Journal of Thermal Analysis, Vol. 52 (1998) 697-703

THERMAL STABILITY OF A PARA-CRESOL NOVOLAC RESIN

A. Hamou[1], *C Devallencourt*[2], *F. Burel*[3], *J. M. Saiter*[2] *and M. Belbachir*[1]

[1]Laboratoire d'Etude des Matériaux Amorphes et des Polymères, Institut de Physique Université d'Oran, Es Sénia, Algérie
[2]Laboratoire d'Etude et de Caractérisation des Amorphes et des Polymères, Université de Rouen, Faculté des Sciences, 76821 Mont-Saint-Aignan Cedex
[3]Laboratoire des Matériaux Macromoléculaires, Institut National des Sciences Appliquées de Rouen, Place Emile Blondel, B. P. 08, 76131 Mont-Saint-Aignan Cedex, France

Abstract

The thermal stability of *p*-cresol novolac resin was studied by means of DSC, X-ray diffraction, thermogravimetry and SEC investigations. After 30 thermal cycles in which the same sample was heated, cooled and heated again, without attainment of the temperature of degradation at any time in the experiment, important structural modifications are observed. At the end of the experiments, the resin, which is initially highly crystalline, exhibits all the characteristics of a semi-crystalline material.

Keywords: DSC, novolac resin, thermogravimetry, X-ray diffraction

Introduction

The *p*-phenol novolac resins have long been known for their applications as insulants in electronic engineering, in the automobile industry, in adhesive production and in the field of chemical coatings [1]. These resins have good chemical and mechanical characteristics, but exhibit a weak thermooxidative resistance. Thus, several structural modifications have been proposed, involving copolymerization with long-chain alkyl phenols, or blending with elastomers or epoxy resins [2, 3]. The complete characterization of such a material requires the use of many experimental methods (DSC, IR spectroscopy, NMR, SEC, etc.) [4] and the thermal stability is often studied by means of thermogravimetry. In this case, it is the value of the highest temperature that the resin can reach without exhibiting a mass loss (i.e. thermal degradation) which is determined. In this work we present results obtained by DSC, X-ray, thermogravimetry and SEC on one of the more simple novolac resins subjected to thermal cycles in which the same sample is heated, cooled and heated again for a long time without attainment of the temperature of degradation at any time in the experiment.

1418-2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental methods

Poly(hydroxy-1-methyl-3-phenylenemethylene) was synthetized by acidic catalysis (oxalic acid), using a reaction mixture with a formaldehyde (37% in H_2O, Aldrich)/*p*-cresol (99%, Merck) molar ratio of 0.85, as described by Koebner [5] (Fig. 1). The final product is a white powder.

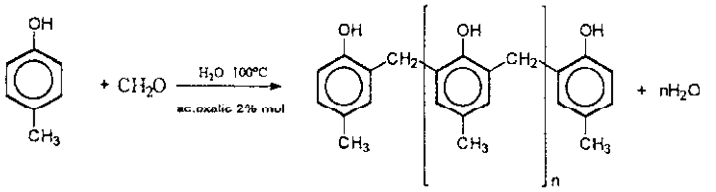

Fig. 1 Formula of poly(hydroxy-1-metyl-3 phenylenemethylene)

By means of size exclusion chromatography (SEC), the average molecular weight was computed, by using a water 510 Gel Permeation Chromatograph with polystyrene standards. The apparatus was equipped with five μStyragel columns (100, 500, 10^3, 10^4 and 10^5 Å) operating in toluene; detection was made with an R 401 Waters refractometric detector.

