

Study of the Pyrolysis of Saturated Chlorinated Polyethylene Fibers

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Synopsis

The thermal degradation of saturated chlorinated polyethylene in powder and fiber form has been studied. Direct observations of fiber length variations have enabled us to prove the reactional mechanisms proposed. In the temperature range of 200°–300°C, the material exhibits some fluidity. Its degradation is explained by intrachain and interchain dehydrochlorination reactions, followed by an arrangement of conjugated double bonds obtained in the shape of polyacenic cycles. Between 300°C and 800°C, the polyacenic cycles react with each other to give a pregraphitic structure which is responsible for the increase in rigidity of the material. The fibers of saturated chlorinated polyethylene can be used as a precursor of carbon fiber.

INTRODUCTION

Previous studies of the preparation and pyrolysis of saturated chlorinated polyethylene (73.2% chlorine content by weight) have indicated that it is possible to obtain from this polymer a chain structure which is that of an ungraphitic carbon.¹⁻³

Irrespective of the original product, chlorinated poly(vinyl chloride) prepared by photochemistry is nonfilm forming, owing to its very low average molecular weight. Indeed, during the chlorination a great number of chain ruptures occurs. Under the same conditions, saturated chlorinated polyethylene gives a product of similar structure but with a higher molecular weight,⁴ hence the polymer can be formed into a thread.

PREPARATION OF THE CHLORINATED POLYMER

Chlorination to saturation level can be easily accomplished only by using the fine powder obtained after precipitation with methyl alcohol from a 10% solution of polymer in ethane tetrachloride. The finely powdered polymer is washed, dried, and then swollen with chloroform gas during 60 hr. The chlorination is carried out in the presence of ultraviolet light, the polymer being maintained in suspension in carbon tetrachloride by chlorine; the apparatus for this chlorination has been described in an earlier publication.⁵ The polyethylene used is the low-density variety, and the

chlorination time is 4 hr, after which the polymer is soluble in the reacting medium. After precipitation by methyl alcohol, it is fractionated with a 70/30 mixture of tetrahydrofuran and methyl alcohol at room temperature. The yield of the operation, calculated from the theoretical quantity of chlorinated polymer corresponding to the initial weight of polyethylene, is 70%. The saturated chlorinated polyethylene contains 73.7% of chlorine by weight; its rough formula is $(C_2H_2Cl_2)_n$; and its two principal components are 1,2-dichloroethylene ($-\text{CHCl}-\text{CHCl}-$) and 1,1-dichloroethylene ($-\text{CH}_2-\text{CCl}_2-$).⁴ The average molecular weights, determined with an automatic osmometer, are between 60,000 and 75,000. The specific gravity measured by a density gradient column is 1.6650 g/cc, and the glass transition temperature, determined by the dilatometric method, is 136°C.

SPINNING

Since chlorinated polyethylene is not a thermoplastic polymer, the spinning has been carried out from a tetrahydrofuran solution by the wet method, using a mixture of water and ethylene glycol in the coagulation bath. The mechanical characteristics of the fiber obtained are those of a rigid but weak material with an amorphous but orientated structure.

THERMAL DEGRADATION

Experimental Procedure

The thermal degradation of the polymer powder has been studied in an inert atmosphere using a thermobalance (Ugine-Eyraud Model B.60) with a horizontal furnace (Heraeus Rok Model A 4/60) and a differential thermal analyzer (Netzsch-Geratebau Model 404 T). The rate of temperature rise is 4°C/min. The pyrolysis of the fibers was undertaken using two types of device: a vertical furnace (Heraeus Rox Model 6.5/60) modified for the purposes of this study for temperatures up to 900°C, and an electron gun (Alcatel), for treatments up to 2400°C.

