Research Paper Chemistry

THE ANALYZES OF COPOLYMER SHELVIS USED AS VISCOSITY IMPROVERS FOR SAE 10W-40 MINERAL OIL

Ioana Stanciu

University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry, 4-12 Elisabeta Blvd, 030018, Bucharest, Romania

ABSTRACT

Copolymer Shelvis is used as automotive for as viscosity improvers for multi-grade oils. The properties chemical and physical of copolymer are: physical state – solid, form – white solid blocks, colour – compressed crumbs, odourless, flashpoint > 150oC, insoluble in water, is not material hygroscopic, stable, density (15oC) – 0.272 g•cm-3 and none hazardous decomposition. In this study we established the physico-chemical analyzes vized of a copolymer Shelvis used as viscosity improvers for SAE 10W-40 mineral oil was: spectroscopy FTIR, thermo-gravimetric differential thermal analysis (TG-DTA). The diagram DSC evaluates the glass transition temperature. The thermogrames TG and DTA to evaluates their heat resistance of copolymer Shelvis. The kinetic parameters of copolymer hydrogenated poly (isoprene-co-styrene) were determination a method of multilinear regression analysis.

KEYWORDS TG-DTA, FTIR, DSC, kinetic analysis, multilinear regression

INTRODUCTION

Copolymer Shelvis is used as automotive for as viscosity improvers for multi-grade oils. The properties chemical and physical of copolymer are: physical state – solid, form – white solid blocks, colour – compressed crumbs, odourless, flashpoint > 150°C, insoluble in water, is not material hygroscopic, stable, density (15°C) – 0.272 g·cm^{-3} and none hazardous decomposition [1-3].

The chemical structure of copolymer Shelvis was determined using spectroscopy FTIR. The differential scanning calorimetry is widely used in the study copolymer hydrogenated poly (isoprene-co-styrene). For the polymer chemist, DSC is a handy tool for studying curing processes, which allows the fine tuning of polymer properties. The cross-linking of polymer molecules that occurs in the occurring process is exothermic, resulting in a positive peak in the DSC curve that usually appears soon after the glass transition [2].

The DSC used a determination the glass transition temperature of copolymer Shelvis [4]. The object of the present paper is the determination chemical structure using spectroscopy FTIR, glass transition temperature using differential scanning calorimetry (DSC), heat resistance and kinetic parameters using thermo-gravimetric differential thermal analysis (TG-DTA) for a copolymer Shelvis – recommended as viscosity improvers for multi-grade oils. The thermogrames TG and DTA to evaluates their heat resistance of copolymer Shelvis. The kinetic parameters of copolymer Shelvis were determination a method of multilinear regression analysis.

MATERIAL AND METHOD

The copolymer hydrogenated poly (isoprene-co-styrene) is Shelvis commercialized by Infineum UK Limited.

FTIR spectra of copolymer measurement using FT-IR GX Perkin Elmer spectrophotometer in the range of 4000 to 500cm^{-1}, with a resolution of 4 cm^{-1}. The curve TG and DTA were determined using DSC DuPont 2000. The experiments were performed in water atmosphere, operated in range 40-600°C and a heating rate 20°C · min^{-1}.

A method of multilinear regression analysis (MLRA) of the kinetic equation was chosen for the simultaneous evaluation of the activation energy, frequency factor and reaction order from a DTA curve. Using a computer simulation program, several DTA curves were obtained, provided with different Gaussian errors, starting from the evaluated kinetic parameters. Since the dependent variable varies within maximum one order of magnitude, constant absolute errors simulate best the naturally occurring spread of experimental data.

RESULTS AND DISCUSSION

Figure 1 present spectre FTIR of a copolymer Shelvis. The characteristic absorption bands of a copolymer appeared at 2921.53, 2852.03, 1461.39 and 1376.70 cm^{-1}. The significant bands, their wavenumbers and the corresponding functional groups are show in Table 1.

TABLE – 1
SIGNIFICANT BANDS AND FUNCTIONAL GROUPS OF A COPOLYMER SHELVIS

Wavenumber cm^{-1}	Absorption Bond
2923.14	C-CH_3 asymmetric stretch
2852.03	C-CH_3 symmetric stretch
1461.39	C-CH_3 asymmetric stretch
1376.70	C-CH_3 symmetric bending

First, the intensity of the absorption band at 2923.14 cm^{-1} associated with the C-CH_3 asymmetric stretch [5-8] had decreased significantly after ages.

The second significant observation about the aged IR spectra is decomposition of the C-CH_3 bond with a symmetric bend at 2852.03 cm^{-1}. The third major observation is in the intensity of the C-CH3 bond with a asymmetric bend around wavenumber 1461.39 cm^{-1}. A similar reduction was also observed for the C-CH_3 symmetric bending absorption at wavenumber 1376.70 cm^{-1}.

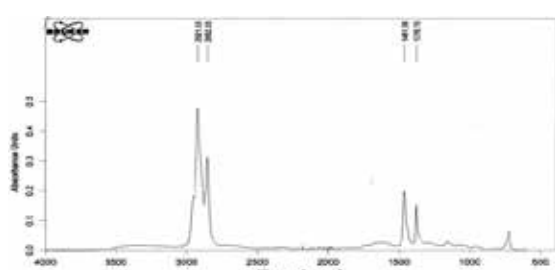

Figure 1: The spectre IR of a copolymer Shelvis

The experimental thermogram was obtained using a differential scanning calorimeter DSC DuPont 2000. The DSC study was carried out with DSC DuPont 2000 equipment. The experiments were performed in nitrogen atmosphere, operated in the range -80 – 140°C at a heating rate 20°C · min-1 and the sample mass 0.1 mg. The glass transition temperature of copolymer Shelvis is at -50.19°C.