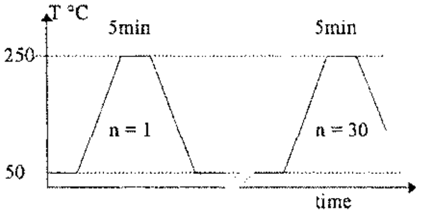

Fig. 2 Thermal cycles performed by DSC; *n* is the number of cycles

Differential scanning calorimetry (DSC) was performed with a Perkin Elmer Series 4 calorimeter. Experiments were carried out under a nitrogen flow at a heating rate of 10°C min^{-1}. To eliminate problems of mass variations during the thermal cycles, the samples were put in sealed capsules in granular form. Calibration of the calorimeter with regard to temperature and energy was achieved by measurement of the temperature and enthalpy of melting of indium as standard material. The thermal stability of the polymer was tested by DSC during 30 consecutive cycles (Fig. 2). During these cycles, the same sample was used and no interruption was allowed during the sequences of measurements. Thermogravimetric measurements were made on a TG, DTA 92 Setaram thermobalance, from 20 to 900°C at 5°C min^{-1} and under a nitrogen flow. Finally, the existence of a crystalline or/and a vitreous phase was checked by X-ray diffraction, with the help of a fast curved detector, using CoK_α radiation.

Results and discussion

From SEC, the average molecular weight of the studied sample was found to be $\overline{Mn}\approx 580$. From the X-ray diffraction pattern (Fig. 3), the existence of rays and the lack of the characteristic vitreous diffuse hump allow the conclusion that the sample exhibits a high crystallinity ratio.

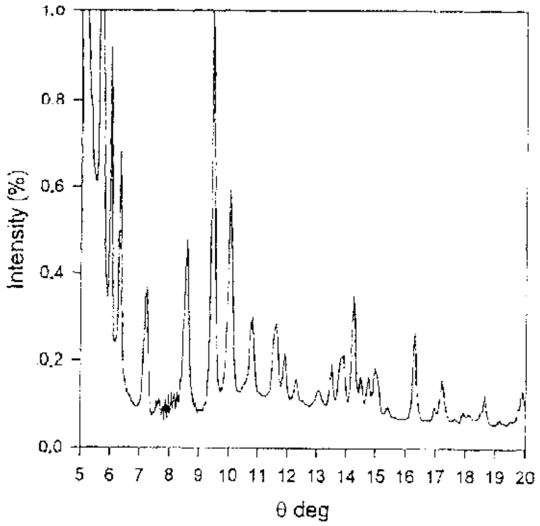

Fig. 3 X-ray diffraction pattern obtained on the sample before the thermal cycles

Figure 4a depicts the enthalpic curve obtained after the first heating period. The endothermic reaction at T_m=205°C (onset temperature), with an enthalpy ΔH_M=135.2 J g^{-1}, associated with melting, is the only reaction observed. This result is consistent with the existence of a crystalline phase in the sample. It should be pointed out that a small shoulder occurs at the beginning of this melting peak. Finally, the thermogravimetric curve (Fig. 5) exhibits only one main degradation process, with a temperature of maximum decomposition close to 477°C. No water evaporation nor other mass loss is observed in the temperature range between 30 and 300°C.

Figure 4b displays the enthalpic curve resulting during the first cooling period. Only the exothermic reaction at $T_c\approx$160.6°C, is observed with an enthalpy ΔH_c=112 J g^{-1}. This reaction is associated with crystallization of the melt. The observations made during the 30 cycles peformed may be divided into three parts:

i) Up to the 15th scan, during the heating or the cooling periods, no reactions other than the first endothermic and exothermic peaks described above are observed. Nevertheless, after each cycle, the temperatures of the melting peak and the crystallization peak decrease as the number of cycle increases. The same variations are observed for the enthalpy of melting (ΔH_M) and for the enthalpy of crystallization (ΔH_c). Finally, the small shoulder observed in the first scan becomes an endothermic peak after the 15th scan.

