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Physico-chemical analysis of two copolymers used as viscosity improvers for SAE 10W mineral oil

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Abstract. Two copolymers available on the market were characterised using FTIR spectroscopy, thermo-gravimetric differential thermal analysis (TG-DTA), and the differential scanning calorimetry (DSC). The aim of these analyses was to demonstrate that SAE 10W mineral oil viscosity was improved using hydrogenated poly (isoprene-co-styrene) (Infieum UK LIMITED) – trade name INFINEUM SV 260 and poly (ethylene-co-propylene) (DSM Elastomers Europe B.V.) – trade name KELTAN 4200. The DSC curve evaluates the temperature of the glass transition. The TG and DTA thermogrames evaluate the heat resistance and the kinetic parameters of the two copolymers. These parameters were determined using the method of multilinear regression.

Keywords: DSC, kinetic analysis, multilinear regression, TG-DTA, FTIR

1. Introduction

KELTAN 4200 and INFINEUM SV 260 are two copolymers used as automotive viscosity improvers for multi-grade oils. The copolymer KELTAN 4200 is recommended for plastics and oil modification, for application in automotive, construction, wire and cable, as well as for general rubber good. The chemical and physical properties of the copolymer KELTAN 4200 are: physical state - solid, form - bales or granulate, colour – natural opaque, brown in case of oil extended grades, odour – weak paraffinic, relative density 860-900 $kg.m^{-3}$, bulk density depending on structure (bale or granulate), insoluble in water, soluble in hydrocarbons such as alkanes: hexane, heptanes, octane, decane, dodecane, iso-octane, isododecane, cycloalkanes: cyclo-octane, decaline, cyclododecane, aromatic substances: butyl benzene, octylbenyene, and oil: paraffinic naphthenic, aromatic [1] .

The copolymer KELTAN 4200 is used as viscosity improver for multi-grade oil. The chemical and physical properties of the copolymer INFINEUM SV 260 are: physical state – solid, form – white solid blocks, colour – compressed crumbs, odourless, flashpoint > 150^0C, insoluble in water, not hygroscopic, stable, density (15^0C) – 272 $kg.m^{-3}$ and none hazardous decomposition [2].

The purpose of the present paper is to determine the chemical structure and the kinetic parameters [3] of thermic degradation for KELTAN 4200 and INFINEUM SV 260 – recommended as viscosity improvers for multi-grade oils – for which the global and partial solubility parameters and radii of interaction sphere [4], glass transition temperature and heat resistance [5], rheological behaviour of concentrated solutions [6] and viscosity indices of solutions copolymers were determined using the ASTM 2270-93 [7] to estimate their efficiency as viscosity improvers for the low viscosity mineral oil SAE 10W.

2. Experimental

The following copolymers were used as viscosity improvers: hydrogenated poly (isoprene-co-styrene) (Infieum UK LIMITED) – trade name INFINEUM SV 260 and poly(ethylene-co-propylene) (DSM Elastomers Europe B.V.) – trade name KELTAN 4200 for low-viscosity oil SAE 10W (INCERP, Romania).

FTIR spectra of copolymers were made using a FT-IR GX Perkin Elmer spectrophotometer in the range of 4000 to 500cm^{-1}, with a resolution of 4 cm^{-1}.

A method of multilinear regression analysis (MLRA) of the kinetic equation was chosen for the simultaneous evaluation of the activation energy,

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frequency factor and reaction order from a DTA curve. Several DTA curves were obtained using a computer simulation program provided with different gaussian errors, starting from the evaluated kinetic parameters. Since the dependent variable varies within maximum one order of magnitude, it can be concluded that constant absolute errors simulate best the naturally occurring spread of experimental data [3, 10].

3. Results and Discussions

The FTIR spectra of copolymer KELTAN 4200 is presented in Fig. 1. The characteristic absorption bands of the copolymer appear at 2921.07, 2851.57, 2361.41, 1460.59, 1376.12, 674.10 and 628.69 cm^{-1}.