The Thermal Stability of Chlorinated Polyethylene Powder

The graphs of isothermal degradation versus time (for constant temperatures) (Fig. 1) and of weight loss versus temperature (for a standard heating rate of 4°C/min) (Fig. 2) show a marked change in the degradation process when the pyrolysis temperature is in the range of 270°–300°C. As for the saturated chlorinated poly(vinyl chloride), two distinct processes of decomposition may be distinguished during the pyrolysis of chlorinated polyethylene. In the first temperature range, the apparent order of the reaction is zero, and the activation energy is single and equal to 50 kcal/mole. The volatile materials liberated are mostly composed of hydrochloric acid.

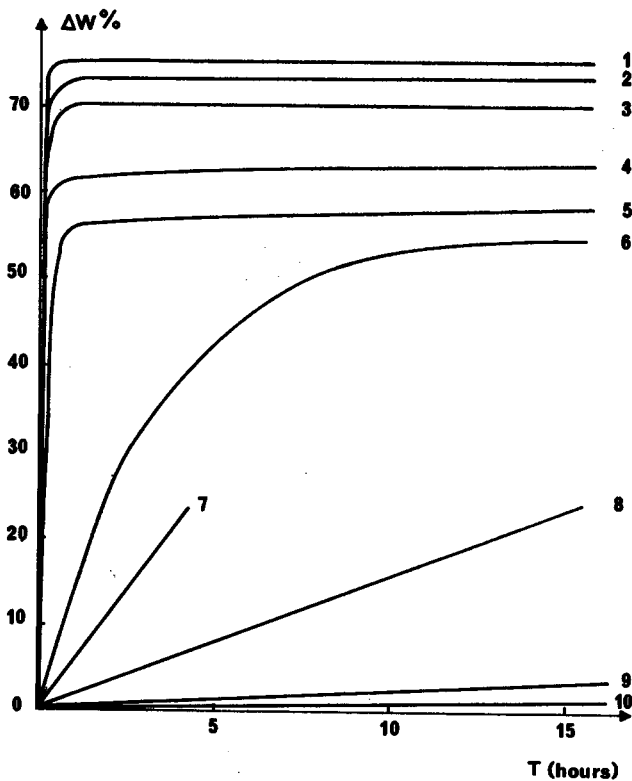


Fig. 1. Isothermal thermogravimetric analysis of saturated chlorinated polyethylene: (1) 800°C; (2) 600°C; (3) 500°C; (4) 400°C; (5) 300°C; (6) 270°C; (7) 250°C; (8) 235°C; (9) 215°C; (10) 206°C.

The general tendencies of the isothermal graphs up to 300°C indicate a level corresponding to a relative weight loss of 60%. The time to reach this level is a function of the degradation temperature. Thus, the relative weight loss after five or ten days of treatment at 235°C is respectively 58.6% and 60.5%.

In the second temperature range, that is to say, above 300°C, the relative weight loss becomes higher than 60%. The isothermal graph of the degradation levels out after 10 min of pyrolysis, and the relative weight loss is independent of the duration of degradation. To increase this weight loss, it is necessary to increase the treatment temperature. For temperatures higher than 800°C, the increase in weight loss is negligible; at this temperature, the chlorine content of the char is lower than 0.1%.

Graphs of relative weight loss versus temperature obtained either by isothermal degradation during 24 hr or by heating with a temperature rise of 4°C/min are similar. Both show a great change of slope at about 300°C and 350°C, respectively, which corresponds to a relative weight loss of around 60%, resulting uniquely from the liberation of hydrochloric acid. Above this value, the degradation rate is markedly reduced; the relative