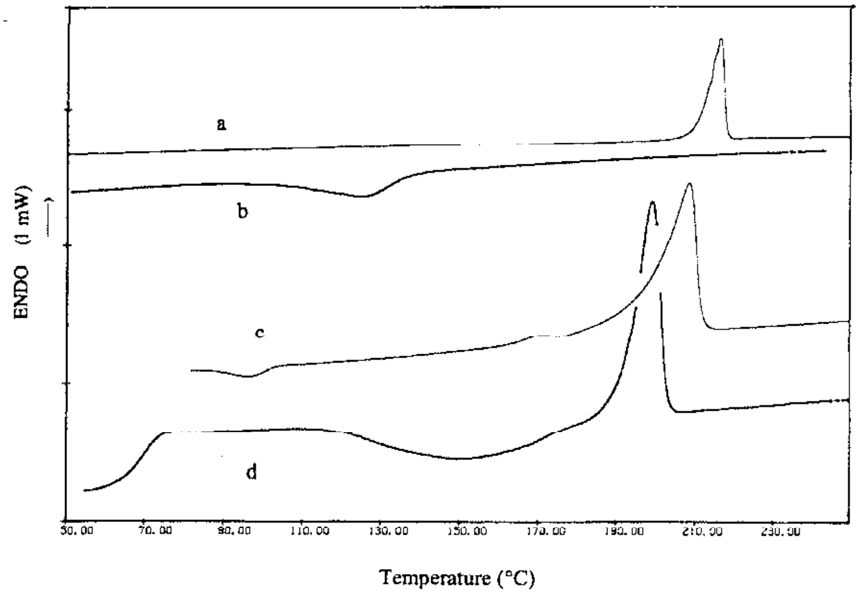

Fig. 4 DSC curves obtained during a) the first heating period, b) the first cooling period, c) the 17th scan, d) the 27th scan. For a, b and c, full X scale=50 to 250°C, while for d, X=30 to 250°C; for a and b, full Y scale=15 mW, for c Y=5 mW, and for d, Y=1 mW

ii) From the 15th up to the 18th scan, the behaviour observed previously remains the same. The decreases in T_m, T_c, ΔH_M and ΔH_c continue. Nevertheless, during the heating period, a new exothermic reaction is observed (Fig. 4c). This

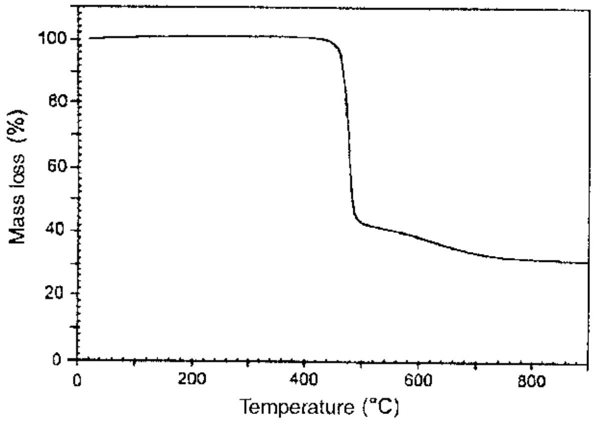

Fig. 5 Thermogravimetric curve obtained on the resin before the thermal cycles

new reaction is attributed to a devitrification process. In spite of the lack of evidence of a glass transition reaction, this indicates that a vitreous phase exists in the sample. We believe that the glass transition is not observed in our curves because it is out of the range of temperatures scanned during the experiments. The last point to be noted at this stage of the protocol is that the temperature of devitrification remains practically constant, while the enthalpy increases. This indicates that, after each scan, the ability to devitrify increases, or the quantity of vitreous phase increases compared to the crystalline phase, or both.

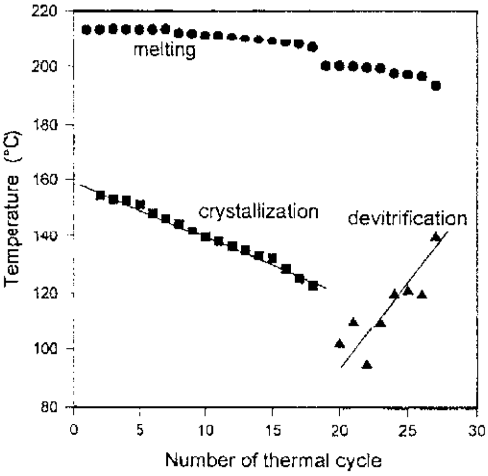

Fig. 6 Temperatures of melting, crystallization and devitrification obtained during each cycle