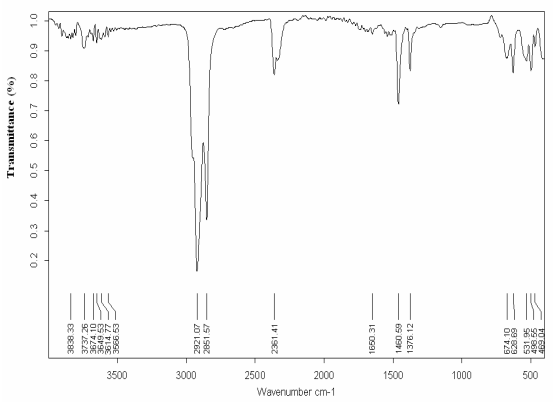

Fig. 1. The IR spectrum of a copolymer KELTAN 4200

The significant bands, their wave numbers and the corresponding functional groups are shown in Table 1.

Table 1. Significant bands and functional groups of KELTAN 4200

Wavenumber cm^{-1}	Absorption Bond
2921.1	CH_2 asymmetric stretch
2851.57	CH_2 symmetric stretch
2361.41	CH_2 symmetric stretch
1460.59	C-CH_3 asymmetric stretch
1376.12	C-CH_3 symmetric stretch
674.10 -628.69	Out of plane CH band

First, the intensity of the absorption band at 2921.07 cm^{-1} associated with the CH_2 asymmetric stretch [8] had decreased significantly after aging. A similar decrease was also observed for the CH_2 absorption band at 2851.57 cm^{-1}, which is associated with the CH_2 symmetric stretch.

The second significant observation about the aged IR spectra is the decomposition of the C-CH_3 bond with an asymmetric band at 1460.59 cm^{-1}. The third major observation is about the intensity of the C-CH_3 bond with a symmetric band around 1376.12 cm^{-1}. A similar reduction was also observed for the out-of-plane CH band absorption at wavenumber 674.10 and 628.69 cm^{-1} .

The FTIR spectra of copolymer INFINEUM SV 260 is shown in Fig. 2. The characteristic absorption bands of a copolymer appeared at 2922.45, 2853.31, 2361.41, 1459.99, 1376.35 and 699.61 cm^{-1}. [9,10].

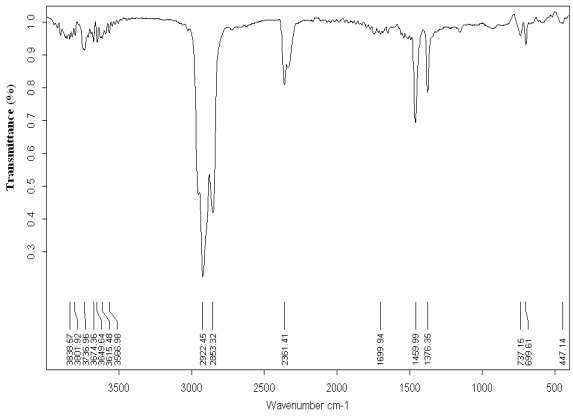

Fig. 2. The IR spectrum of a copolymer INFINEUM SV 260

The significant bands, their wave numbers and the corresponding functional groups are shown in Table 2.

Table 2. Significant bands and functional groups of INFINEUM SV 260

Wavenumber cm^{-1}	Absorption Bond
2922.45	CH_2 asymmetric stretch
2853.31	CH_2 symmetric stretch
2361.41	CH_2 symmetric stretch
1459.99	C-CH_3 asymmetric stretch
1376.35	C-CH_3 symmetric stretch
699.61	Out of plane CH band

The copolymers TG and DTA curves were plotted using a DuPont differential scanning calorimeter (DSC) in nitrogen atmosphere, in the range of 80 – 1400^{0}C, with a heating rate of 20°C · min-1 and the sample mass 0.1 mg. The glass transition temperatures of copolymer KELTAN 4200 is at 54.17^{0}C and at 53.40^{0}C. For copolymer INFINEUM SV 206 the glass transition temperature is at 50.19^{0}C [6].