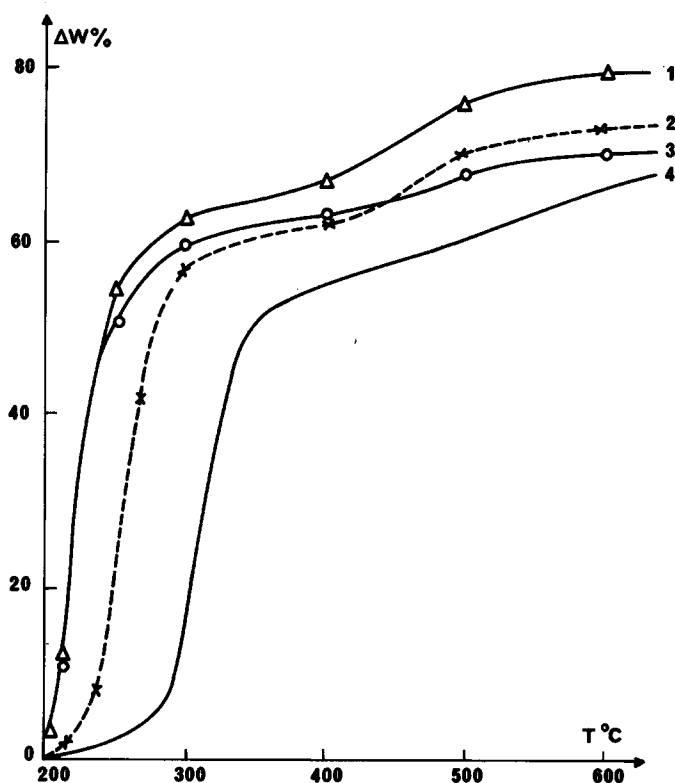


Fig. 2. Curves 1 and 3: Isothermal furnace degradation of saturated chlorinated polyethylene powder, each point being the result of 24 hr of pyrolysis at the corresponding temperature; curve 1 represents total weight loss, curve 3 represents hydrochloric acid evolution which is part of the total weight loss. Curve 2: Isothermal thermobalance degradation of saturated chlorinated polyethylene powder, each point being the result of isothermal 5 hr of treatment at the corresponding temperature. Curve 4: Dynamic thermogravimetric analysis of saturated chlorinated polyethylene powder at a rate of 4°C/min.

weight loss after 24 hr at 500°C is 79%, 70% of which is hydrochloric acid. The difference between these two values corresponds to the release of hydrocarbons which are condensed on the cold parts of the furnace in the form of tar. Since the polymer samples are introduced into a furnace which is already at a high temperature, the phenomenon of "pyrolysis flash" can occur.

Thermal Degradation of Fiber

Dynamic Thermogravimetric Analysis of Powder and Fiber. To compare the thermal degradation of the fiber with that of the powder, a skein of the fiber is hooked onto the hanging arm of the thermobalance. A quartz counterweight is attached to the lower end of the skein to keep it under a weak stress. The results are presented in Figure 3, together with those for the isothermal degradation of the powdered polymer, after 24 hr of fur-

