

Thermal Analysis of Alumina Grafted with Acrylic Acid and It's Polymeric Schiff-Base Derivatives

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Abstract

The thermal behaviors of the alumina-grafted acrylic acid monomer and its extended poly (acrylic acid) polymers (A), alumina-grafted 1-acryloxy-4-butoxybenzylideneaminophenyl, polymer (B) and alumina-grafted 1-acryloxy-4-octoxy benzylideneamino phenyl, polymer (C) were investigated using differential scanning calorimetry (DSC), Thermal gravimetric (TG) and differential thermal gravimetric analysis (DTG). The thermal properties of all synthesized materials are discussed related their structural formula.

Introduction

Thermal Analysis is a well-established set of techniques for obtaining qualitative and quantitative information about the effects of various heat treatments on materials of all kinds, including new chemical compounds, plastics, ceramics, alloys, construction materials, minerals, foods and medicines. Heating is performed under strictly controlled conditions and can reveal changes in structure and other important properties of the material being studied. Such studies are of great practical importance in the use of materials (Menczel and Prime, 2007).

Most organic polymeric materials melt below 200°C and most of them begin to degrade rapidly at temperatures only slightly above 200°C. Thermally stable polymers are generally considered to be those which will withstand much higher temperatures without loss of strength or change of structure. In general we expect these materials to withstand at least 300°C in air and up to 500°C or higher in inert atmospheres.

Polymers which show these properties are usually highly aromatic in structure, often with heterocyclic units, high melting, sometimes infusible and usually with low

solubility in all solvents (Menczel, 2009). Macroscopic Thermal Analysis of Polymeric Materials systematically treats measurements by thermal analysis and the quantitative link to microscopic, molecular structure and mobility. Reversible and irreversible thermodynamics, kinetics, quantum mechanics, and statistical thermodynamics are the roots of the described thermal analysis (Wundeslich, 2005).

Synthesis and free-radical alumina-grafting polymerization of acrylic acid monomer and their Schiff-base derivatives using benzoyl peroxide as initiator was attempted. All the prepared compounds and grafted polymers were characterized by different analytical and spectroscopic techniques, with all details reported in our previous work (Sultan et al, 2010).

In this work we study the liquid crystalline properties to the organic compounds in polymers, and thermal behavior to all compounds prepared. The present work, focusing on thermal characterization and behaviour of the entire grafted polymer will be explored using Differential Scanning Calorimeter (DSC) and Thermo Gravimetric (TG) and Differential Thermal Analysis (DTA).

Experimental

Preparation of Alumina-graft acrylic acid monomer

(21 g) Alumina was weighted and placed in one-neck round bottom flask, followed by addition of (30) ml dry-toluene.

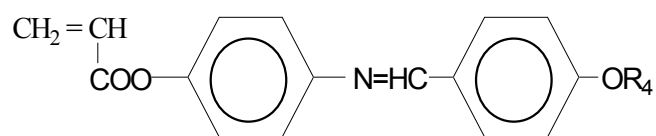
The monomer acrylic acid (7) g was added to the standard solution of Alumina-toluene drop wise at room temperature, then the mixture was left stirring for (3) hours. The product was filtered and washed with (20) ml distilled water, then (20) ml of acetone. The solid product was left to dry at room temperature.

Preparation of polymers by free radical polymerization.

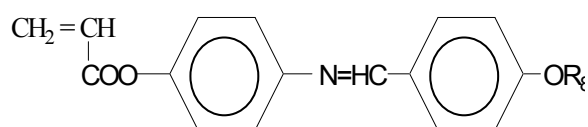
Benzoyl peroxide was used as initiator. It was purified by dissolving certain amount in minimum quantity of chloroform until got a clear solution. Petroleum ether (60-80) °C was added drop wise until white precipitate started to appear, then the solid product filtered and left to dry in descanter at room temperature.

Graft polymerization was carried out the following polymers were obtained:

- 1) Extending alumina-graft acrylic acid with additional acrylic acid monomer to get polymer (A).
- 2) Extending alumina-graft acrylic acid with 1-acryloxy-4-butoxy benzylidene amino phenyl (II) to get polymer (B).



- 3) Extending alumina-graft acrylic acid with 1-acryloxy-4-octoxy benzylidene amino phenyl (III) to get polymer (C).



