

Synthesis of the Fatty Acid Compounds Obtained from Sunflower Oil Refining Products

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ABSTRACT: In our study the effects of various factors in the reaction of chlorination and copolymerization of fatty acid wastes were investigated and optimum conditions were determined. The first purpose of this study is to investigate the electrochemical chlorination reaction of fatty acid wastes in the electrolysis of HCl, then to obtain composite materials by the products of this reaction, and finally to determine physicochemical properties, heat resistance, and the effect of chloride to the fire strength of these composite materials. At that time the glycide ester of fatty acid (GEF) was synthesized and used as modifcator for the

determination of thermal and heat properties of composite materials. And the properties of composite materials that are obtained were compared. Styrene-fatty acid copolymers (SFC) were also synthesized by interacting wasted product with styrene. Molecular weight of copolymer, number of carboxyl groups in its structure, its adhesion capability and thermal properties were investigated. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 541–547, 2008

Key words: fatty acid; copolymerization; composites; thermal properties

INTRODUCTION

Fatty acids are long-chain carboxylic acids that often contain an even number of carbon atoms up to 24. More than half of the naturally occurring fatty acids in plants and animals are mono- or polyunsaturated.¹

Chemical modification of vegetable oils is an important route to obtain industrial products using renewable feedstock.² Recycling perhaps is going to be one of the most essential waste management strategies in the contemporary world. There is still a high potential to develop new efficient and environmentally friendly reaction pathways leading to new products or to find new applications for already existing oleochemicals. One of the functionalities that plant oils offer for the chemical modification is the ethylene group. It can undergo reactions such as acylation, isomerization, hydrogenation, hydroxylation, oxidative cleavage, carboxylation and epoxidation, among many others.^{3–6}

Fatty acid alkyl esters are extensively used as valuable intermediates in oleochemistry for the synthesis of a variety of products such as superamides and fatty alcohols, biosurfactants, hydraulic and drilling fluids, and biodegradable polyesters. Other industrial applications comprise their usage as lubricants, antirust agents, and plasticizers. Special attention is

given to methyl fatty acids as potential substitutes of conventional diesel fuel. The synthesis of alkyl esters is accomplished by chemical trans esterification from which short reaction times and high yields are obtained.^{7–10} Fatty acid cellulose esters (FACE), recently identified as potential biodegradable plastics, have been synthesized via a novel vacuum-acid chloride process.¹¹

Most papers deal with the modification of fatty acids. Production of fatty acid alkyl esters by lipase-catalyzed alcoholysis of waste plant oil from oil processing industry with primary alcohols was investigated by Lara and Park.¹² The classical method of fatty acids methyl esters production is based on triglyceride transesterification to methyl esters.¹³ Hydrogenation of vegetable oils is an important practice in the modification of fats and oils.¹⁴

Fatty acids and triglycerides have been used in a number of polymeric applications. Epoxidized and acrylated triglycerides have been used as plasticizers and toughening agents. In fact, the largest nonfood use of triglycerides is the use of epoxidized soybean and linseed oils as plasticizers in poly(vinyl chloride).¹⁵ Pressure sensitive adhesives have been made from fatty acid methyl esters.¹⁶ In addition, thermo-setting liquid molding resins, similar to vinyl ester resins, have been made using plant oils as the cross-linkers.^{17–19}

In this respect, the synthesis of the glycide ester of fatty acid (GEF), chlorinated combinations and styrene-fatty acid copolymers (SFC) from fatty acids that is derived from the refining process of sun-

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flower oil, is important both for the prevention of environmental pollution and for reprocessing of the waste into useful products.

MATERIALS AND METHODS

The waste of sunflower oil as fatty acid and soap stock (SS) was supplied from Zade Chemical Industry, Konya, Turkey.

Styrene, epichlorohydrin (ECH), and benzoyl peroxide (BP) were received from Merck. Triethylenetetramine (TETA) was purchased from Fluka.