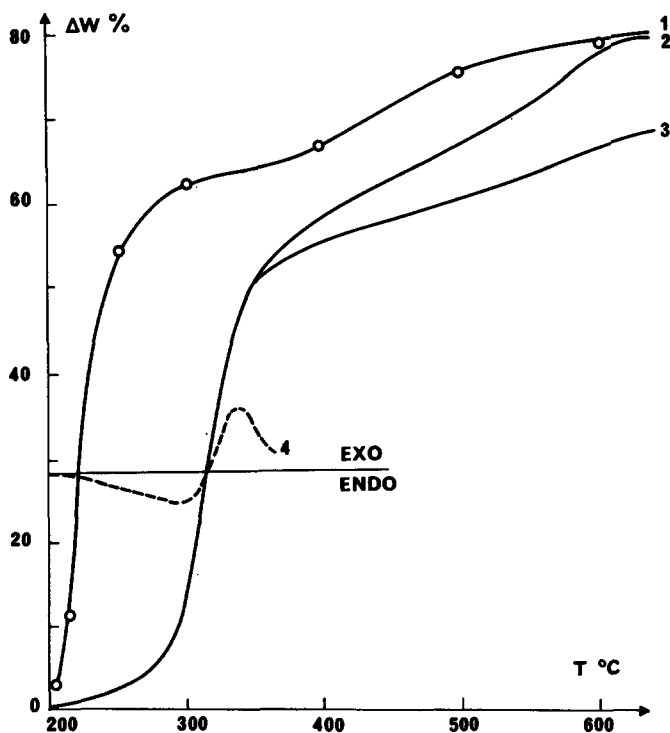


Fig. 3. Curve 1: Isothermal furnace degradation of saturated chlorinated powder, each point being the result of 24 hr of pyrolysis at the corresponding temperature. Curve 2: Dynamic pyrolysis of the fiber in a thermobalance at 4°C/min. Curve 3: Dynamic pyrolysis of the powder in a thermobalance at 4°C/min. Curve 4: Differential thermal analysis at 4°C/min.

nance treatment. After 350°C, the thermal behavior is different, the powder being less easily degradable than the fiber. From 600°C on, the relative weight loss is identical to that obtained for the powder after 24 hr of furnace pyrolysis. This difference of thermal behavior between the fiber and the powder may be a consequence of the physical aspect of the samples rather than a difference of reactional processes; indeed, the fiber reaches thermal equilibrium faster.

Variations of Fiber Length During Pyrolysis. With regard to the variation of fiber length, the behavior of the fiber during the pyrolysis may differ according to the value of the stress applied during the thermal treatment (Fig. 4). If the stress is high, a large relative elongation of the fiber is observed, followed by rupture (Fig. 4, curve 1). If the stress is sufficiently high, it provokes an elongation but not rupture; this elongation is then followed by a relative shrinkage (Fig. 4, curve 2). If the applied stress is sufficiently low, a shrinkage occurs. In this case, the representative graph of the process is not uniform. There is first a shrinkage; then, at around

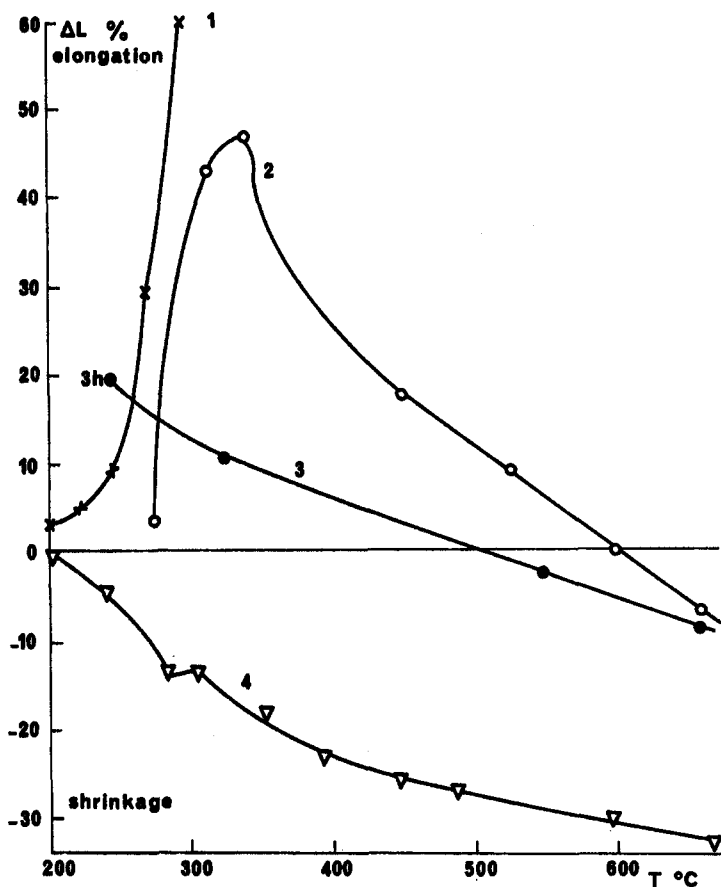


Fig. 4. Length variations of fiber during dynamic pyrolysis at $4^{\circ}\text{C}/\text{min}$; (1) constant high load applied; elongation is observed, followed by rupture at $\Delta L/L = 60\%$; (2) constant weak load applied; elongation is observed, followed by shrinkage; (3) pre-treatment of reticulation during 3 hr at 245°C ; without load applied shrinkage is observed; (4) without load applied, shrinkage is observed.