In all of those preparation a two neck round-bottom flask contain (20) ml of dry toluene as a solvent was placed in controlled water bath at (75°C) (± 2) under nitrogen atmosphere, after (5) minutes (0.1) g benzoyl peroxide was added, followed by addition of (5) g of alumina-graft acrylic acid monomer, after that (5) g of each of the following monomers was added, (i.e. I, II, III) separately. So we will have three different reactions, with stirring for (1) hour. The product was filtered and washed firstly with (15) ml of toluene and secondly with (15) ml of acetone, then left to dry at room temperature.

All the prepared materials were characterized by FTIR spectroscopy and some of those pure materials were characterized by $^1\text{H-NMR}$ (Sultan et al, 2010).

Differential Scanning Calorimeter (DSC)

DSC measurements were recorded on Netzsch STA (University of Trento, Italy). Temperature range up to 450 °C with a heating rate of 10 °C / min in argon atmosphere was reached. Sensitivity curve was carried out performing thermal analysis on different standard materials in order to evaluate changes in enthalpy during the thermal treatments.

Thermo gravimetric (TG) and differential analysis (DTA).

TG and DTA were performed on a Labsys Stream Thermobalance (University of Trento, Italy), operating in the range (20 -700)

°C, with a heating rate of (10) °C min⁻¹. Thermal analysis was recorded under 100cm³ min⁻¹ helium flux (99.99%). Powdered samples were analyzed using alumina crucibles and $\alpha\text{-Al}_2\text{O}_3$ as reference.

Results and Discussion

DSC thermograms for grafted monomer and polymers are illustrated in Figures (1) to (4) and thermal properties are summarized in Table (1) The DSC thermogram of alumina-graft acrylic acid monomer, Figure (1), showed two endothermic peaks. The first big one centered at 215 °C followed by a small one at 286 °C. These peaks could be arises from the degradation of high molecular weight chains accompanying with high value of enthalpy (46.46 Jg⁻¹) compared with the other one.

The thermogram of alumina-graft monomer polymerized with acrylic acid monomer showed two peaks, exo- and endothermic, Figure (2). The first exothermic peak centered at 139 °C could be attributed to the crystallization transition temperature. This resulted semi crystalline polymers with crystals of different sizes and orientation. Thus, the crystallization temperature brought about crystals to the same sizes and perfection. The second endothermic peak at 240 °C which is almost the half way of the grafted monomer gave as overlapping peaks representing the degradation of the entire

polydispers polymer. The enthalpy of melting is also high compared with crystallization exothermic value.

Table (1): DSC data for grafted monomer and polymers A, B and C

Polymer	1 st - Transition Temperature / °C ($\Delta H/J/g$)	2 nd - Transition Temperature / °C ($\Delta H/J/g$)	3 rd - Transition Temperature / °C ($\Delta H/J/g$)
Graft Monomer	215(46.46)	286(3.52)	
Polymer A	139(11.63)	230(47.71)	
Polymer B	149(4.38)	204(22.97)	285(4.05)
Polymer C	138(3.67)	213(25.27)	286(4.38)

The thermograms of polymers B and C, Figures (3) and (4), showed three endothermic transition peaks. The first peak centered at 149 °C and 138 °C for polymers B and C respectively, represent the crystal to crystal transition temperature (obtaining crystalline perfection). The second peaks (204 °C and 213 °C) due to the crystal to liquid

crystal transition temperatures. While, the third transition peaks (285 °C and 286 °C) belong to the transition from liquid crystal to isotropic liquid phase for polymers B and C respectively. The liquid crystalline properties of these polymers are discussed in our previous work (Demos, 1988).