Synthesis of glycidyl ester of fatty acid

Glycidyl ester of fatty acid (GEF) was obtained by the esterification reaction of sodium salt of fatty acid (SS) with ECH in the alkaline medium. Ten gram of SS and 10 mL benzene were taken to the flask for the reaction and 4 mL 40% NaOH solution was added to this mixture. Three gram of ECH was supplemented to the mixed solution drop-by-drop at 40°C within 20–30 min. After this addition the temperature was increased to 70–80°C and the mixture was boiled for 5 h. The ester, that is obtained, was distilled under vacuum (Fig. 1).

Synthesis of chlorinated compounds of fatty acid

The electrochemical chlorination process of fatty acid wastes took place in the electrolysis of HCl. For the implementation of the reaction, 250-mL electrolyzer without diafragma [installed with a medium-type anode (rutenium oxide and titanium oxide) and graphite cathode] is used. The gas Cl₂ is formed by the separation of HCl acid through electric current, and this Cl₂ in turn is combined with unsaturated bonds by turning into hypochlorous acid.

The temperature of the reaction was kept stable by the water running through the outer side of the electrolyzer, controlled by the thermostat. The products of the reaction were mixed with the help of a magnetic mixer. After the reaction, the chlorohydrins of fatty acids were separated from the electrolyte solution by ether solution and they were dried with

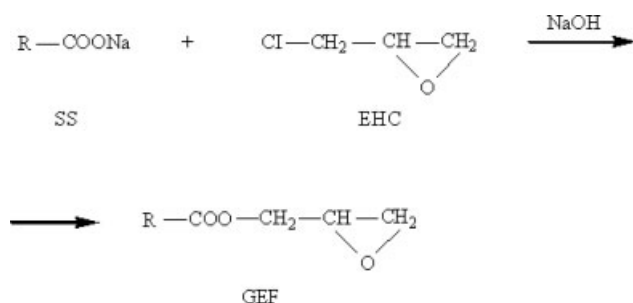


Figure 1 Reaction scheme of synthesis of GEF.

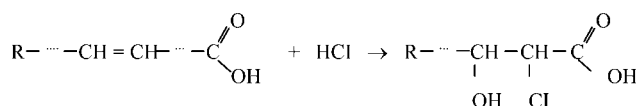


Figure 2 Reaction scheme of chlorination of fatty acids.

Na₂SO₄ and purified in the distillation process under vacuum with a pressure of 250–260°C/15 mmHg. The values obtained, for distillate $d^{20} = 1.0938$; $n^{20} = 1.4945$; for fatty acid $d^{20} = 0.9529$; $n^{20} = 1.4945$ (Fig. 2).

Synthesis of styrene-fatty acid copolymer

The experiments were performed at different ratios of fatty acid and BP just to investigate copolymerization of styrene and fatty acid in the presence of radicalic catalyzer BP. The weighted quantities were installed into the bulbs and kept in the salt-water bath. After cooling treatment, the top of the bulbs was covered up. The bulbs were kept at 80°C for 1 h, at 100°C for 2 h, and at 120°C for 4 h for synthesizing copolymers (Fig. 3)

Modification of epoxide resin

Chlorinated fatty acid and glycidyl ester of fatty acid were used as modifier. The industrial product epoxide resin containing 20% of epoxide groups was used for obtaining epoxide composites and then various epoxide composites were obtained through the modification with the inclusion of TETA in 15%. After the component were mixed thoroughly, the mixture was poured into molds and let go hard for a duration of 2 h at 80°C, 1 h at 100°C, and 1 h at 120°C. The thermal resistance, destruction, and the level of being fire-proof of the composites were examined.

Measurements

The fatty acid and SS samples were analyzed with the Shimadzu Gas Chromatograph (model GC-15A).

