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ATTEMPTS TO APPLY DIFFERENTIAL THERMAL ANALYSIS WITH THERMOGRAVIMETRY FOR THE INVESTIGATIONS OF ASPHALT–POLYMER SYSTEMS

B. Liszyńska and *A. Łukowski*

INSTITUTE OF CHEMISTRY, PŁOCK BRANCH OF WARSAW
TECHNICAL UNIVERSITY, 09-400 PŁOCK, ŁUKASIEWICZA 17, POLAND

Attempts were made to apply DTA together with TG for the investigation of asphalt–poly(methyl methacrylate) systems. Compositions were made by photopolymerization of methyl methacrylate in the presence of asphalt or asphalt components.

The value of thermal analysis was demonstrated especially for determining the structures asphalt–polymer systems.

The modification of asphalts, with polymers leads to bituminous materials having improved properties, and allows the utilization of macromolecular by-products and waste-products [1].

Due to the very complex chemical and physicochemical structure of asphalts, the theoretical background of asphalt–polymer systems has not been fully investigated so far [2].

The aim of this study was to examine the possibility of applying differential thermal analysis with thermogravimetry to investigate systems composed of petroleum asphalt and poly(methyl methacrylate) (PMM). The practical aspect of the work was to evaluate the chance of utilizing waste products formed during methyl methacrylate (MM) production for asphalt modification.

Experimental

MM polymerization initiated by ultraviolet radiation was conducted by means of the block method in the presence of non-separated petroleum asphalt D 35, and in the presence of its group components, i.e. asphalt oils, asphalt resins and asphaltenes. Due to their inhibitory influence on the course of polymerization, the contents of the asphalt components present in the reaction medium did not exceed 25 wt.% [3].

The products obtained were subjected to fractionation in order to learn more about their composition and structure. One of the methods applied was asphalt elution from the examined product or its group component with a selective (in comparison with PMM) solvent, carbon disulphide. It was observed that asphalt present in the product was not eluted completely.

Another technique used was polymer precipitation by cyclohexane from the composition solution in benzene, and its further fractionation by fractional precipitation. The fractions obtained were named in accordance with their colouring: a "dark" fraction (with asphalt predominance) and a "light" fraction (with PMM predominance).

The residue after elution of reaction products with the selective asphalt solvent was subjected to thermal analysis, as were the dark and light polymer fractions isolated from the reaction products. For the sake of comparison, the PMM thermal curves was recorded.

The analysis was carried out on a G-425 derivatograph made in Hungary, under the following conditions: reference material Al_2O_3, heating rate 10 deg/min, maximum temperature 1273 K, nitrogen atmosphere.

It was found that the thermal curves of the residue formed after washing with carbon disulphide and those of the light polymer fraction were similar, and did not differ significantly from those of pure PMM.

The effects of three endothermic transitions are indicated in the curves. The product of MM polymerization in the presence of asphalt resins was eluted with CS_2. These thermal curves are presented as examples (Fig. 1). The characteristic transition temperatures from the DTG curves and the calculated total mass losses of the samples during analysis for the chosen products are listed in Table 1.

The mass loss of pure PMM is 100% and the same is observed for the light polymer fraction. These data indicate that the light polymer fraction is PMM homopolymer.

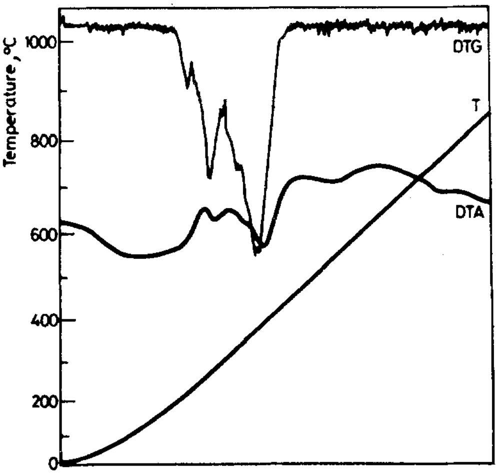

Fig. 1 DTA and DTG curves of product eluted with CS_2, obtained in presence of asphalt resins