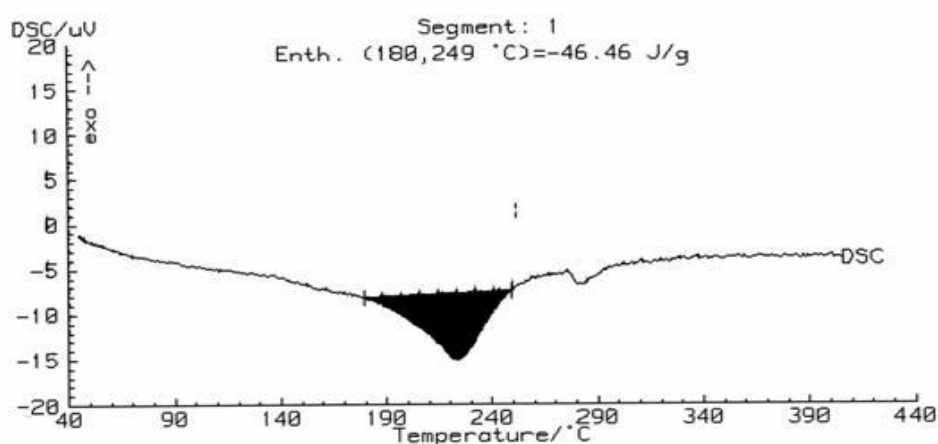


Figure (1): The DSC thermogram of trace for Alumina-graft acrylic acid monomer

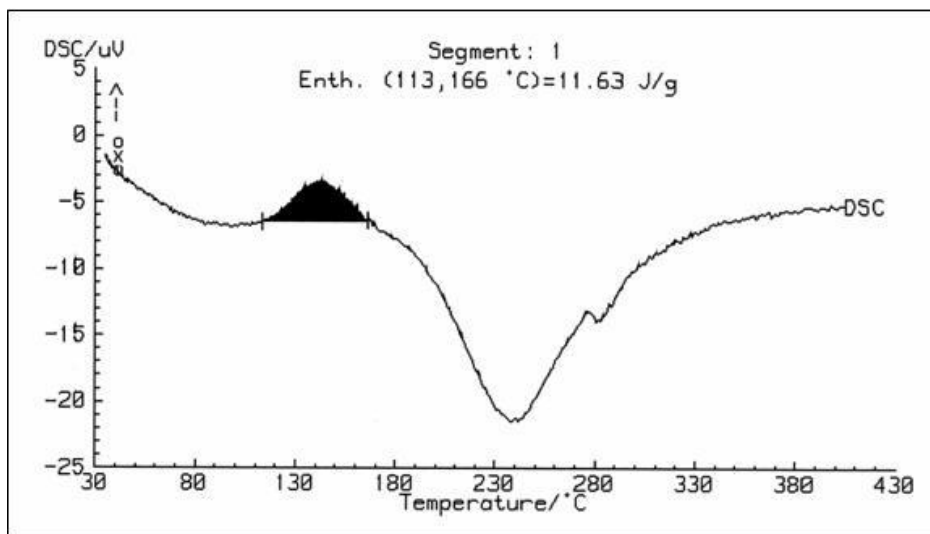


Figure (2): The DSC thermogram of trace for polymer A.

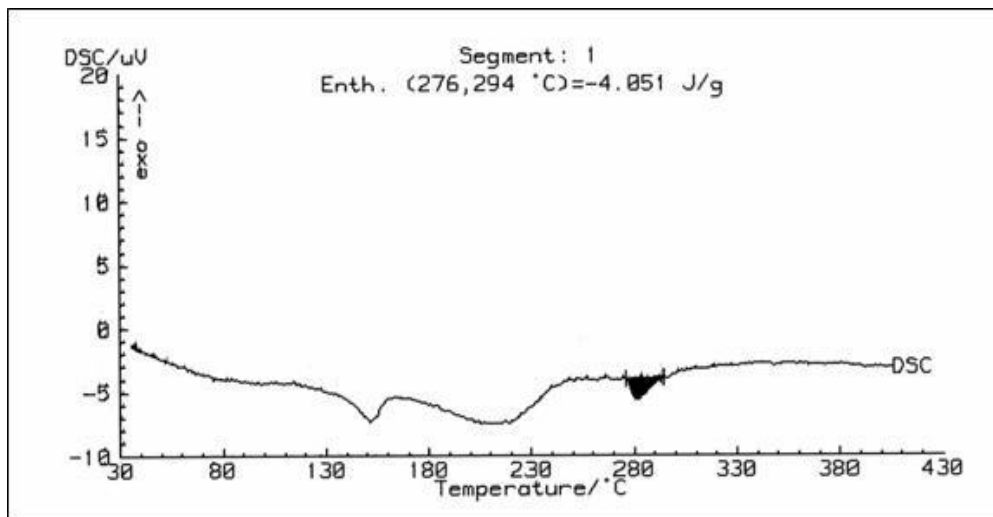


Figure (3): The DSC thermogram of trace for polymer B.