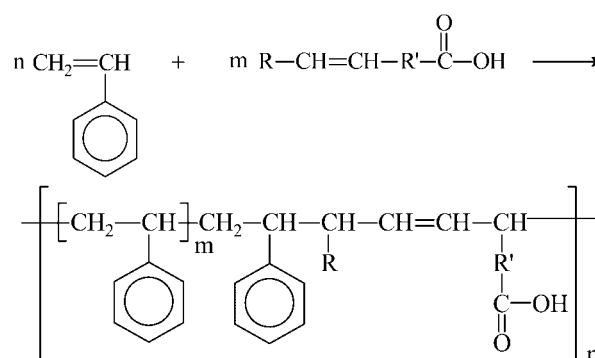


Figure 3 Reaction scheme of copolymerization of fatty acids with styrene.

TABLE I
The Composition of Fatty Acids (%)

%	Soap stock	Fatty acid
C _{12:0}	0.01	0.26
C _{14:0}	0.04	0.34
C _{16:0}	8.75	7.95
C _{16:1}	0.07	0.38
C _{18:0}	4.69	3.97
C _{18:1}	32.48	24.41
C _{18:1 cis}	–	0.93
C _{18:2 trans}	–	0.5
C _{18:2 cis}	65.75	54.59
C _{20:0}	–	0.33
C _{18:3 trans}	–	0.57
C _{18:3 cis}	1.05	0.15
C _{20:1}	0.54	1.56
C _{22:0}	–	0.97
C _{22:1}	–	2.29
C _{24:0}	–	0.61

In the analysis, the column, GC-15A Glass that was sized ID 3.0 mm × 15 mm and filled with 80/100 mesh was used. The temperature of the column and the flow rate was adjusted to 200°C and 30 mL/min, respectively, and nitrogen was used as carrier gas.

The IR spectrum of the chlorinated fatty acid films was recorded with a UNICAM SP 1025 spectrometer. FTIR spectrums of GEF and SFC were recorded with a Mattson 1000 FTIR spectrometer.

Chemical analysis

Determination of chlorine group

The sample was burnt and the free chlorine generated was converted to KCl with H₂O₂ and KOH to determine the amount of chlorine groups of the chlorinated fatty acid. Then this solution was titrated with Hg(NO₃)₂ solution in the presence of diphenylcarbazone as an indicator, until the appearance of pink color. The percentage of chlorine was calculated as follows:

$$CI\% = \frac{(v_1 - v_2) \times f \times 0.35457}{W} \times 100$$

where, v_1 and v_2 are the volumes (mL) of 0.01N Hg(NO₃)₂ in the titration procedures for the blank and

sample, respectively, f is a titration factor for Hg(NO₃)₂ solution, 0.35457 is the equivalent amount of chlorine corresponding to 1 mL of 0.01N Hg(NO₃)₂, and w is the amount of chlorinated fatty acid (mg).

Determination of molecular weight of copolymer

Mark–Haunwick formula was used for appointment of molecular weight of copolymer:

$$\log [\eta] = \log K + \alpha \log M$$

Ostwald Viscosimetry was used in the determination.

Determination of acid number

The copolymer (1 g) was dissolved with 20 mL benzene in a globular flask and an ethanol solution of 20 mL 0.1N KOH was added. Then, the mixture was boiled under a reflux condenser in a water bath. After it was cooled, the surplus KOH was titrated with 0.1N HCl. The concentration of carboxyl groups was calculated from the wasted amount of KOH with the following formula:

$$AN(\text{mg KOH/g copolymer}) = 56.1 \times (V_1 N_1 - V_2 N_2) / m$$

where V_1 is the volume of the added 0.1N KOH (mL), N_1 is the normality of the KOH solution, V_2 is the volume of wasted 0.1N HCl, N_2 is the normality of the HCl solution, and m is the amount of the sample (g). Acid number (AN) (56 mg equiv of KOH/g of polymer) could be calculated in this way too.

