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THERMAL CHARACTERISTICS OF AROMATIC PETROLEUM RESINS

V. JARM, G. BOGDANIĆ, A. ALAJBEG and J. MÜHL
INA-Industrija nafte, Research and Development, Zagreb (Yugoslavia)

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ABSTRACT

Some thermal characteristics (T_g, T_s, T_M) and kinetic parameters of thermal decomposition (E_A, log A, mechanism) of three low molar mass aromatic petroleum resins (PRs) were determined from DSC, TG and DTG analysis. The differences in the results were correlated with the molar mass, structure and thermal history of the PRs. PRs were prepared under different reaction conditions from the same C_9 fraction of pyrocondensate containing 63.7 mass% of alkenylaromatic monomers.

INTRODUCTION

Petroleum resins (PRs) are a group of synthetic low molar mass resins obtained from a mixture of monomers present in crude oil pyrolysis fractions [1,2]. They are used as modifiers in various multicomponent systems such as adhesives, coatings, polymer blends and rubber compounds, where they improve compatibility, processability, rheological and mechanical properties and thermal stability during processing and application [1,2]. Because of the rather complex structure of PRs their applications are more a result of practical experience than knowledge of structure–property relationships.

Little is published about the thermal properties of PRs in the current literature. It is known that aromatic PRs have better thermal stability than aliphatic ones [1,2]. The softening point is used as a characteristic for the classification of solid PRs [1,2]. Tsatschev and Rustschev [3] compared the thermal stabilities of the cumarone–indene resins and their copolymers with the crude oil pyrolysis fraction using TG, DTG and DTA techniques.

In this work some thermal characteristics (T_g, T_s, T_M, E_A, log A) of aromatic PRs were determined from TG, DTG and DSC analyses and correlated with their structure.

EXPERIMENTAL

A fraction of aromatic hydrocarbons of pyrocondensate (liquid byproduct in ethylene production from gasoline), boiling point 403–473 K, consisting

TABLE 1

Characteristics of low molar mass aromatic petroleum resins (PRs) obtained by free radical (P), cationic (C) and thermal (T) polymerisation of a monomer mixture in the C_9 fraction of pyrocondensate

Characteristic of PR	PR-P	PR-C	PR-T
Polymerisation conditions	0.5% TMPH[a] 403 K, 20 h	1% BF_3OEt_2, 303 K, 2 h	503 K, 10 h
Mass fraction of precipitated PR in original PR	0.83	0.78	0.55
$\overline{M}_n$, (g mol^{-1})	4280	1695	1710
Bromine number	3.3	2.4	2.4
Transition temperature, T_g (K)	375	381	330
Softening point, T_s (K)	400	420	395
Temperature of maximum rate of decomposition[b], T_M (K)	660	653	653
Activation energy of decomposition, E_A (kJ mol^{-1})	244.65 ± 8.77	211.23 ± 5.15	150.25 ± 4.13
Pre-exponential factor, log A (min^{-1})	23.55 ± 0.04	$20.51 \pm 0.12^+$	16.08 ± 0.06
Reaction mechanism	Random degradation, $L = 2$	Random degradation $L = 3$	Random degradation, $L = 2$

[a] TMPH, 2,4,4-trimethylpenthyl-2-hydroperoxide.

[b] At a heating rate of 10 K min^{-1}.

of 63.7 mass% of alkenylaromatic monomers (styrene 13.6, vinyl toluene 30.9 and indenes 19.7 mass%) and 36.3 mass% of aromatic hydrocarbons was used for PR synthesis. The monomer solution was polymerised in the presence of the free radical initiator 2,4,4,-trimethylpenthyl-2-hydroperoxide (PR-P) or cationically with boron trifluoride etherate (PR-C) and thermally (PR-T) as indicated in Table 1. The resins were separated from the solutions by steam distillation, precipitation (benzene–methanol) and drying in vacuum at 333 K to constant mass. The molar masses of PRs were determined cryoscopically in benzene; the softening points were determined using a ring-and-ball apparatus; the bromine numbers of PR solutions in CCl_4 were determined on a Beckman KF4 aquameter (Table 1).

Details of the polymerisation and characterisation of PRs are described elsewhere [4–6].

TG and DTG analyses of PRs were performed on a Perkin–Elmer TGS-2 instrument in nitrogen and in air at a flow rate of 8 ml min^{-1}, a temperature range of 333–873 K, heating rates of 5, 10 and 20 K min^{-1}, and a sample size of 4 mg. Before analyses, samples, in the form of fine powder, were briefly preheated to 373 K.