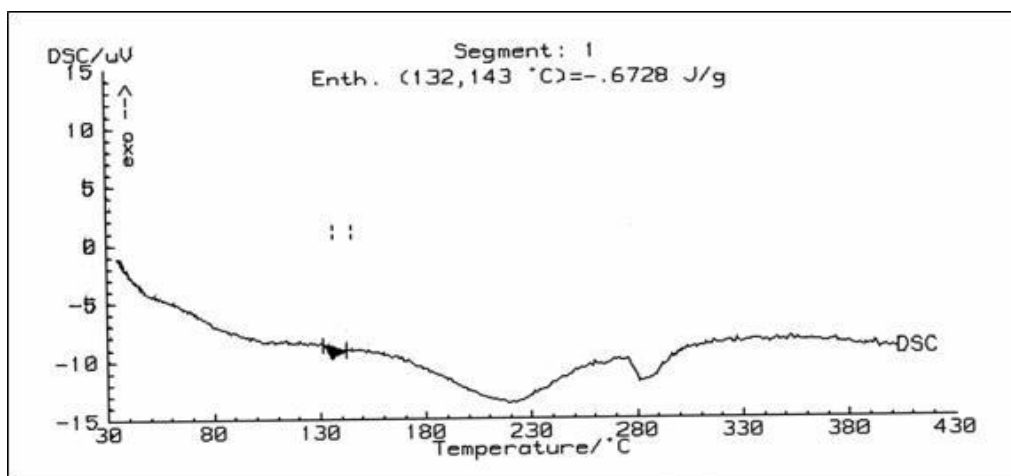


Figure (4): The DSC thermogram of trace for polymer C.

Thermal Gravimetric (TG) and Differential Thermal Gravimetric (DTG) Analysis

The thermal stability of grafted monomer and polymers was measured by thermogravimetry using TG and DTG instruments under N₂ gas atmosphere with heating rate 10 K/min.

All samples were heated from room temperature to the maximum temperature indicated by DSC measurements. In order to exclude thermal degradation during the

heating period the maximum temperature are examined under the hot-stage polarizing microscopy and choosing depending on these observations (Sultan, 2007).

Figures (5) to (8) exhibit TG thermograms and the first derivatives of thermogravimetry traces for grafted monomers and polymers. Table (2) listed the thermal properties of grafted monomer and polymers A, B and C together with weight percentage loss.

Table (2): TG and DTG data of weight loss% and temperature of occurring for graft monomer and polymers

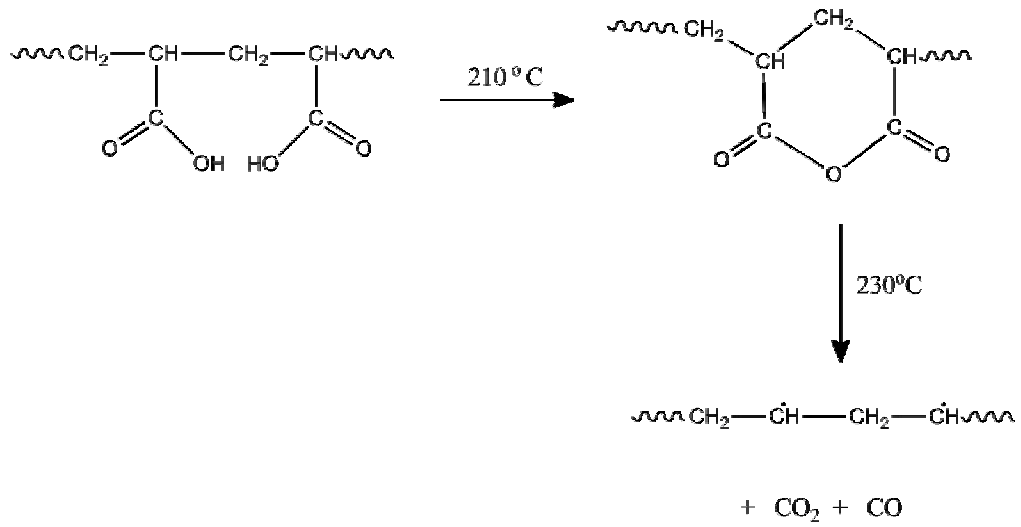
Polymer	First-weight loss %(T ^o C)	Second -weight loss %(T ^o C)
Graft Monomer	11.716(210)	3.527(470)
Polymer A	18.497(225)	10.155(450)
Polymer B	11.288(210)	7.939(420)
Polymer C	14.777(235)	5.543(460)

The general features of these thermograms showing the weight loss trace of two distinguishable maxima. The first one centered around 210-220 °C with average percentage weight loss 11.3 – 18.4% and the second peak centered at 420-470 °C with average percentage weight loss 3.5-10.1%. By calculation the percentage weight loss of the original molecular weight, it seems that the bond breaks at oxygen-Al₂O₃ position (Sultan, 2007).