Fig. 3 presents the thermograms of two copolymers KELTAN 4200 and INFINEUM SV 260 [5].

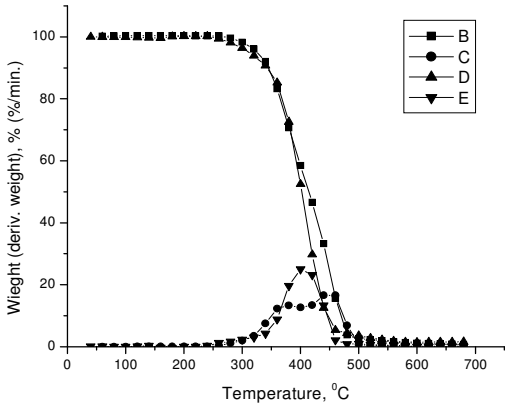

Fig. 3. The experimental thermograms for copolymers KELTAN 4200 and INFINEUM SV 260: B - TG of KELTAN 4200, C – DTA of KELTAN 4200, D – TG of INFINEUM SV 260 and E – DTA of INFINEUM SV 260 [5]

The thermal degradation mechanism of a copolymer poly (ethylene-co-propylene) is:
1. Between 0 and 270^{0}C copolymer is stable thermic;
2. In the 252-380^{o}C temperature range the copolymer is thermal degraded (elimination propylene).
3. In the 380-470 ^{o}C temperature range the thermal degradation continues (elimination ethylene).

The mechanism of thermal degradation for the poly (isoprene-co-styrene) copolymer is:
1. In the 0-231^{0}C temperature range the copolymer is thermal stable.
2. In the 231-470^{0}C temperature range the INFINEUM SV 260 copolymer is thermal degraded.

Starting from experimental TG and DTA curves and using the kinetic equation (1) [11]:

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

where n is the reaction order with respect to reactant, α is the conversion, t the time, T the absolute temperature, A is the frequency factor, E the activation energy and R the molar gas constant.

$$d\alpha/dt = A\alpha^n(1-\alpha)^m e^{-E/RT} \quad (2)$$

where m is the reaction order, the kinetic parameters (E, A, n and m) were evaluated by a multilinear regression method, using the linearized form of the equations (1) and (2).

Table 3 presents the values of the kinetic parameters for the thermal decomposition of KELTAN 4200 obtained by multilinear regression.

Table 3. The kinetic parameters obtained with equation kinetic for the experimental TG and DTA curves of a KELTAN 4200

Kinetic equation	Frequency factor, sec^{-1}	Activation energy, kJ/mol	n	m
2	9.791E-01	2.186E+01	0.54	0.99
1	1.591E-15	-1.735E+02	2.35	-

Table 4 shows the values of the kinetic parameters for the thermal decomposition of INFINEUM SV 260 obtained by multilinear regression [11].

Table 4. The kinetic parameters obtained with the kinetic equation for the TG and DTA experimental curves of INFINEUM SV 260 [11].

Kinetic equation	Frequency factor, sec^{-1}	Activation energy, kJ/mol	n	m
2	7.552E+00	3.264E+01	0.50	1.06
1	2.514E-15	-1.692E+02	2.51	-

The DSC experimental curve of the KELTAN 4200 copolymer in the temperature range of 40-600^{o}C, obtained using a CAHN DSC 550 with the heating rate 10°C min^{-1} in the air atmosphere, is presented in Fig. 4.