Determination of adhesion properties of the coatings

The adhesion property of the copolymer was determined by the Lattice Notch Method. Coatings of 10% toluene solution of copolymers on metal surfaces were divided into equal and small squares (1 mm × 1 mm) by a razor blade. An insulating tape (10–100 mm) was applied to these squares and the tape was suddenly pulled. As a result of this operation, the adhesion percentage was calculated from

TABLE II
The Characteristics of the Modified Epoxide Resin Products

Modifier	Thermal destruction, loss of weight (%)					Softing point (°C)	Fire resistance (s)
	150 ^a	200	250	300	350		
CIFA	2	5	7	13	18	120	3
GEF	3	5	8	15	32	90	–

^a 150, 200, 250, 300, and 350 are temperatures (°C).

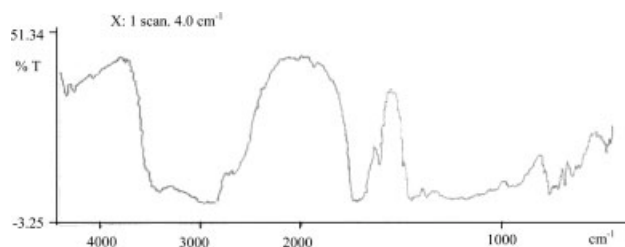


Figure 4 IR-spectrum of CIFA.

TABLE III
Quantity of Styrene-Fatty Acid

Sample	Styrene (g)	Fatty acid (g)	Benzoil peroxide (g)
SFC1	3.9	1.5	0.06
SFC2	3.9	0.2	0.04
SFC3	3.9	0.4	0.08
SFC4	3.9	0.6	0.02
SFC5	3.9	0.8	0.10

the number of squares removed from the coating by the following expression:

$$\text{Adhesion(\%)} = [(a - b)/a] \times 100$$

where, a is the total number of squares, b is the number of squares removed from coating.

Thermal analysis

The thermal analysis experiments were performed with a NETZCH-Geratebau GmbH model thermogravimetric analyzer. Samples were heated under nitrogen atmosphere from 250 to 450°C at a heating rate of 10°C min⁻¹.

Softening points of fatty acids compounds were measured with a CEAST HDT-VICAT model apparatus. The heat rate was 50°C/h.

RESULTS AND DISCUSSION

The results of the gas chromatography analysis of fatty acid and SFCs were given in Table I. As seen from Table I, the isomers between C₁₂-C₂₄ were determined and it was confirmed that the majority of the isomerism was formed because of the C_{18:2}-cis isomers.

The optimum temperature was found as 50–60°C for the electrochemical chlorination reaction of the fatty acid waste. When the temperature was lower than these temperature frontiers, the separation speed of chloride from the electrode and of the reaction of its conversion into hypochloric acid is

decreased. However, when the temperature was higher than these temperature frontiers, the position was opposite to that, the vaporization speed of HCl increased, thus, it affected the productivity.

The optimum density of the electric current on anode was observed as 10–15 A/dm² in the reaction. This current density may account for an acceleration of the separation speed of anode.

The optimum concentration of HCl was found as 10–15%. When the concentration was more than 15%, the amount of di- and tetrachlorides of fatty acids that were obtained from the reaction as by-products were increased. The structures of chlorohydrins were evaluated with data from spectral and chemical analysis.

As a result of this study, 25–35% Cl content was determined in the chlorinated derivations of fatty acids, and these were used as a modifier in epoxide resin to produce composite materials, having high physicomechanical properties, under the suitable reaction conditions. The amount of chlorinated fatty acids, which were used as modifiers in obtaining fire-proof composites, changed between 10 and 30% and the optimum amount was determined as 20%.

It was determined that the content of the electrochemically synthesized fatty acid derivatives also had an effect on the heat properties of the epoxide resin composites. The obtained results can be seen on Table II and Figure 9. As seen from Table II and Figure 9, both epoxide resin composites were stable to thermal destruction up to 250°C.