300°C , a relative extension of 2% occurs, followed by a new shrinkage which reaches 32% near 700°C .

As for the weight losses, the length variations of the fibers indicate two temperature ranges in which the behavior of the fiber is different: (1) 200°C – 320°C , in which either a shrinkage or an elongation of the fiber occurs, depending upon the value of the applied stress; (2) above 320°C , in which range an extension is never observed; further, if the test fiber is held between two fixed points (to prevent shrinkage), then rupture occurs at about 350°C .

In order to limit this tendency to shrink, we have tried to reticulate the fiber by a heating treatment of between 3 and 40 hr at 245°C . During the first few minutes only, a shrinkage or an elongation is observed depending upon the applied stress. However, irrespective of the value of the stress

or the duration of the heating treatment, it is impossible to carry out afterward a pyrolysis with no shrinkage without breaking the fiber as soon as the temperature approaches 350°C.

In all cases, for temperatures above 800°C the fiber is constituted uniquely of carbon and the shrinkage observed is a maximum. In fact, the fiber exhibits no further variation in length, either by continued heating at 800°C or by heating to 1000°C.

PROPERTIES OF THE FIBER AFTER PYROLYSIS ABOVE 800°C

In the temperature range of 800°C–2400°C, the thermal treatment has been carried out using an electron gun (Alcatel) working under high vacuum. This kind of device is far from ideal for this study, owing to the focalization of the energy and the need to work under vacuum. However, the x-ray diffraction spectrograms for the fiber obtained at 800°C, 1500°C, and 2400°C indicate the evolution of their structure, which becomes progressively that of a graphitic carbon (Fig. 5). Simultaneously, a net increase in rupture strength is observed, thus fibers treated at 2000°C have a tenacity five times that of fibers treated at 800°C. Their average properties are: tenacity, 25 daN/mm²; modulus of elasticity, 200 daN/mm²; elongation at break, 1%. These results could certainly be improved by using a more suitable device for the thermal treatment.

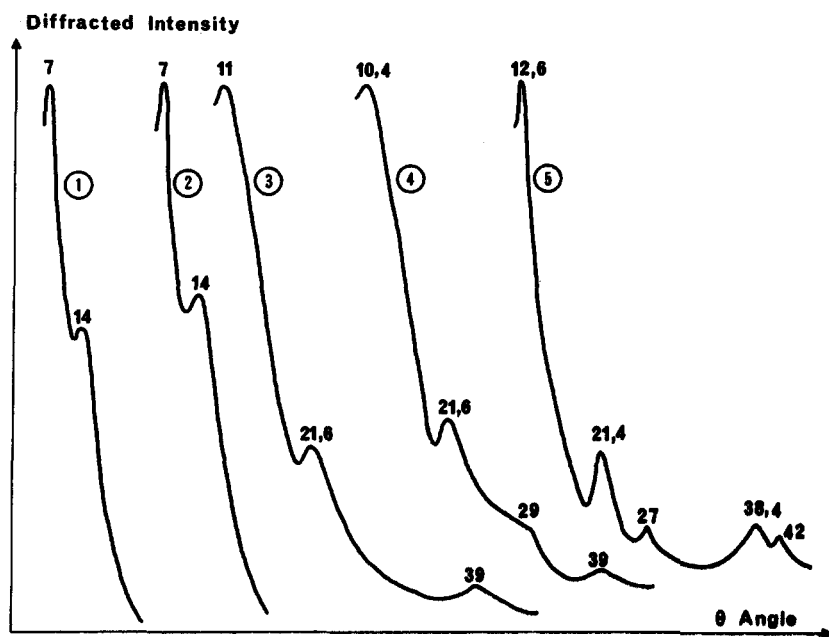


Fig. 5. X-Ray diffraction spectrograms: (1) unstretched fiber; (2) stretched fiber; (3) fiber after pyrolysis at 800°C; (4) fiber after pyrolysis at 1500°C; (5) fiber after pyrolysis at 2000°C.