The T_g values were determined from DSC curves obtained on a Perkin–Elmer model DSC-2 instrument in nitrogen with a heating rate of 20 K min^{-1}.

TABLE 2

Products of the pyrolytic decomposition of aromatic petroleum resins (PRs) at 773 K (PRs were prepared by free radical (P), cationic (C) and thermal (T) polymerisation of the same monomer mixture in the C_9 fraction of pyrocondensate)

Component	PR-P	PR-C	PR-T
Benzene	2.33	2.28	2.31
Toluene	10.64	8.19	10.8
Ethylbenzene	4.49	4.05	2.95
Xylenes	5.61	5.48	5.67
Styrene	21.31	14.80	18.48
m-, *p*-Methylstyrenes	15.91	8.05	10.73
Indenes	2.81	10.67	2.64
Other identified components	6.24	5.15	4.13
Sum of 28 identified components	69.34	58.64	57.49
Sum of 22 unidentified components	30.66	41.36	42.51

Samples of PRs underwent thermal decomposition in a flow tube reactor [7] under the following conditions: reactor temperature, 773 K; carrier gas, nitrogen with a flow rate of 150 ml min^{-1}. The products were collected in *n*-hexane at 248 K and identified (Table 2) by GC–MS and high resolution GC with flame ionisation detection [5].

RESULTS AND DISCUSSION

Primary thermograms of aromatic PR in nitrogen (Fig. 1) have only one decomposition stage in the range 473–723 K with mass loss above 90% at a heating rate of 10 K min^{-1}. In air, PRs decompose in two stages, the first at 480–720 K and the second at 760–850 K with approximate mass losses of 75 and 25% respectively, at a heating rate of 10 K min^{-1}.

For determining the decomposition kinetic parameters only the TG data obtained in nitrogen in the range 473–723 K were used. Degrees of conversion, c, were defined as the mass of the sample remaining at any time divided by the total decomposed mass of the sample. Application of the Ozawa method [8,9] for calculation of the decomposition kinetic parameters of PRs consists of two steps: calculation of E_A and determination of the mechanism and pre-exponential factor A.

Integral TG curves for three heating rates (5, 10 and 20 K min^{-1}) were obtained by plotting $1 - c$ vs. $1/T$. From the readings of temperature at constant conversion for three heating rates, a plot of log hr vs. $1/T$ was drawn. The slope of the straight line was used for the calculation of E_A according to