The structure of the chlorinated compounds of fatty acid (ClFA) was evaluated with data from IR-spectroscopy. Consequently, it was observed on the spectrum that following the reaction of chlorination, the peak points indicating unsaturated fatty acids had disappeared and peak values between 2900 and 3000 cm⁻¹ for acid OH⁻, 1770 cm⁻¹ for acid C=O, and 800–600 cm⁻¹ for Cl⁻ were recorded (Fig. 4).

Quantity of materials, which were used for synthesizing of SFC, were given in Table III. It was demonstrated that if the ratio of styrene: fatty acid was

TABLE IV
Properties of Styrene-Fatty Acid Copolymers

Samples	Molecular weight (g)	Amount of carboxyl (%)	Adhesion (%)	Loss of weight (%)				
				150 ^a	200	250	300	350
SFC1	70 × 10 ³	9	99	–	–	–	–	–
SFC2	110 × 10 ³	1.1	99	–	–	–	–	–
SFC3	100 × 10 ³	1.7	100	–	–	–	–	–
SFC4	95 × 10 ³	2.4	90	3	5	7	18	47
SFC5	90 × 10 ³	5.6	91	4	7	10	21	52
PS	–	–	0.2	20	34	42	50	46

^a 150, 200, 250, 300, and 350 are temperatures (°C).

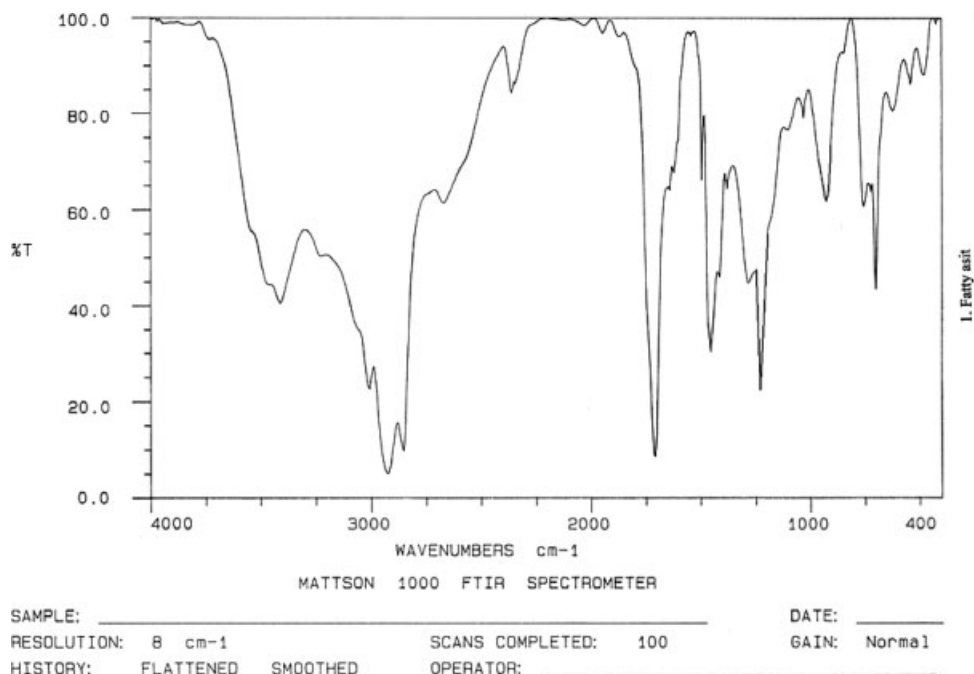


Figure 5 FTIR-Spectroscopy of GEF.

70 : 30% and quantity of BP was enhanced from 0.05 to 15%, amount of carboxyl groups in the copolymer would be raised from 5.6 to 9%. It was seen that the physical and mechanical properties of SFCs depend on the ratio of styrene-fatty acid-BP (Table IV).