DISCUSSION

Direct observation of the length variations of fibers obtained from saturated chlorinated polyethylene has allowed us to determine the temperature at which viscous flow of the material occurs. The graphs indicate that this flow arises in the temperature range corresponding to the onset of degradation (Fig. 6) and that the whole process is endothermic (Fig. 3). Thus, a partial fusion of the products appears, which, owing to the greater mobility of the chains or segments of chains, induces the initiation of the degradation reaction. The linearity of the isothermal graphs of degradation in the temperature range of 200°C–260°C (Fig. 1) seems to indicate that the total kinetics of the degradation reaction is controlled either by physical factors or by the rate of the initiation reaction, as long as the fluidity of the material is insufficient.

When the temperature is high enough to permit a considerable viscous flow, not only is the order of the reaction no longer zero, but a process of autoacceleration begins. The graphs representing weight loss versus time are S-shaped (Fig. 7).

The observation of this process of viscous flow is an experimental confirmation of suggestions made by Guyot et al.⁶ concerning poly(vinyl chloride) and Berticat et al.³ concerning chlorinated poly(vinyl chloride). Ac-

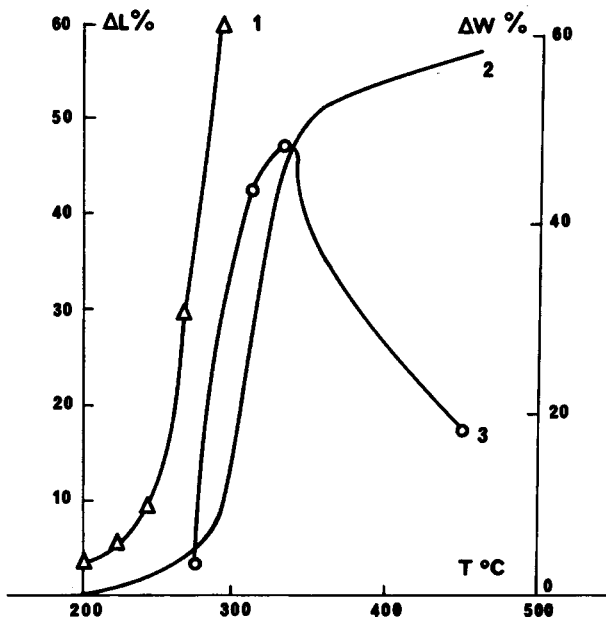


Fig. 6. Viscous flow at temperature of initial degradation during dynamic pyrolysis of fiber at 4°C/min.: (1) constant high load is applied during the pyrolysis of fiber; elongation is observed, followed by rupture at $\Delta L/L = 60\%$; (2) weight loss of fiber during pyrolysis; (3) weak load is applied during pyrolysis of fiber; elongation is followed by shrinkage.

