

Comparison of Dynamic and Static Degradation of Poly(vinyl Chloride)

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Synopsis

The thermal degradation of PVC was measured under dynamic and static conditions. The UV and IR spectra, as well as the molecular weight distribution of the PVC samples, taken after different time intervals were measured. It was established that during the dynamic PVC degradation, performed in a mixing chamber, two stages with different degradation rates can be distinguished both in extinction and torque vs. time curves. While oxygen does not, dissolved HCl does play an important role in the dynamic degradation: HCl steps into reaction with the formed polyenes and has a catalytic action. The chemical degradation, particularly the crosslinking, produces the changes in the rheological behavior of the material. Results were compared with those obtained under static conditions in argon, air, and HCl atmosphere.

INTRODUCTION

PVC can be processed only in the presence of stabilizers because of its relatively low decomposition temperature. Much experimental and theoretical work has been done to discover the degradation characteristics of this valuable material and to find new ways for proper stabilization.

Most of the experimental work was accomplished with powder or film samples of PVC or in solution, but mostly under static conditions.¹⁻⁵ However, the first step on the way of PVC utilization is the processing where the raw material is exhibited to heat, shear, and oxygen, always under dynamic conditions.

Although measuring equipment which is suitable to test PVC under dynamic conditions exists, the first aim of these—like the HAAKE Rheocord, the Brabender Plastograph, rheometers, and extrusimeters—is to determine the rheological and processing characteristics of PVC compounds. Even the widespread Brabender stability test determines only the end of stabilizer effectivity and the beginning of severe crosslinking and says nothing about the processes which result in these phenomena nor about the effect of the different factors such as heat, shear, oxygen, etc.

In an attempt to compare Brabender stability with a static test, King and Noel⁶ took samples from a Brabender mixing chamber and from the mill and determined the optical changes (color and lightness difference, absorbance, etc.) of the samples. Menges and Müller⁷ determined the maximal residence time in the processing machine based on Brabender measurements. They examined also the effect of N₂ and O₂ on this residence time. Cohen⁸ concluded from this static and dynamic tests that the latter are more informative in the evaluation of PVC compounds. Schramm⁹ measured some of the volatile degradation products during the Brabender test using a gas stream to carry these products

into distilled water the conductivity of which was measured. He established that the conductivity continually increases from the beginning of the measurement and that at a certain point it shows a sharp break.

The above workers, who made their experiments mostly on stabilized PVC compounds, agreed on two points: (1) correlation between static and dynamic tests can be found only in the case of hard PVC compounds, and (2) oxygen increases the rate of degradation also in dynamic tests. Their opinion, however, differs on whether the beginning of degradation can be assigned to a certain point of the torque vs. time curve⁷ or not.^{6,8}

The aim of our work was to get insight into the processes and phenomena of PVC degradation under dynamic conditions and to compare these with those taking place in static tests. With these experiments, we wanted to get nearer to an understanding of the dynamic stability and stabilization of PVC, with special consideration of the processing of PVC.

EXPERIMENTAL

The dynamic measurements were carried out in a Rheomix 600 mixing chamber of a HAAKE Rheocord Type EU-10 V equipment with 180°C set temperature (187–190°C material temperature), 20 rpm, and 60 g charge.

The PVC used in the study was an Ongrovil S 5061 type suspension PVC powder made by Borsod Chemical Works, Hungary. No additives were added to the powder in any of the experiments.

The experiments were carried out according to the most common way: by loading the cold material into the preheated chamber and measuring the change in torque and temperature. During the measurements, according to the characteristic changes of the torque vs. time curve, samples were taken at different intervals. The samples were tested by IR and UV spectroscopy and GPC. The IR spectra of PVC films, pressed at 190°C, 30 s, were recorded using a Nicolet 7199 Fourier Transform IR spectrometer. UV spectra were taken on 5 g/L tetrahydrofuran solutions.

