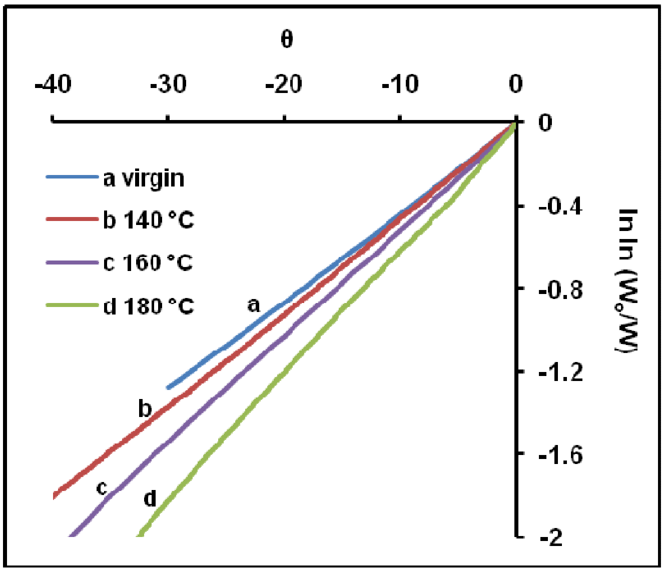

Figure 3. Plots of lnln(W_0/W) vs. θ for virgin and heat treated samples of CR-39 polymer

The calculated values of activation energies are listed in Table 1.There is an evident increase in the values of activation energy with the increase annealing temperature. Such an increase may be attributed to the increase in packing density, organized molecular arrangements [14, 16, 19, 23] etc. in the polymeric sample which signifies the increased thermal stability of the polymer.

3.1.2. Determination of frequency factor

The corresponding values of frequency factor for the virgin and the heat treated samples of CR-39 have been determined by substituting the values of activation energies in the expression [18]

$$-1 = -\frac{A}{\beta}\frac{RT_s^2}{E_a}\exp\left(-\frac{E_a}{RT_s}\right)$$

where A is the frequency factor and β is the constant rate of heating.

The values so obtained are listed in Table 1. Corresponding to the increase in values of activation energies, the values of frequency factor increases [23]. Such an increase in the frequency factor signifies the increase in the rate of reaction [14-15, 23]. This may be due to the rearrangements of molecular states producing new interstates which facilitate the reaction as a result of heat treatment.

3.1.3. Determination of entropy of activation

The difference between the entropy of the transition state and the sum of the entropies of the reactants is called entropy of activation (ΔS) and is calculated as [14]

$$\Delta S = 2.303R\log\left(\frac{Ah}{kT_z}\right)$$

where h is Planck's constant and k is Boltzmann constant.

The calculated values of entropy of activation are listed in Table 1. There is a clear cut increase in the values of entropy of activation with the increase in the annealing temperature which again supports the relative fast nature of reaction [23].

3.1.4. Determination of free energy of change of decomposition:

This is given as the difference between the enthalpy of the transition state and the sum of the enthalpies of the reactants in the ground state. It may be considered to be the driving force of a chemical reaction. ΔG determines the spontaneity [23] of the reaction. The values of ΔG are calculated using the expression [14]

$$\Delta G = E_a - T_s \Delta S$$

and are listed in Table 1.The positive values of ΔG signify the non spontaneity of the degradation reaction.

3.1.5. Determination of rate coefficient

It can be calculated using Arrhenius equation [14]

$$K = A \exp\left(-\frac{E_a}{RT_s} \right)$$

The calculated values of rate coefficients are listed in Table 1.

Table 1: Values of various kinetic parameters for virgin and heat treated CR-39 polymer

S.No.	Heating temperature(°C)	E_a (kJ/mol)	A (s^{-1})	ΔS (J/mol/K)	ΔG (kJ/mol)	K (s^{-1})
1.	virgin	137.9	7.3E10	-43.14	165.1	0.25
2.	140	149.2	5.9E11	-25.81	165.5	0.27
3.	160	157.9	3.7E12	-10.46	164.4	0.28
4.	180	166.6	1.2E13	-1.06	167.3	0.29

The increasing trend in these values again confirms the fast nature of reaction [23] with increasing annealing temperature.

CONCLUSION

The increase in activation energies for thermal degradation and other related kinetic parameters like the frequency factor, entropy of activation and rate coefficient with the increase in heating temperature clearly indicate the enhancement in thermal stability of CR-39 as an effect of heat treatment. Thus, it can be concluded that the thermal stability of CR-39 can possibly be improved as per requirement through heat treatment.

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