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POLYMERIC MODIFIERS FOR BITUMINOUS BINDERS

Abstract. *Polymer-modified binders (PMB) have found wide application in improving the durability and performance properties of asphalt pavement. To establish the prospects for modifying bituminous binders with polymers, it is necessary to study the basic physical and chemical characteristics of these materials. This paper presents the results of studying the main structural and thermophysical properties of polyethylene terephthalic waste. It was revealed that the presence of functional groups and the corresponding thermal characteristics of the polymer waste open the possibility of using them as modifiers in road construction.*

Keywords: *bitumen, modification, polymers, waste, polyethylene terephthalate.*

Introduction

Currently, the paving industry needs high quality bitumen to meet the demand for durable pavements with low maintenance and repair costs. The most interesting works in this direction are the technologies for modifying the structure of bituminous binders with various additives-polymers used as modifiers of binder properties, the method for obtaining polymer-modified bitumen (PMB). Scientists have been engaged in these studies since 1970 [1] and it has already been established that the use of polymer modifiers mitigates the main causes of accidents in asphalt concrete pavement [2–5], improves the properties of bitumen, which include stiffness at high temperatures, cracking resistance at low temperatures, and moisture resistance, and fatigue life [6, 7].

Polymeric materials used as bitumen modifiers can be divided into two categories: elastomers and plastomers [8]. Elastomeric modifiers extend the range of low and high operating temperatures, while plastomers are known to be effective modifiers at high operating temperatures [9-11].

Plastomers increase the viscosity and stiffness of bitumen, forming rigid mesh structures that resist deformation, in turn, elastomers have a positive effect on the elastic properties of bitumen: they resist permanent deformation under the action of tensile forces and restore their original shape after loading [12, 13].

The most used plastomers are polyethylene (PE), polypropylene (PP), ethylene vinyl acetate (EVA), ethylene butyl acrylate (EVA).

Ethylene vinyl acetate (EVA) semi-crystalline copolymer finds wide application for the workability of the asphalt concrete mix during construction and its resistance to deformation during operation. It was revealed [14] that the introduction of EVA significantly improves the stiffness of asphalt pavements and, consequently, reduces the degree of their permanent deformation caused by large traffic loads at high temperatures. However, despite extensive research conducted in the field of plastomers, their effect on the high temperature performance of PMB has not been studied in sufficient detail due to the complex nature of the interaction between asphalt and polymer [15].

Among elastomers, styrene-butadiene-styrene (SBS) has been widely used [16-18]. Styrene-butadiene (SB) polymer is one of the first commercially successful used as modifiers [19, 20], which is due to its ability to give asphalt excellent resistance to permanent deformation, fatigue, and low-temperature thermal cracking [21]. The properties of polymer-modified binders (PMBs) strongly depend on the concentration [22], molecular structure [23], and chemical composition of the real polymer [24], however, in works [25] it is noted that it is necessary to limit the use of SB polymers with styrene content outside the range of 25-35%.

To modify bitumen, reactive (reactive) polymers containing various functional groups (for example, succinic anhydride, etc.) capable of forming chemical bonds with asphalt molecules are also actively used [26]. In some cases, the chemical interaction between binder and modifier can be facilitated by the addition of low molecular weight compounds such as sulfur [27] or mineral acids [28]. However, in most cases, binder-polymer interactions are physical in nature and depend mainly on the structure of the polymer, molecular weight, and chemical composition.

Despite the numerous works done, research in the field of eliminating the shortcomings of polymer-bitumen materials continues. The main disadvantages of polymer modifiers include their thermodynamic incompatibility with asphalt due to large differences in density, polarity, molecular weight, and solubility between the polymer and asphalt [29], which in turn can lead to delamination of the composite during heat storage and has a negative effect for the use of the resulting material in construction. At the same time, researchers are still looking for methods to reduce the cost of production and the sensitivity of PMB to high temperatures, as well as to increase the elasticity of binders [30], which in turn emphasizes the relevance of searching for new cheap bitumen modifiers.

This article presents studies of the main physical and chemical properties of PET waste (PET flakes), which are planned to be used as bitumen modifiers.