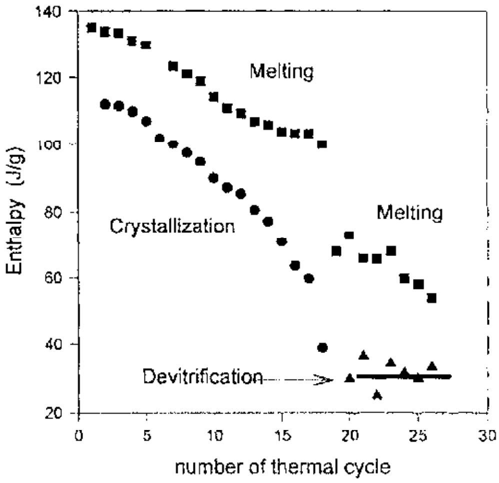

Fig. 7 Melting, crystallization and devitrification enthalpies determined during each cycle

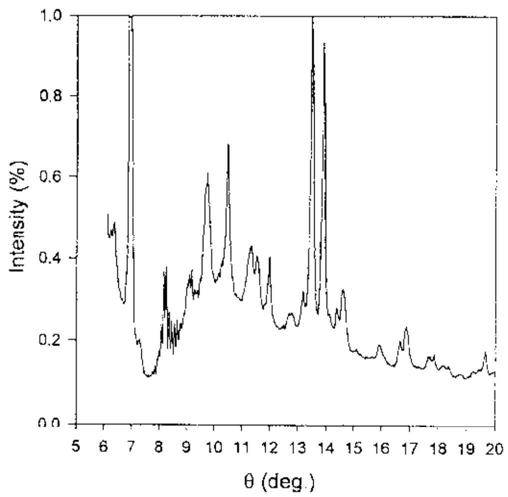

Fig. 8 X ray diffraction pattern obtained on the sample after 30 cycles

iii) From the 18th up to the 30th scan, the crystallization observed during the cooling period vanishes and the melting enthalpy continues to decrease. For the devitrification process, the enthalpy remains constant, but its temperature increases drastically in such a way that the peaks of devitrification and melting are superimposed by the 24th scan. We observe the glass transition, which remains at the same temperature (T_g≈40°C), while the melting enthalpy continues to decrease. All the values detemined during these thermal cycles are reported in Figs 6 and 7.

X-ray diffraction (Fig. 8) and SEC analysis were performed on the sample which had undergone the 30 thermal cycles. The X-ray diffraction pattern showed rays and evidence of a diffuse hump, which indicates that part of the sample remained crystallized while another part was vitreous. This is consistent with our DSC data. From the SEC analysis, we observed the existence of two new small peaks, indicating a new distribution of $\overline{Mn}$ at $\overline{Mn}$≈900 and ≈720. This indicates that the lengths of some chains increase, but as regards the magnitudes of the new peaks, this transformation involves a very small volume of the sample. Thus, a polymerization reaction of low magnitude may occur during these thermal cycles.

Conclusions

The thermal stability of a *p*-cresol novolac resin was investigated. Thermogravimetry revealed no degradation before 400°C, which demonstrates the good thermal stability of this resin. Nevertheless, when experiments were performed in another way, by heating, cooling and heating again during 30 thermal cycles, without attainment of the temperature of degradation at any time in the experiment, it was found that structural modifications can occur. The previous highly crystalline structure of the resin becomes semicrystalline with a value of T_g close to 40°C, leading to the possibility of physical aging during room-temperature storage.

* * *

Our thanks to FICU (AUPELF UREF) for financial support.

References

1 P. M. Kopf and A. D. Little, Encyclopaedia of Polymer Science and Engineering, Vol. 11, 2nd ed. John Wiley & Sons, Inc., 1988 p. 45.
2 C. P. Reghunadhan Nair, R. L. Bindu and V. C. Joseph, J. Polym. Sci., Part A, Polym. Chem., 33 (1995) 621.
3 C. N. Cascaval, Eur. Polym. J., 30 (1994) 969.
4 C. Devallencourt, J. M. Saiter, A. Fafet and E. Ubrich, Thermochim. Acta, 259 (1995) 143.
5 M. Koebner, Brit. Plastics, 11 (1939) 43.