It is known for poly(acrylic acid) that had two step mechanisms for thermal degradation as discussed by Maurer et. al.,

1987 which is connected with anhydride formation (dehydration at approximately 210 °C) and CO₂ evolution due to anhydride decomposition (start at 230 °C) as shown in scheme (1). The temperature decomposition is a function of the tacticity. The maximum of the decomposition temperature is reached at 415°C and it occurs thus at lower temperatures compared to our polymer components. Previous results indicated that the decomposition should start at lower temperature in grafted acrylic acid polymers compared to the pure components (Takegoshi,

and Kichi, 1992). These data are in agreement with our measurements.



Scheme (1)

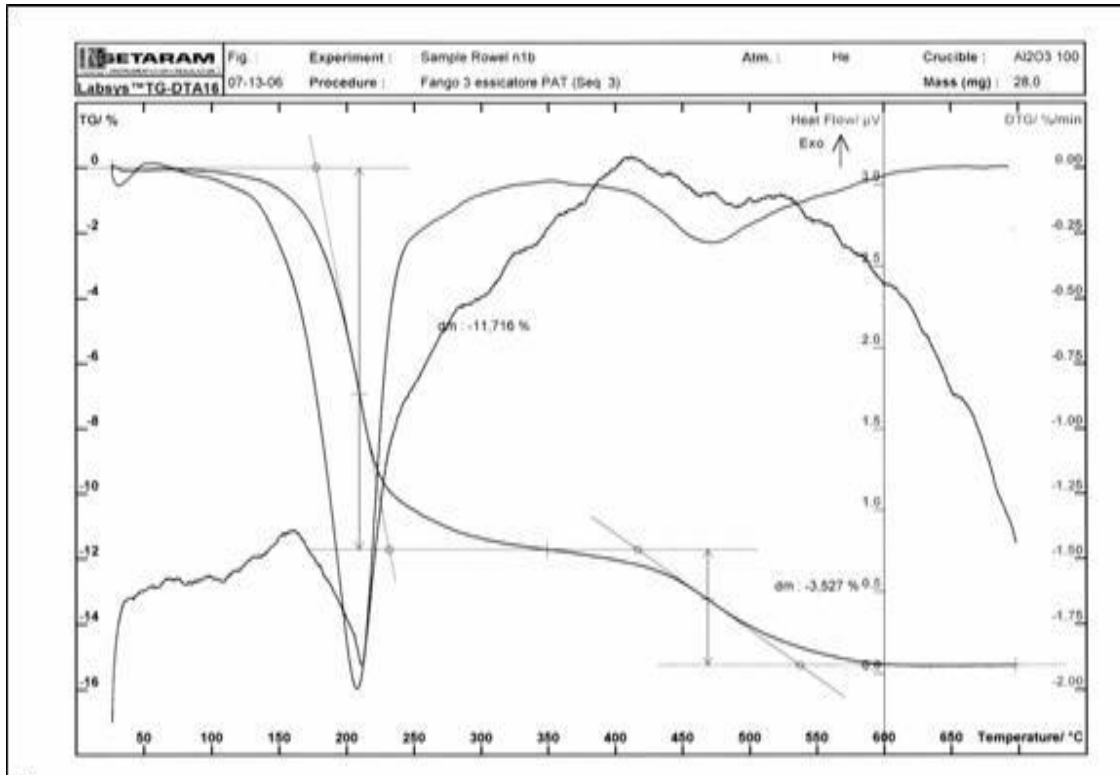


Figure (5): TG and DTG thermograms of trace for graft-acrylic acid monomer.