The choice of PET was driven by the popularity of packaging materials made from this plastic, which has an extremely short lifespan and generates a huge amount of waste that needs to be disposed of.

Materials and methods

Polyethylene terephthalate (PET), the fourth most produced polymer in the world [31], is a thermoplastic polymer that, due to its high strength barrier and easy thermoforming, is widely used to produce soft drink bottles, food packaging, textile fibers [32], etc. Polyethylene terephthalate waste used in this study were obtained from water bottles, separated, washed, and ground.

Study of the structural features of PET waste using IR, NMR spectroscopy. The infrared spectra of the PET sample were obtained on a Bruker Tensor II IR Fourier instrument. 1H and 13C NMR spectra of PET waste were taken on a JNM-ECA 400 nuclear magnetic resonance spectrometer. Study of the thermo-destructive properties of PET waste on a thermal analyzer TGA/DSC 3+, Mettler Toledo.

The molecular weight of waste polyethylene terephthalate was determined by the viscometric method using an Ubbelohde viscometer in m-cresol at a temperature of 25°C. The average molecular weight (Mn) was determined using the Mark-Houwink equation:

$$M_n = \sqrt[\alpha]{\frac{[\eta]}{K}},$$

where α and K are constants for the polymer-solvent system.

Results and discussion

In the IR spectrum of PET flex, shown in Figure 1, high-intensity stretching vibrations of the carbonyl group are observed in the range of 1715 cm-1. It is known that the stretching vibrations of the C–O group give several strong bands in the range of 1300-1000 cm-1: in the spectrum of the PET flex one can distinguish the average vibration frequencies νC-O for a number of esters with a long hydrocarbon chain with strong peaks at 1270 and 1130 cm-1. The peak in the region of 1666 cm-1 is typical for double C=C bonds in aromatic compounds, and the bands of out-of-plane bending vibrations of the unsaturated C-H bond lie in the region of 1000-800 cm-1, which confirms the presence of a benzene ring in the PET sample.

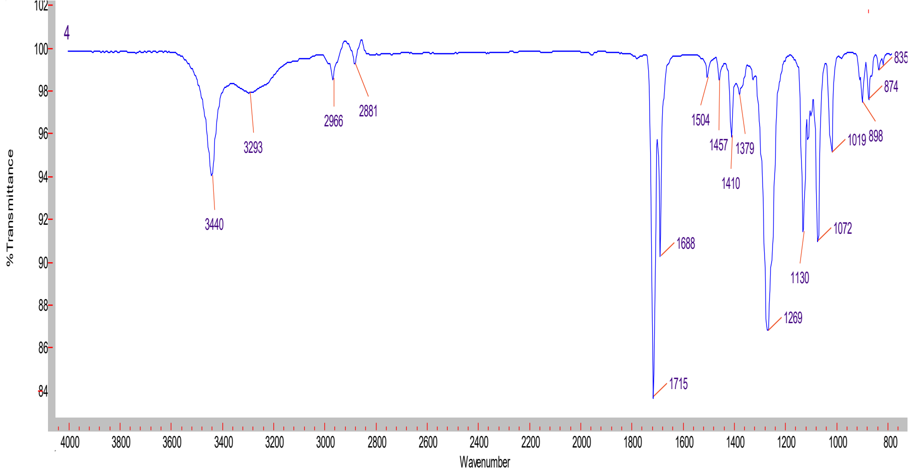

Figure 1 – IR-spectrum of PET waste [author's material]