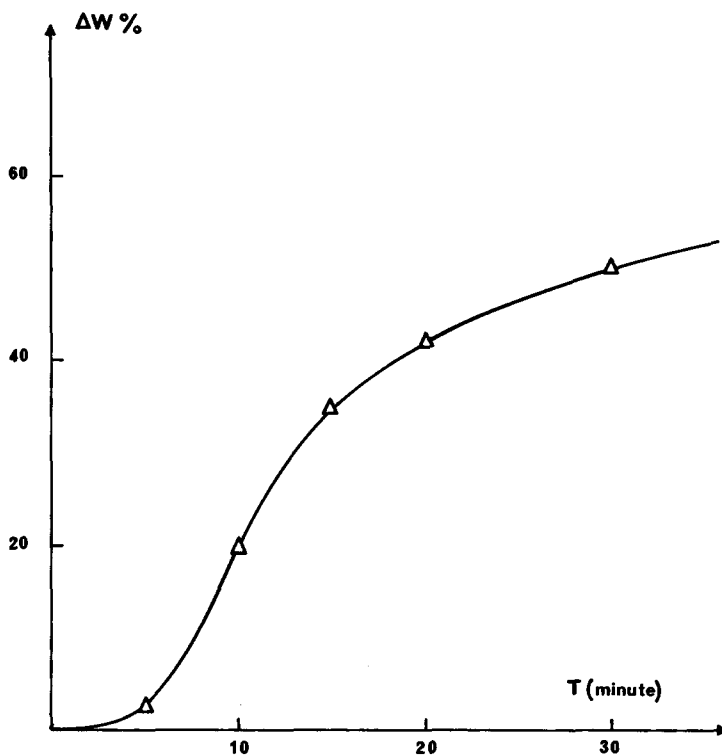


Fig. 7. Isothermal thermogravimetric analysis of saturated chlorinated polyethylene at 300°C.

According to these authors, the autoacceleration of the degradation comes from an intermolecular dehydrochlorination made possible by the reduction of the rigidity of the medium. Thus, there is a formation of tertiary carbon carrying labile atoms of chlorine or hydrogen which constitute new initiation points, followed by the liberation of hydrochloric acid and the formation of double bonds.

The reticulation of the medium does not decrease the number of intermolecular reactions because the autoacceleration subsists, so it must be admitted that the reticulated chains arrange themselves to permit new condensations with the liberation of hydrochloric acid. Further, since the material remains reasonably fluid up to 320°C, the reticulation which appears at lower temperatures ought not lead to too rigid structures, as would be the case if Diels-Alder reactions took place between sequences of conjugated double bonds according to the diagram presented in Figure 8. A unidimensional polymer such as A can no longer easily lose any hydrochloric acid. The graphs of degradation versus temperature ought, therefore, to show a change of slope at the appearance of such a product. That is to say, when the weight loss of the initial polymer reaches 56.7%; then the chlorine content (by weight) of the char ought to be 42.1%. Experi-

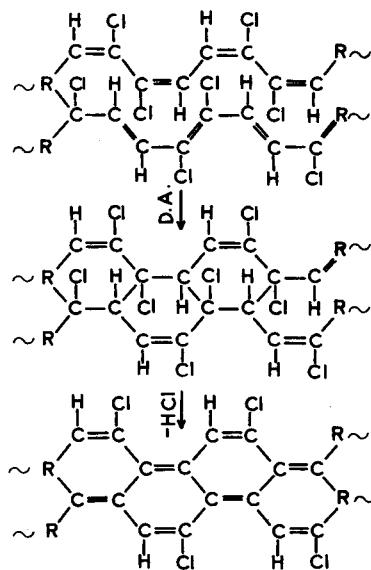


Fig. 8. Reactional process of thermal degradation of saturated chlorinated polyethylene in the first range of temperature.

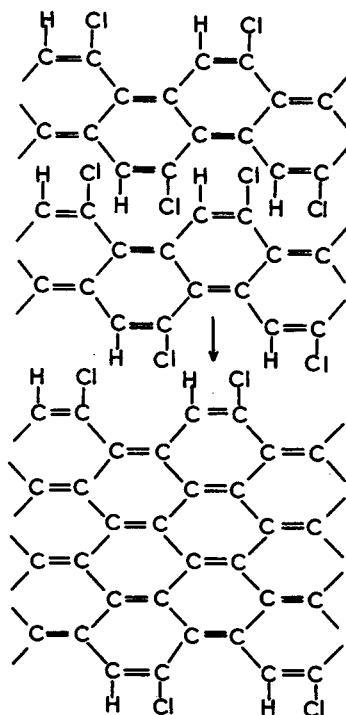


Fig. 9. Reactional process of thermal degradation of saturated chlorinated polyethylene in the second range of temperature.