The comparative static tests were carried out on powder samples and films cast from 1,2-dichloroethane solution. The experiments were carried out at 180°C under argon and air atmosphere, as well as in sealed evacuated glass tubes under the evolved HCl. The formation of polyenes and the HCl elimination were measured. For further experimental details, see Refs. 10–13.

RESULTS AND DISCUSSION

The torque and temperature vs. time curves (an example of which is shown in Fig. 1), measured under the given conditions, are well known. The different characteristic changes of the torque vs. time curves can be explained as follows: The first part of the curve characterizes the fusion process. The applied high temperature and the friction cause quick fusion of the homogeneously distributed material. As the melt temperature increases, the torque decreases. Later, because of crosslinking processes, the torque rises again.

The degradation (HCl evolution, polyene formation, discoloration) starts very early, already in the phase of decreasing viscosity. During the degradation, the torque at first rises moderately, then the increase becomes more pronounced.

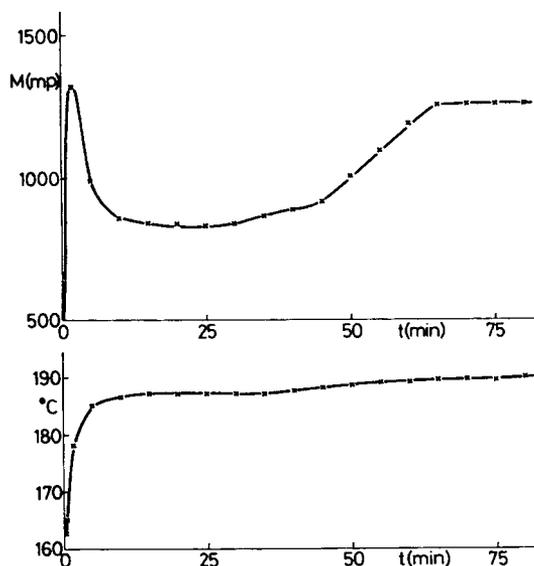


Fig. 1. Torque vs. time and temperature vs. time curves of Ongrovil S 5061 PVC powder (set temp. 180°C, 20 rpm, 60 g).

Finally, the torque does not change further; a limiting value is reached. Although these stages of the torque curves can be definitely distinguished in each measurement, the transitions between them are continuous.

The temperature curve is simpler: at the beginning of the measurement it increases quickly (due to outer heating and high friction). After melting of the material, the temperature reaches a stationary value, then (as degradation proceeds and crosslinking becomes significant) slowly rises again to reach a limiting value. This second increase is caused by the higher friction of crosslinked material.

During the measurements, the formation of polyenes was followed. The UV spectra of the samples dissolved in THF were taken, and the extinctions at different wavelengths, characteristic of polyenes of different lengths, were noted. These extinctions are shown in Figure 2 as a function of time.

In the change of the extinctions, which are proportional to the polyene concentrations, three stages can also be distinguished: two increasing stages with different rates and a decreasing one, after the gel point. This latter can be explained readily (the crosslinked portion of PVC cannot be solved¹¹), but the presence of the first two stages, representing two different degradation rates, is not so evident; however, they can be distinctly seen in each measurement and at each polyene length. It is obvious that there is a definite relation between the torque and the extinction vs. time curves measured on samples taken from the mixing chamber. On the other hand, such two different rates cannot be observed in the static measurements when carried out in argon atmosphere. An example of extinction vs. time curves in static measurements is shown in Figure 3: the extinction increases constantly until the gel point, then decreases.