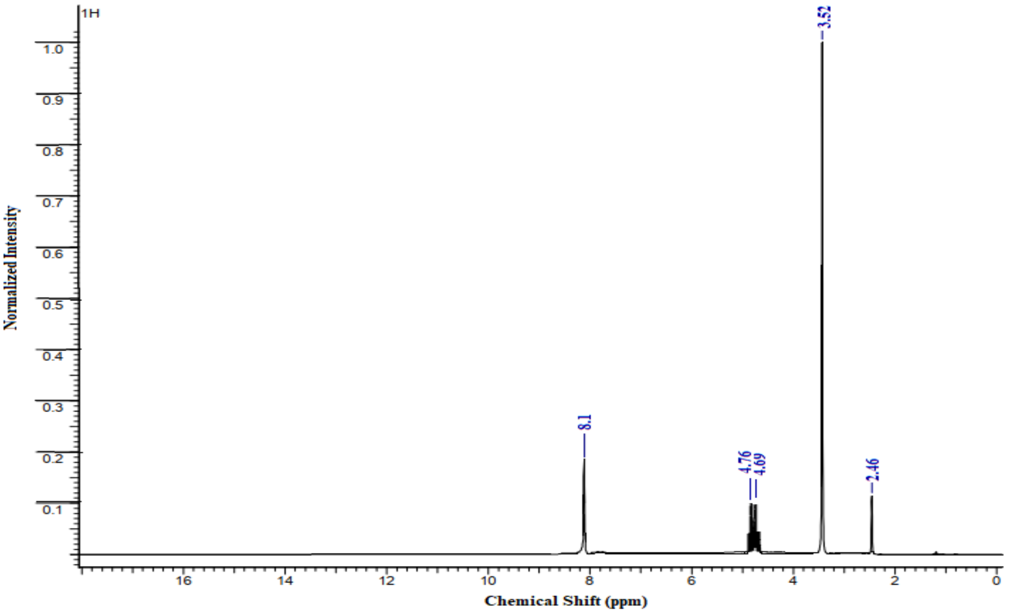

Figure 2 – 1H NMR spectrum of PET waste sample [author's material]

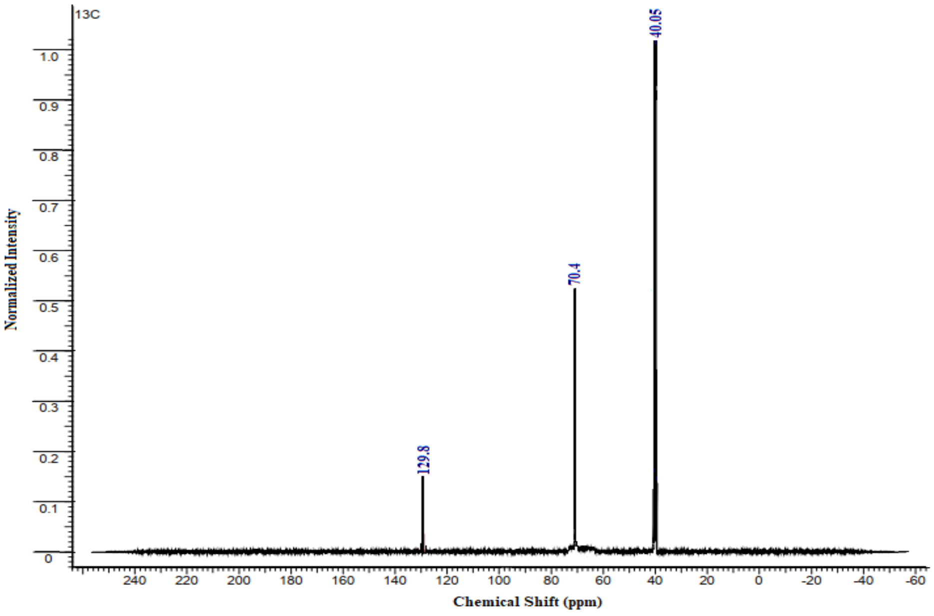

Figure 3 – 13C NMR sample of waste PET [author's material]

The 1H NMR spectrum of the PET sample is shown in Figure 2. A singlet at 8.1 ppm corresponds to the protons of the aromatic ring, a triplet at 4.7 ppm, corresponding to the methylene group (-CH2-), adjacent to the ester bond [33, 34].

The peak at 3.52 ppm refers to the methylene groups, referred to as protons in the methylene group in -CH2-OH.

On the 13C-NMR spectrum of the PET waste (Figure 3) there is a band in the region of 129.8 ppm, corresponding to the signals of carbon of aromatic groups, a peak in the region of 70.4 ppm – to vibrations of carbon in the O-CH2- bond. The peak at 40.05 ppm is attributed to the signals of carbon nuclei of various alkyl groups CH3, CH2, and CH in the region of shifts at 40 ppm.