Table 1 Transition temperatures and mass losses for PMM and the investigated products

Product	Critical temperature, °C				Mass loss, wt, %
PMM	220	300	380	–	100.0
Products eluted with CS_2, obtained in presence of					
5 wt % asphalt	150	300	400		99.0
10 wt % asphalt	150	310	390		99.0
15 wt % asphalt	225	310	400		89.7
10 wt % oils	170	310	390		100.0
10 wt % resins	150	300	395		97.4
10 wt % asphaltenes	245	300	410		93.1
Light polymer fraction from product obtained in presence of					
5 wt % asphalt	220	280	380		98.7
15 wt % asphaltenes	220	280	380		100.0
Dark polymer fraction from product obtained in presence of					
15 wt % asphaltenes	230	275	380	460	74.7
25 wt % asphaltenes	240	280	380	460	60.2

For the products eluted with carbon disulphide the mass loss during the analysis decreases together with the amount of asphalt component used to obtain these products. The residue obtained should be interpreted as the result of coking of asphalt compounds present in this fraction. This in agreement with the fact that the lowest mass loss is characteristic of the products obtained in the presence of asphaltenes.

The temperature of the first transition of pure PMM is 220°. The first transition of the products obtained in the presence of non-separated asphalt, oils and resins occurs at a lower temperature than that for pure PMM. This can be explained by the plasticizing influence of these substances. The lowest temperatures are characteristic of the products containing resins. On the other hand, for the products obtained in the presence of asphaltenes, the first transition occurs at a higher temperature than for pure polymer. This fact can be explained by the considerable thermal resistance of the asphaltenes.

The curves of the dark polymer fraction (Fig. 2) differ from those discussed so far, as they reveal a fourth transition. This indicates a different character of this fraction in comparison with the light polymer fraction.

Conclusions

The results of the investigations demonstrate the value of thermal analysis in the determination of the structure of asphalt–polymer systems.

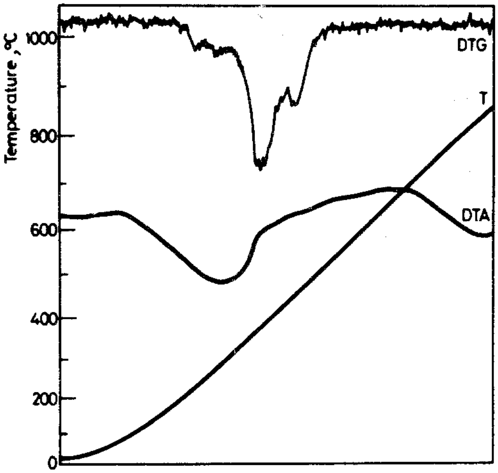

Fig. 2 DTA and DTG curves of dark polymer fraction isolated from product obtained in presence of asphaltenes

This method provides indications of the asphalt compound contents in the investigated compositions. However, it should be stated that application of the method is quite complicated, as it requires taking of calibration curves for each system.

References

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Zusammenfassung — Versuche wurden unternommen, um DTA und TG zur Untersuchung von Asphalt—PMM-Systemen heranzuziehen. Die in dieser Arbeit untersuchten Kompositionen wurden durch Photopolymerisation von in Asphalt oder Asphaltkomponenten eingebrachtem MM hergestellt. Die thermische Analyse ist besonders zur Bestimmung der Struktur von Asphalt—Polymer-Systemen geeignet.

Резюме — Предприняты попытки применения ДТА и ТГ для исследования систем асфальт—ПММ. Образцы для исследования были приготовлены фотополимеризацией ММ в присутствии асфальта или его компонент. Установлена полезность термического анализа в особенности, для опреледения структуры систем асфальт—полимер.