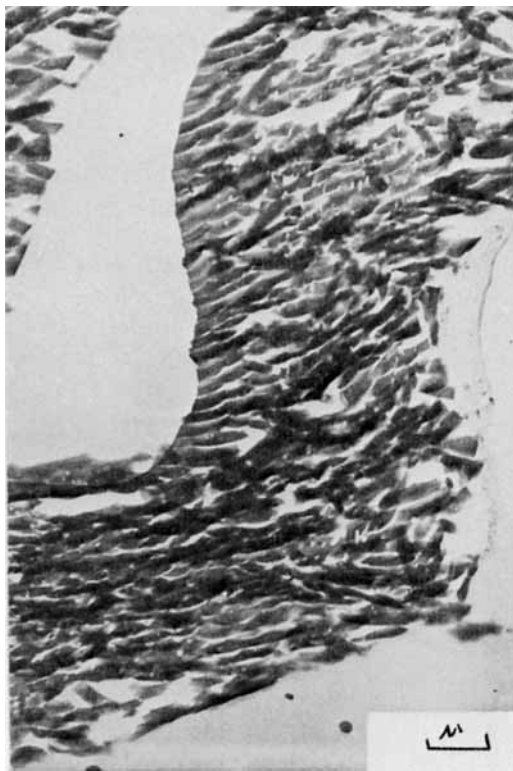


Fig. 10. Microscopic view of a transversal section of fiber after pyrolysis at 800°C.

mentally, the change in slope is observed for a relative weight loss of 57.5%, while the chlorine content of the char is 42%.

The second stage of pyrolysis provokes a reaction of polycondensation concerning essentially the chlorine or hydrogen atoms which are on the periphery of the A-type sequences. At the end of the first process, these units are randomly distributed inside the char. It is necessary that these units orientate themselves, side by side in the same plane, so that they may react with each other to form B-type units (Fig. 9). This arrangement necessitates an increasingly greater activation energy since the medium becomes progressively more rigid with the beginning of the plane organization. This explains why the relative weight loss cannot exceed 60% for degradation temperatures lower than 300°C and why any temperature increase above this limiting value produces a new level of relative weight loss.

These mechanisms are in agreement with the variations observed in fiber length. From 200°C on, depending upon the applied stress, the fiber undergoes either a viscous flow or a shrinkage, but in either case the fluidity of the medium increases to reach a maximum in the temperature range of 300°C-320°C. The A-type units, which only grow in a linear fashion,

could still be sufficiently flexible and mobile with respect to each other to explain this. Above 320°C, the temperature is high enough for the initiation of the condensation reaction, leading to B-type structures, and the material becomes progressively more rigid owing to the pregraphitic organization following this reaction.

Plane structures such as B can pile up in certain zones at equal distances to each other, in the same plane but in different directions, thus producing crystallites of turbostratic carbon. Examination by electron microscopy shows that this arrangement is already visible on the transversal sections of a carbon fiber pyrolyzed at 800°C (Fig. 10).

When the temperature is raised to 2000°C, it is logical to think that the chains linking the crystallites together are broken, at least partially, permitting the orientation of the crystallites in a parallel sense and the rotation of their planes, and thus bringing about the appearance of an almost graphitic carbon with a nonporous structure.

The pyrolysis of saturated chlorinated polyethylene fibers seems, therefore, to present all the theoretical conditions necessary for the preparation of high-modulus carbon fibers. Our results could, no doubt, be considerably improved by the use of a more suitable device for the thermal treatments above 1000°C.

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