It is known [26] that when modifying a binder to improve the compatibility of a polymer, the possibility of forming a chemical interaction is considered, which is achieved by the presence of reactive functional groups. The functional groups are characterized by the ability to chemically interact with the less compatible asphaltene fraction, which is rich in ether atoms and reactive groups. This fact indicates the possibility of using PET waste as a modifier due to the presence of carbonyl -CO - groups in their composition.

It is known that the temperature characteristic of semicrystalline polymers is measured by phase transitions using the method of differential scanning calorimetry (Figure 4). Table 1 presents the main data of the thermal analysis of the PET sample.

Table 1 – Physical and chemical properties of PET

Molecular weight, Da	Tmelt, °C	Tglass, °C
47300	253	87

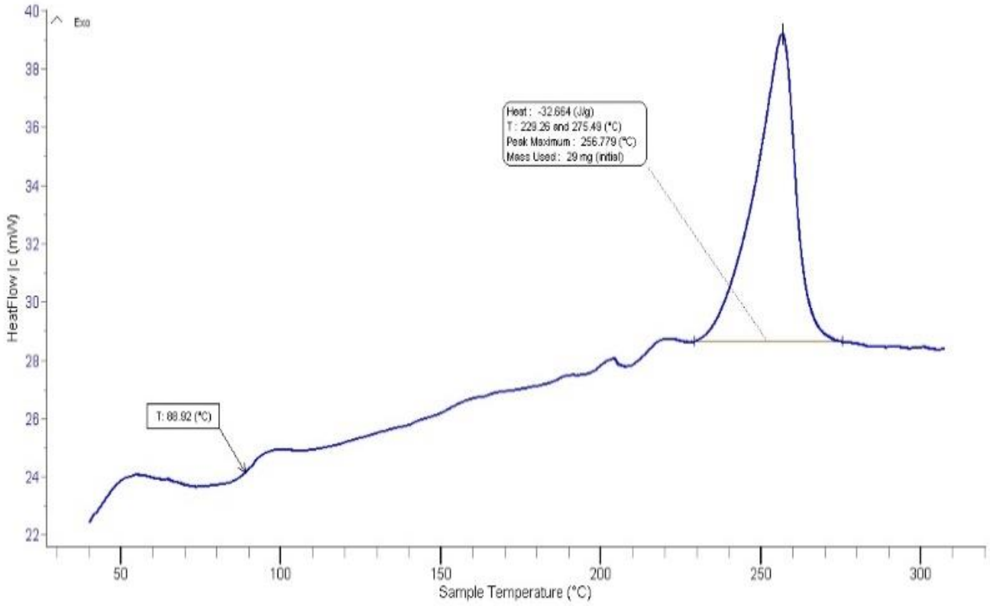

Figure 4 – PET DSC curve [author's material]

Based on the data in Table 1 and Figure 4, it was found that the melting and glass transition temperatures of the sample are 253°C and 88°C, respectively, which are slightly higher than the temperature characteristics of initial PET, this is due to the presence of additives in them and opens new opportunities for the safe operation of materials on their basis at higher temperatures.

A PET waste sample was also analyzed by DTA/TG and DTG to establish thermal behavior over a temperature range of 20-650°C.

It is observed that during dynamic heating in the range of 20-185°C, it left a slight slope of its line on the thermogravimetric (TG) curve in the direction of decreasing the initial weight by 2.52% (Figure 5). The mass loss is due to emissions of weakly bound carbon matter into the atmosphere. A further increase in temperature in the derivatograph furnace led to the development of an endothermic reaction in the charge, which left a shallow peak at 215°C on the DTA curve, which proceeded without weight loss. Such a thermal manifestation is usually typical for polymorphic transformations and for the processes of melting of the heated substance.