The spectra obtained in static tests under argon atmosphere are quite different from those obtained under dynamic conditions. In Figure 4, the UV spectra of a sample taken after 80 min from the static test and a sample taken after 25 min

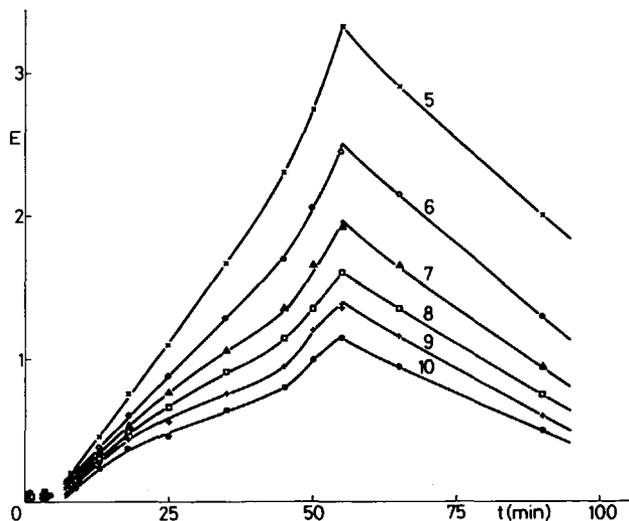


Fig. 2. Extinction of polyenes with different lengths (n) as function of time, measured under dynamic conditions (set temp. 180°C, 20 rpm, 60 g). Extinctions were calculated to 1%, 1 cm: (X) $n = 5$; (O) $n = 6$; (Δ) $n = 7$; (\square) $n = 8$; (+) $n = 9$; (\bullet) $n = 10$.

from the dynamic test are compared. Because of the different degradation conditions (temperature, shear, rate, etc.) in the two types of tests, we have chosen the gel points (i.e., 159 and 55 min, respectively) as references, and we have compared the spectra taken at times about half of these values.

As can be seen in Figure 4, the concentration of the longer polyenes is much higher in the static test than in the dynamic test. Thus, it is obvious that the degradation under dynamic and static conditions proceeds differently. How can the speeding up be explained in the second stage of both (torque and extinction vs. time) curves of the dynamic test? What is the cause of the differences between the dynamic and static measurements? These are the questions which must be cleared first to get nearer to the understanding of the problem of dynamic stability.

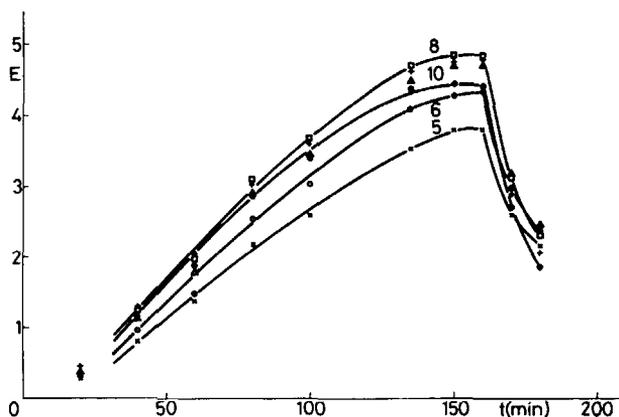


Fig. 3. Extinction of polyenes with different lengths (n) as function of time, measured under static conditions (180°C, argon). Extinctions were calculated to 1%, 1 cm: (X) $n = 5$; (O) $n = 6$; (Δ) $n = 7$; (\square) $n = 8$; (+) $n = 9$; (\bullet) $n = 10$.

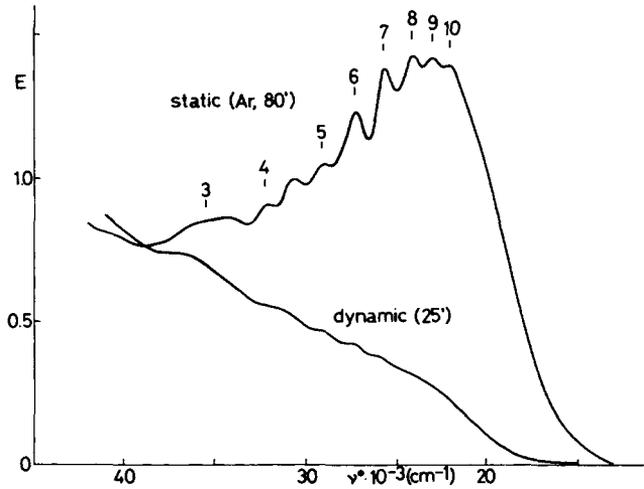


Fig. 4. UV spectra of samples degraded under dynamic and static (Ar) conditions (5 g/L THF, $l = 1.0$ cm).