$$\frac{\log \text{hr}}{1/T} = 0.4567\frac{E_A}{R} \qquad (1)$$

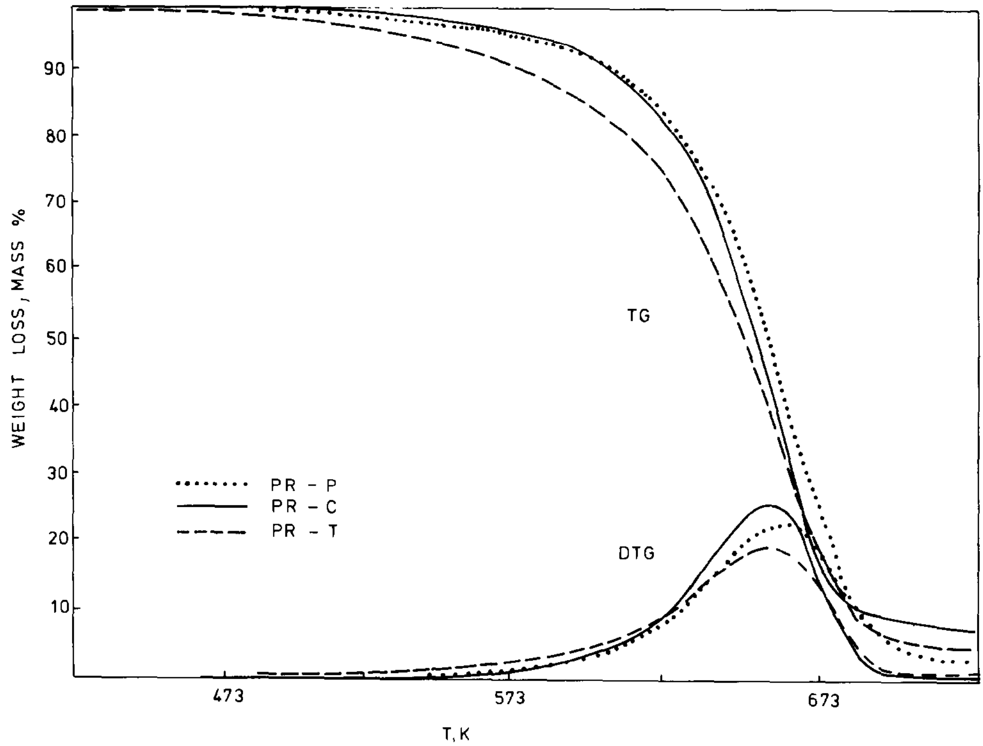

Fig. 1. Primary TG and DTG curves of aromatic petroleum resins. Nitrogen, heating rate 10 K min^{-1}.

where hr is the heating rate (K min^{-1}), T is the absolute temperature (K), E_A the activation energy of decomposition (kJ mol^{-1}) and R the universal gas constant (8.314 J mol^{-1}).

By using the estimated E_A and the TG curves at three heating rates the experimental master TG curve of each PR was drawn (Fig. 2) and compared with the theoretical TG curves [8]. The mechanism and pre-exponential factor were elucidated from this comparison.

The values of E_A and log A and the decomposition mechanism of the PR samples (PR-P; PR-C; PR-T) are presented in Table 1. An approximate agreement between experimental master TG curves and TG curves calculated from the estimated kinetic parameters is seen in Fig. 2.

The differences in the values of the thermal characteristics of the three aromatic PRs (T_g, T_s, T_M, E_A, log A) could be explained by various molar masses, compositions, and thermal histories of the samples.

In the range of low molar mass polymers there exists a correlation between M_n on the one hand and T_g, T_M and E_A on the other [10,11]. For example, PR-P has the highest M_n and E_A, among the three analysed PRs, just as all original (non-precipitated) PRs have lower M_n and E_A values than precipitated PRs.

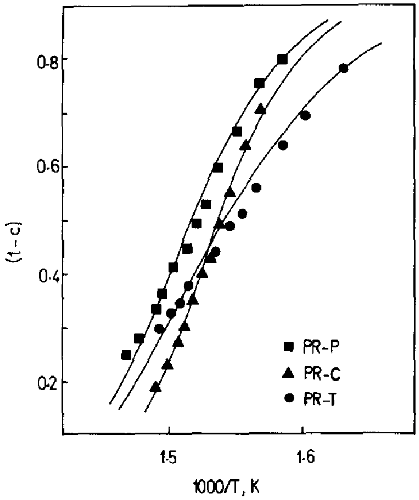

Fig. 2. Comparison of experimental master TG curves (———) with TG curves obtained from estimated kinetic parameters of decomposition of aromatic petroleum resins.

Although PRs were prepared from the same mixture of monomers their compositions differ because of the different reactivities of monomers under various polymerization conditions. Structural variations in differently prepared PRs were already detected in the ratios of aromatic-to-aliphatic signals of ^1H and ^{13}C NMR spectra [6], as well as in various compositions of unreacted monomers after polymerisation, determined by GC analysis [5]. The different products of pyrolytic decompositions of PRs at 773 K are shown in Table 2. Among 28 identified decomposition components the content of styrenes is significantly higher in PR-P and PR-T than in PR-C, while the content of indenes is significantly higher in PR-C. The PR-C has lower M_n, E_A and T_M values than PR-P. The presence of cyclic indene units in PR-C molecules increases its stiffness as well as its T_g and T_s values. The average rate of decomposition, in the temperature range 624–673 K and at a heating rate of 10 K min^{-1}, is the highest for PR-C, 1.36% K^{-1} (for PR-P 1.11 and for PR-T 1.13% K^{-1}), with the highest number of repeating units, $L = 3$, in non-volatilised polymer.

The PR-T has lowest E_A, T_g, T_s and T_M values. It was prepared under the most severe conditions (503 K). Although its unsaturation is not significant it probably contains "weak links" and begins to decompose at the lowest temperature. The thermal stability of PR-T is the lowest.

CONCLUSION

The analysed low molar mass aromatic PRs belong to the same type of carbon chain polymer. The small differences in estimated T_g, T_s and T_M

values as well as more significant differences in the values of kinetic parameters of thermal decomposition (E_A, log A), for the three PRs prepared under different conditions, are consequences of differences in M_n, structure and thermal history of the PRs.

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