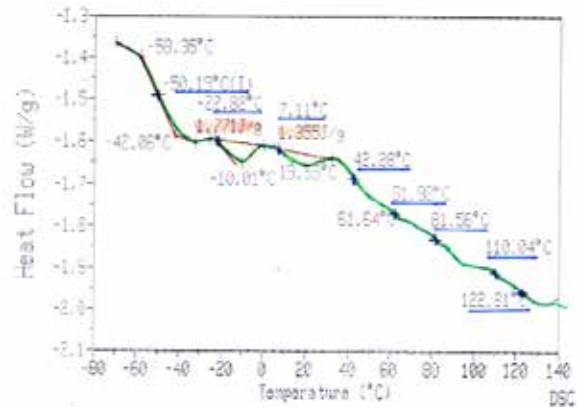

Figure 2: The diagram DSC of a copolymer Shelvis

The TG and DTA curve in the air atmosphere for a copolymer Shelvis is the present in figure 3.

The figure presents: the modified weight in the temperature range 238.94-470oC; the temperature initial of a decomposition thermic is 238.94oC; the modified weight with temperature: 238.94-407.21oC–5.552 %, 407.21-470oC – 90.05 %, 470-600oC – 3.154 % and residue – 1.595 %; the curve present of one maximum, DTG curve we one point of a inflexion at temperature 407.2oC and the temperature final on a decomposition thermic is 470oC.

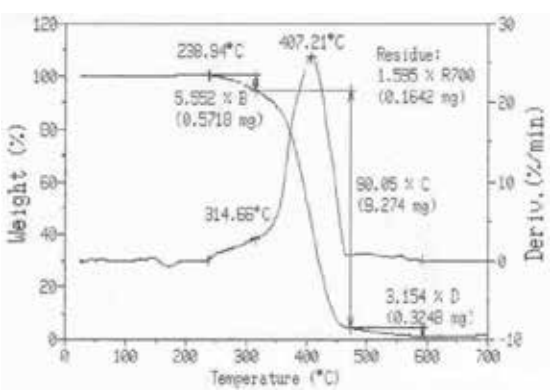

Figure 3: The experimental TG and DTA curves for copolymer Shelvis

The kinetic analysis a thermic degradation of copolymer Shelvis is present paper. The kinetic calculations from the experimental data usually proceed from the basic kinetic equation:

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where α is the conversion, t the time and T the absolute temperature. Arrhenius equation is generally used for the dependences of rate constant k(T) on the absolute temperature:

$$k(T) = Ae^{-E/RT} \quad (2)$$

where A is the frequency factor, E the activation energy and R the molar gas constant.

The conversion function is dependent on the assumed reaction mechanism. Various from of this function have been published [9, 10]. In this work the following from of the conversion function was used:

$$f(\alpha) = (1- \alpha)^n \quad (3)$$

where n is the reaction order with respect to reactant, describing best our experimental data.

Inserting equations (2) and (3) in equation (1), the kinetic equation in the following form is obtained:

$$d\alpha/dt = Ae^{-E/RT}(1 - \alpha)^n \quad (4)$$

Under non-isothermal conditions the explicit temporal dependence in equation (4) is eliminated through the transformation:

$$d\alpha/dt = (A/\beta)e^{-E/RT}f(\alpha) \quad (5)$$

where β = dT/dt is the heating rate.

From experimental TGA the weight of temperature can be also determined using for following equation:

$$d\alpha/dt = A\alpha^n(1-\alpha)^m e^{-E/RT} \quad (6)$$

where m is the reaction order.

Starting from experimental DTA curve, the kinetic parameters (E, A, n and m) were evaluated by a multilinear regression method, using the linearized from of equation (6).

Table 2 shows the values of kinetic parameters for the thermic decomposition copolymer hydrogenated poly (isoprene-co-styrene) of at 20°C min^{-1} heating rate, obtained by multilinear regression.

TABLE – 2

THE KINETIC PARAMETERS OBTAINED WITH EQUATION KINETIC FOR THE EXPERIMENTAL TG AND DTA CURVES OF COPOLYMER SHELVIS

Kinetic equation	Activation energy, kJ/mol	n	m	Correlation Coefficient
$\alpha^n(1 - \alpha)^m$	3.266E+01	0.52	1.04	0.9414
α^n	-1.694E+02	2.51	-	0.9035

The negative value obtained for activation energy of the thermic decomposition with equation (4) has not a physical sense, which means that the kinetic function is not adequate for is description.

The value that is higger than one reaction order can be explained through average molecular polydispersity, can guide to such stoechiometry.

The composition copolymer Shelvis is: 90.05 % isoprene, 5.552 % styrene and 3.154 % other aliphatic compounds.

CONCLUSIONS

The spectre IR of a copolymer Shelvis: C-CH_3 asymmetric stretch, C-CH_3 asymmetric stretch and C-CH_3 symmetric bending. The copolymer was the glass transition temperature -50.19°C. The temperature initial of a thermic decomposition is 240°C and temperature final 470°C. The composition copolymer Shelvis is: 90.05 % isoprene, 5.552 % styrene and 3.154 % other aliphatic compounds. The copolymer Shelvis as having a bit lower glass transition temperature and higher heat resistance.

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