The structure of the GEF and SFC were evaluated with data from FTIR-spectroscopy (Figs. 5 and 6). The characteristic peaks of the functional groups

were observed: aromatic —C=C group at 1580 cm^{-1} , aromatic C—H group at 3040 cm^{-1} , and acid —CO group at 1730 cm^{-1} for the SFC. The characteristic peaks of the epoxy group in the spectrum of GEF at 910 and 1230 cm^{-1} showed the binding of this group to the structure of the copolymer.

The results of the thermograph analysis of SFC4 and SFC5 were given in Table IV and Figures 7–9. It

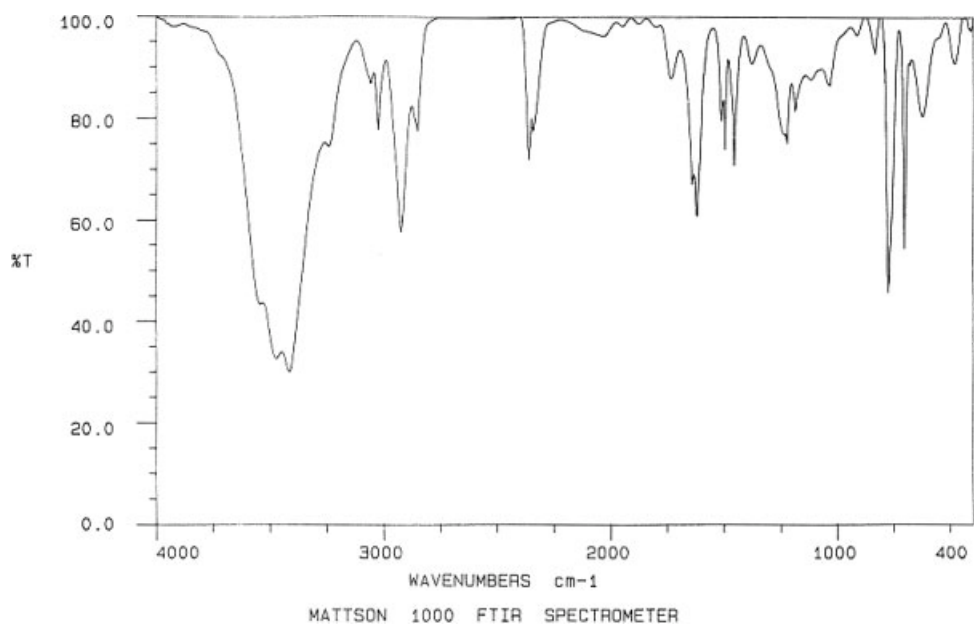


Figure 6 FTIR-Spectroscopy of SFC.

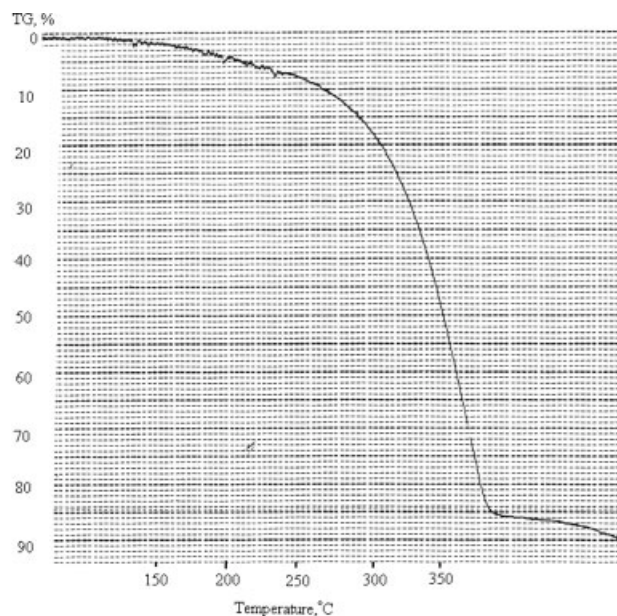


Figure 7 TGA curve of SFC 4.