It could be assumed that the relatively abrupt rheological changes in the second stage cause the change in the degradation rate. The change in torque might originate from reaching a “critical” crosslink density which causes a severe decrease in mobility and so a more pronounced, further crosslinking. The increase in molecular weight and the decrease in molecular mobility increase friction and frictional heat. The increased torque and the elevated temperature speed up all the chemical processes: HCl elimination, polyene formation, and crosslinking.

Thorough examination of the results does not confirm this assumption. The changes in the torque take place later than the changes in the chemical process: as is shown in Figure 5, both the rate increase and the gel point in the extinction

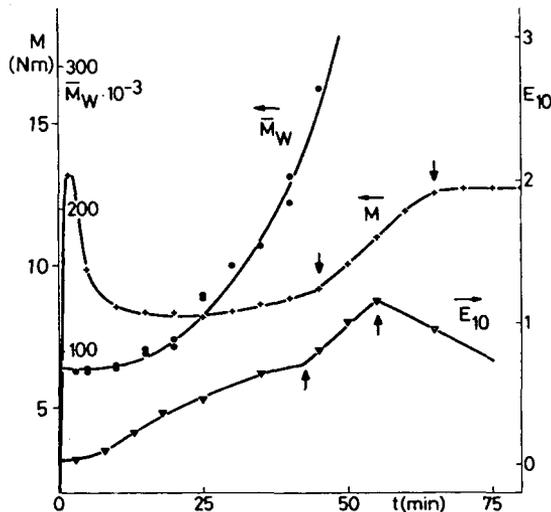


Fig. 5. Torque (M), molecular weight (\bar{M}_w), and extinction of polyene $n = 10$ (E_{10}) vs. time curves (set temp. 180°C , 20 rpm, 60 g). Arrows indicate times where sudden changes occur.

vs. time curve occur earlier than the corresponding changes in the torque vs. time curve. Based on the data in Figure 5, the conclusion can be drawn that the cause of these changes must be looked for in the chemical processes and that these bring forth the changes in the molecular structure and rheological behavior, just inversely as supposed above.

This conclusion is confirmed by the change in molecular weight during the measurement (Fig. 5). The weight-average molecular weight (\bar{M}_w) of the samples taken at different intervals from the mixing chamber does not change at the beginning of the measurement, but after a short period it begins to increase. At the gel point, \bar{M}_w tends to infinity. (It is to be noted that the molecular weight data determined by GPC are not always strictly exact due to long-chain branching in the degraded samples.) These changes seem to be connected with the chemical processes and especially with the changes in the polyene concentration. The polyene concentration begins to grow immediately after the start of the measurement; the increasing polyene concentration brings forth cross-linking, and the molecular weight increases. The material with higher molecular weight has different rheological characteristics, which shows up in the torque changes.

However, all these considerations do not clear up the cause of the differences observed between dynamic and static measurements. To explain these, the effect of two factors must be taken into consideration: under dynamic conditions, oxygen and HCl are present during the mixing of the PVC melt. As was shown earlier,^{13,15} both gases take part in reactions with the formed polyenes. These reactions result in a relatively lower amount of long polyenes and could cause the characteristic differences between the UV spectra measured under static and dynamic conditions.