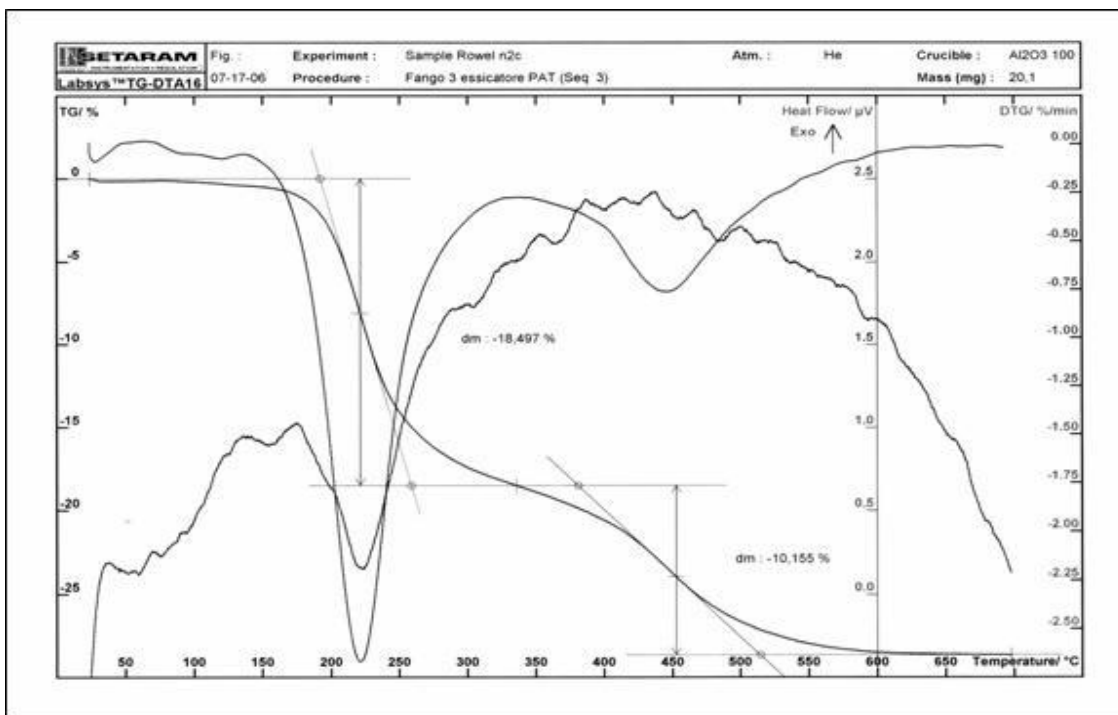


Figure (6): TG and DTG thermograms of trace for polymer A.

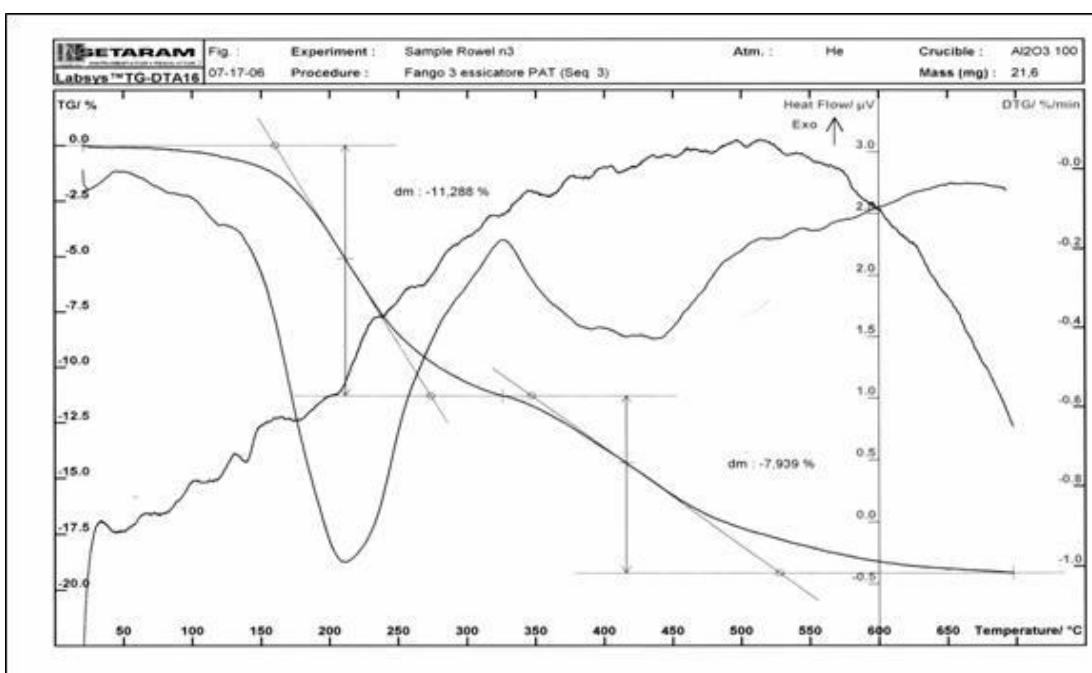


Figure (7): TG and DTG thermograms of trace for polymer B.