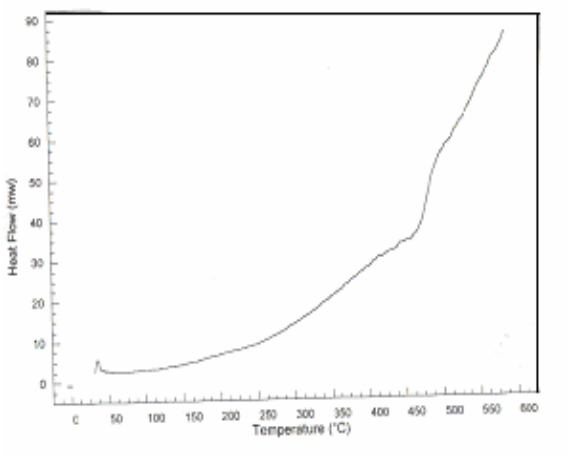

Fig. 4 The experimental DSC curve in the range of temperature 40-600^{0}C for KELTAN 4200

The composition copolymer of a KELTAN 4200 is: 45% propylene and 55% ethylene.
For the INFINEUM SV 260 copolymer the thermal decomposition is confirmed by the DSC diagram (Fig. 5).

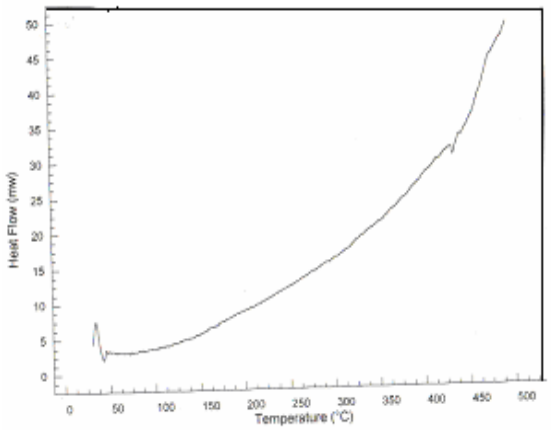

Fig. 5 The experimental DSC curve in the range of temperature 40-600^{0}C for INFINEUM SV 260

4. Conclusions

The FTIR spectra of two studied copolymer present characteristic chemical functional groups: CH_3, CH_2 and CH aliphatic band.

Thermal degradation of the KELTAN 4200 copolymer is placed in the range of temperature 252-470^{0}C. For INFINEUM SV 260 copolymer thermal degradation is placed in the range of temperature 231-470^{0}C.

The negative value obtained for the activation energy of the thermic decomposition with equation (1) has not a physical sense, which means that the kinetic function is not adequate for this description.

The value that is higher than of the first reaction order can be explained through average molecular polydispersity that can guide to such stoechiometry.

The glass transition temperatures as well as the heat stabilities of the two copolymers are very close, the KELTAN 4200 having a bit lower glass transition temperature and a higher heat resistance. Taking account of the functioning temperatures of engines, both copolymers are convenient to be used as viscosity improvers.

5. References

* E-mail address: ioasta@yahoo.com

[1] ***fisa tehnica EPDM
[2]****fisa tehnica INFINEUM SV 260
[3] H.D.Jr. Johnson, *Computational Chemistry An Emphasis on practical Calculations,* Ch. 12.5, Elsevier, 1998
[4]. I. Stanciu and M. Leca, Materiale Plastice, **42**, 4 268-271 (2005).
[5]. I. Stanciu, Buletin UPG – Seria Tehnica, **LX**, 4B (2008).
[6]. I. Stanciu and M. Leca, Materiale Plastice, **43,** 3 236 -240 (2006).
[7]. I. Stanciu and M. Leca, Buletin UPG – Seria Tehnica, **LIX**, 1 69-72 (2007).
[8]. A. Pticek, Z. Hrnjak-Murgic and J. Jelencic, eXPRESS Polymer Letters, **1** (3) 173-179 (2007).
[9]. J. Morshedian, M. Taheri, M. Esfandeh and A. Vahidi, Iranian Polymer Journal, **15**, 955-965 (2006).
[10]. A. Pticek, Z. Hrnjak-Murgic, J. Jelencic and M. Mlniac-Misak, eXPRESS Polymer Letters, **1** (6) 370-376 (2007).
[11]. I. Stanciu, Buletin UPG – Seria Tehnica, **LIX**, (4) 81- 84 (2007).