In Figure 6, three UV spectra can be seen. The samples were prepared under static (in argon and air) and dynamic (in the mixing head) conditions; the spectra shown are taken again at times about half of the corresponding gel points. As an effect of oxygen, the spectrum becomes more similar to the spectra measured on samples taken from the mixing head. On the basis of these spectra, it could be accepted that the oxygen present during the degradation plays an important

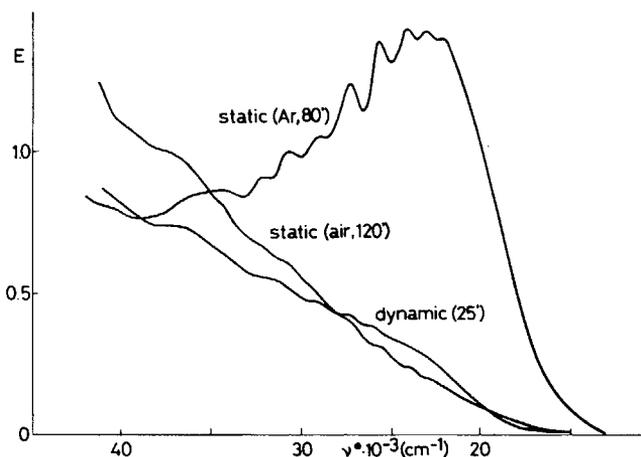


Fig. 6. UV spectra of samples degraded under static (Ar and air) and dynamic conditions (5 g/L THF, $l = 1.0$ cm).

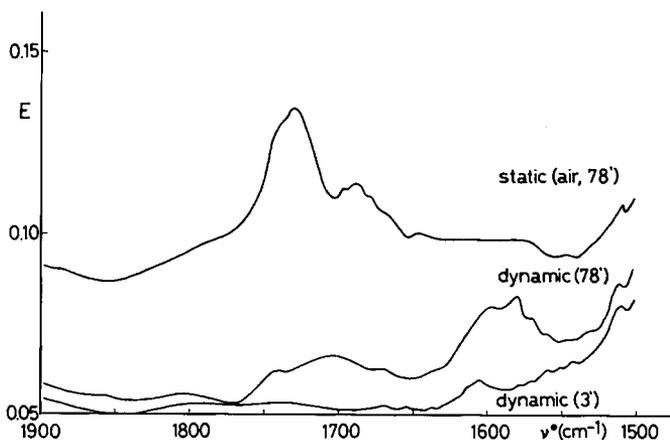


Fig. 7. IR spectra of samples degraded under static (air) and dynamic conditions. The spectra were normalized to 80 μm film thickness. The dynamic (3') sample serves as reference.

role and that the secondary reactions between oxygen and polyenes change the feature of the degradation process and the UV spectra. But thermo-oxidative degradation of PVC results in carbonyl groups¹⁵ which can easily be observed in the IR spectra of the samples. However, in the samples from the mixing chamber, the amount of carbonyl groups was several times smaller than in the samples degraded under static conditions in air (Fig. 7). The comparison here was made at identical degradation times, although the material temperature was 7–10°C higher in the mixing chamber. The peak at about 1600 cm^{-1} in the spectra of dynamic samples can be assigned to unsaturation.¹⁶ The concentration of double bonds is much lower in the sample degraded in air, as oxygen consumed most of the double bonds, and also the rate of degradation is lower.

The UV spectra of PVC samples measured under static conditions in argon atmosphere and in sealed evacuated tubes under the evolved HCl are compared with the spectrum obtained under dynamic conditions in Figure 8. Again,

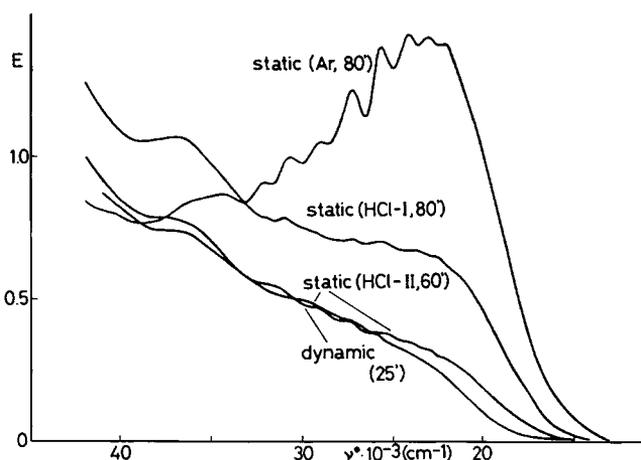


Fig. 8. UV spectra of samples degraded under static conditions in Ar and in atmospheres with different HCl partial pressures as compared to the spectra of a sample degraded under dynamic conditions (5 g/L THF, $l = 1.0 \text{ cm}$).