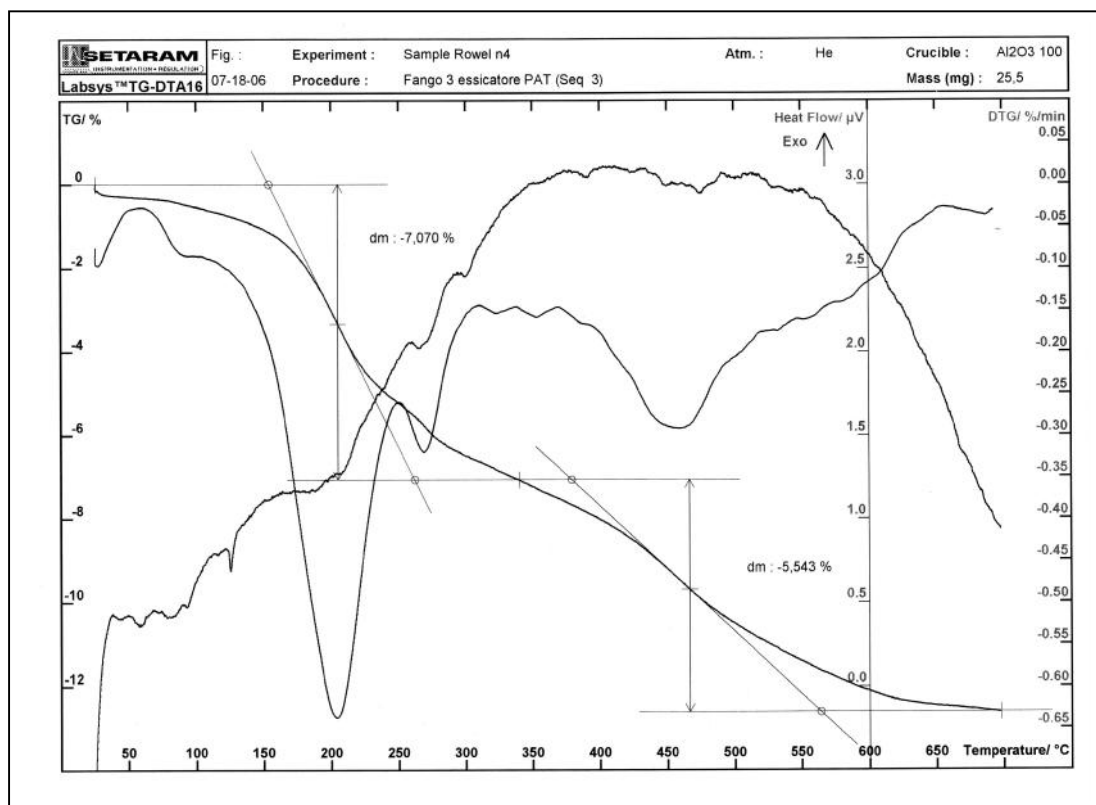


Figure (8): TG and DTG thermograms of trace for polymer C.

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دراسة حرارية لالومينا المطعمة بحامض الاكريلك ومشتقاتها لقواعد شف البوليمرية

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كلمات المفتاح: التحليل الحراري للبوليمرات، الالومينا المطعمة

الخلاصة

تم دراسة السلوك الحراري بواسطة المسعر الحراري التفاضلي (DSC) والتحليل الحراري الوزني (DTG) والتحليل الحراري التفاضلي (TG) للألومينا المطعمة بمونمر حامض الأكريلك وكذلك بيولي (حامض الأكريلك، بوليمر A) والألومينا المطعمة بمركب (1-acryloxy-4-butoxy benzylideneamino phenyl ، بوليمر B) والألومينا المطعمة بمركب (1-acryloxy-4-octoxy benzylideneamino phenyl، بوليمر C). تم مناقشة المخططات الحرارية بالاعتماد على التراكيب الهيكلية للبوليمرات المحضرة.