was established that SFCs were more stable to thermal destruction than polystyrene (PS). In the SFCs decomposition begun (3–4%) at 150°C, the loss of weight was in the range of 7–10% at 250°C, but the loss of weight of PS was 42% at the same temperature. It was found that the loss of weight and adhesion capability increased according to increase of AN of SFC. The best results among the all fatty acids

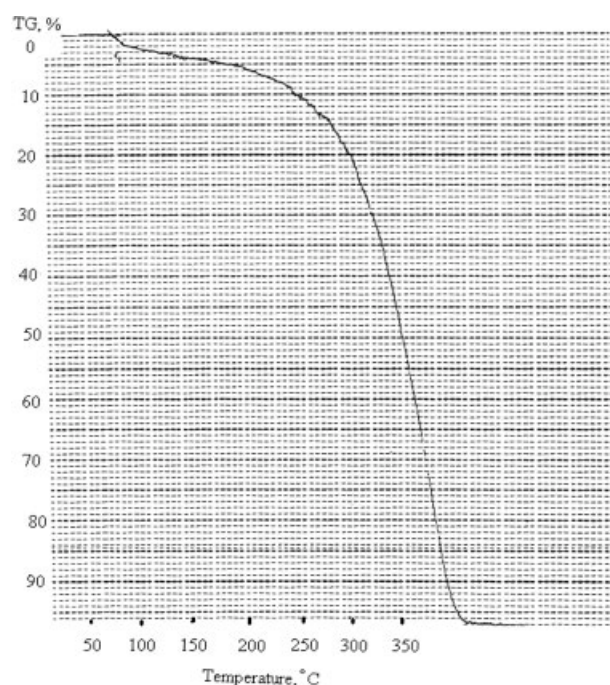


Figure 8 TGA curve of SFC 5.

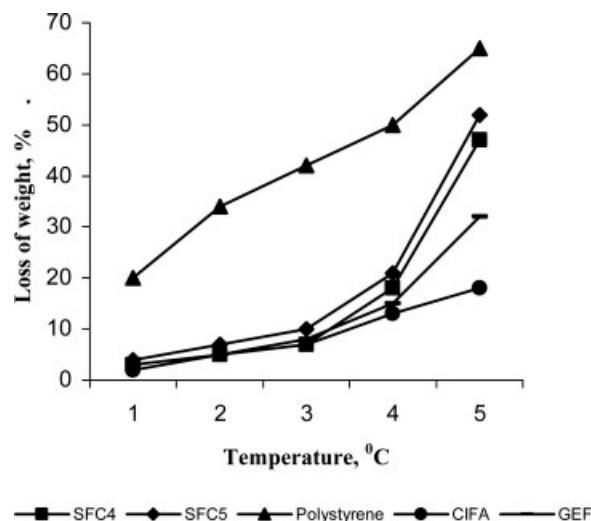


Figure 9 The thermograph analysis of fatty acid compounds.

derivatives was obtained with CIFA-modified epoxide resin.

CONCLUSIONS

Twenty to thirty-five percent increase of the chlorine content in the modifier structure increases the heat resistance of the materials obtained from epoxide resin. Furthermore, it was found that when chlorinated fatty acid was used as modifier, the fire resistance of the composite increased and these materials could put out itself in 3–4 s. Chlorinated fatty acid increases its heat resistance for higher temperature too. Epoxide resin composite with GEF was stable to thermal destruction as CIFA composite up to 250°C.

In the SFCs the loss of weight increased according to increase of AN. Adhesion capability raised with the number of the carboxyl in the styrene-fatty acid copolymer too. The best thermal results among the all fatty acids derivatives were obtained with CIFA-modified epoxide resin.

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