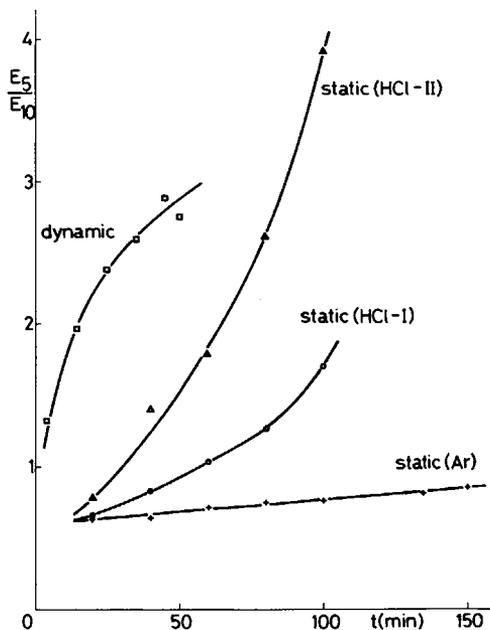


Fig. 9. Relative extinctions (E_5/E_{10}) of samples degraded under static (Ar and HCl) and dynamic conditions.

spectra taken at times about half of the corresponding gel points are shown. Two series of experiments were conducted with 8.2-cc sealed tubes completely immersed in the 180°C silicon oil bath. In series I, 0.75 g PVC was degraded in the tube; the HCl loss conversion at 80 min was about 1%, corresponding to 0.58 atm HCl pressure at 180°C. In series II, 2.5 g PVC was placed in the tube; the conversion was about 0.8%, corresponding to 1.86 atm HCl at 180°C, 60 min.

It can be established that with increasing HCl pressure, the UV spectra of samples from the static measurements approach that of the sample treated in the mixing chamber. This shows that the HCl present in the system plays an important role in the degradation process taking place in the mixing chamber. Although the mixing head is not hermetically sealed and so the HCl pressure cannot exceed significantly the atmospheric pressure, the relatively low melt viscosity and the large charge probably make possible the dissolution of a considerable amount of HCl. This dissolved HCl changes the shape of the UV spectra, and at the same time, its catalytic action^{13,14} can result in the characteristic increase in the degradation rate clearly visible on the extinction vs. time curves. The rate of crosslinking (a secondary reaction of polyenes¹²) increases, too, causing the increase in torque.

The differences in the degradation processes taking place under static and dynamic conditions are well demonstrated in Figure 9, where the relative extinctions of polyenes containing 5 and 10 double bonds are shown. The values and tendencies of the curves in the static test show the effect of HCl. The higher slope of E_5/E_{10} vs. time curves in the dynamic test is a result of several factors, e.g., the higher temperature, the relatively high HCl concentration already at the early stages, and also the shear.

CONCLUSIONS

A comparison of the dynamic and static PVC degradation shows that there are significant differences in the two cases. On the basis of the examinations, the following conclusions can be drawn:

During the degradation of PVC under dynamic conditions, two stages can be distinguished with different degradation rates. The different rates can be observed both in the extinction and torque vs. time curves.

Although oxygen must be present during the dynamic degradation, a much lower amount of carbonyl groups was formed than in the comparative static test performed under air atmosphere.

The HCl, especially the dissolved HCl, plays a determining role in the degradation through its catalytic action.

The rheological behavior of the PVC continuously changes during the degradation owing to the chemical reactions (polyene formation and crosslinking).

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