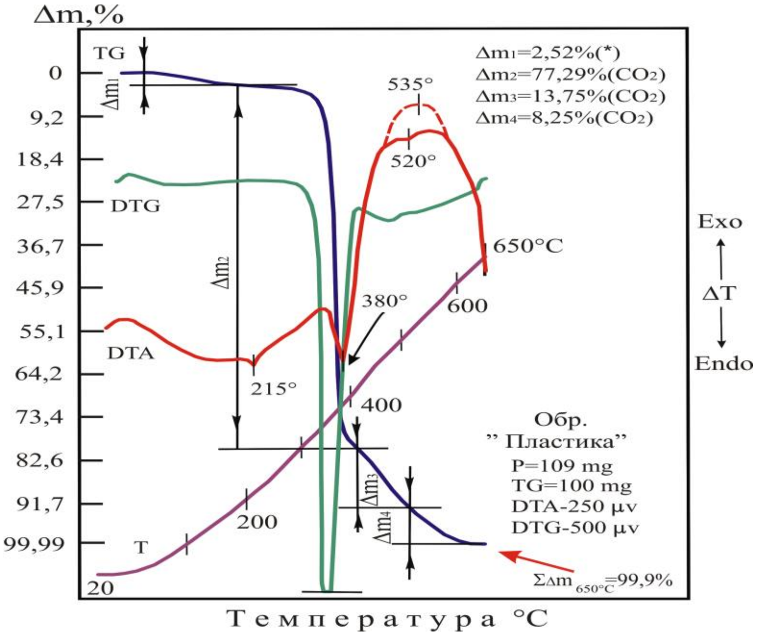

Figure 5 – Derivatogram of PET waste [author's material]

Subsequent heating of the sample to 650°C was accompanied by an influx of heat from the combustion of organic matter into the system. This process took shape on the DTA curve with an exothermic peak at 535°C, Figure 5 (dashed line). This reaction is interrupted twice by counter flows of heat carried out of the system by carbon dioxide. Within the exothermic rise of the DTA curve, these (CO2) emissions left a deep endothermic peak at 380°C and a less intense manifestation at 520°C. These effects were accompanied by weight losses Δm2, Δm3 and Δm4 and corresponding peaks in the differential thermogravimetric (DTG) curve (Figure 5).

The thermogravimetric analysis (TGA) curve of the waste polymer modifier indicates that the PET flex is thermally stable up to 185 ºC with virtually no weight loss. This suggests that the present modifier can be safely used up to this temperature for the production of polymer-bitumen mixtures.

Conclusion

Based on the results obtained from the study of the functional and temperature characteristics of PET flexes, it can be concluded that these wastes can be used to obtain new polymer-modified bitumen. The effect of increasing the compatibility of two components (polymer, bitumen) is expected with a high degree of probability without additional production stages of special functionalization of polymers, which is more cost-effective and solves several environmental problems associated with the disposal of plastic waste.

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БИТУМ БАЙЛАНЫСТЫРҒЫШТАРҒА АРНАЛҒАН ПОЛИМЕРЛІ МОДИФИКАТОРЛАР

Аңдатпа. *Полимерлі модификацияланған байланыстырғыштар (ПМБ) асфальт жабынының беріктігі мен пайдалану қасиеттерін арттыруда кеңінен қолданылады. Битумды байланыстырғыштарды полимерлермен модификациялау перспективаларын анықтау үшін осы материалдардың негізгі физика-химиялық сипаттамаларын зерттеу қажет. Бұл жұмыста полиэтилентерефталат қалдықтарының негізгі құрылымдық және термофизикалық қасиеттерін зерттеу нәтижелері келтірілген. Функционалды топтардың болуы және полимерлі қалдықтардың тиісті жылу сипаттамалары оларды жол құрылысында модификатор ретінде пайдалануға мүмкіндік беретіні анықталды.*

Түйін сөздер: *битум, модификация, полимерлер, қалдықтар, полиэтилентерефталат.*

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ПОЛИМЕРНЫЕ МОДИФИКАТОРЫ ДЛЯ БИТУМНЫХ ВЯЖУЩИХ

Аннотация. *Полимерно-модифицированные вяжущие (ПМВ) нашли широкое применение в повышении долговечности и эксплуатационных свойств асфальтового покрытия. С целью установления перспектив модифицирования битумных вяжущих полимерами необходимы исследования основных физико-химических характеристик данных материалов. В настоящей работе представлены результаты изучения основных структурных и теплофизических свойств отхода полиэтилентерефталата. Выявлено, что наличие функциональных групп и соответствующие термические характеристики полимерного отхода открывают возможности применения их в качестве модификаторов в дорожном строительстве.*

Ключевые слова: *битум, модификация, полимеры, отходы, полиэтилентерефталат.*