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*I. Krutko, K. Yavir, V. Kaulin***THE INFLUENCE OF THE NATURE OF STABILIZER ON THE DEGRADATION OF COAL TAR PITCH****Donetsk National Technical University, Pokrovsk, Ukraine**

We studied the influence of the stabilizers on thermo-oxidative degradation of the main component (coal tar pitch) of a new material, pitch-composite. Based on the data of gravimetric and FTIR spectral analyses, it was established that individual stabilizers (irganox, melamine, calcium stearate and zinc stearate) in the amount of 2% interact with coal tar pitch at 150°C in the presence of air. Melamine, calcium stearate and zinc stearate decelerate (in contrast to irganox) destructive processes in the pitch which is accompanied by the formation of low-molecular compounds. It was shown that irganox initiates the degradation reactions with the formation of volatile compounds when interacting with pitch. When interacting with pitch components, zinc stearate and calcium stearate were stated to reduce the condensation of the system forming methylene bridges between the aromatic rings. Due to the reduced condensation of the aromatic pitch systems, the formation of low-molecular volatile compounds is inhibited and the weight loss diminishes in the presence of calcium and zinc stearates. The obtained results should be taken into account when developing a complex stabilizer for basic stabilization of the pitch-composite.

Keywords: coal tar pitch, thermo-oxidative degradation, irganox, melamine, calcium stearate, zinc stearate, FTIR spectroscopy.

Introduction

Coal tar pitch (CTP) is the residue formed during the distillation of coal tar. CTP is a cheap raw material which is widely used in various industries to produce composite and carbon materials [1–3].

CTP by its nature has high reactivity as it was confirmed by many researchers [2–4]. CTP is a multicomponent mixture of condensed aromatic hydrocarbons and heterocycles with active functional groups that can be activated under certain conditions and enter into chemical interaction.

Composite material based on CTP-pitch-composite is a new class of thermoplastics [5]. It can be used as a precursor to obtain a wide range of carbon materials [5,6]. Pitch-composite is a multicomponent disperse-heterogeneous system where pitch-polymer matrix serves as a dispersion medium and the filler is a dispersed phase [7].

Pitch-polymer matrix is a product of low-temperature modification of CTP by active polymers. CTP has weak polymeric properties. To strengthen them, CTP is subjected to a low-temperature modification by polyvinylchloride (PVC) [8]. Polyvinylchloride is the most studied, it has a high modifying effect and is well-compatible with the CTP

polymer additive. The minimum content of PVC, at which the modifying effect is observed, is 3 wt.% relative to CTP [9].

When obtaining and processing pitch-composite, thermal and thermo-oxidative degradation is observed. This can lead to the change in properties of the composite material.

Pitch-polymer matrix consists of reactive substances that are subjected to the greatest impact of aggressive factors leading to deterioration in the material properties. Therefore a detailed study and understanding of the mechanisms of destruction and stabilization are very important.

Thermal and thermo-oxidative degradation of CTP and polyvinylchloride occurs according to the laws of chain radical reactions [3,10]. To decelerate or prevent these reactions in the pitch-composite, it is necessary to suppress them by adding stabilizers at the stage of its preparation.

We analyzed the mechanism of destruction and stabilization of pitch-polymer matrix components and considered various stabilizers, particularly their properties, structure, application area, advantages and disadvantages, and compatibility with components of pitch-composite. On the basis of our findings, we

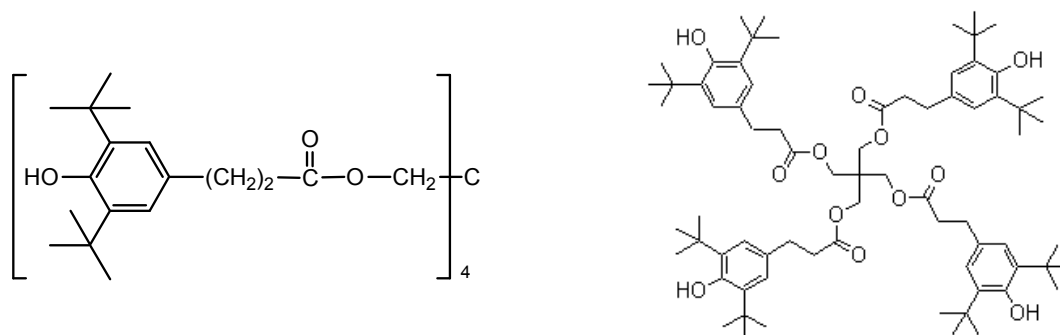


Fig. 1. The chemical formula of Irganox 1010

selected several stabilizers: irganox 1010, calcium stearate, zinc stearate and melamine [10].

Antioxidants (i.e. oxidation inhibitors) irganox 1010 and melamine are introduced into polymeric materials in order to decelerate oxidation processes. Their action involves absorbing the emerging radicals and stopping the development of chain reaction or destroying peroxides that do not have time to decompose with the formation of new radicals.

Calcium stearate has an ionic character; it is believed that it acts as a PVC stabilizer, primarily by neutralizing HCl. Zinc stearate can neutralize HCl and act as primary stabilizers in the nucleophilic mechanism of substitution of labile chlorides.

Pitch-polymer matrix determines the properties of the pitch-composite and is also the most vulnerable to the exposure of external factors in the process of obtaining or processing the material. Therefore, the researches were aimed at studying the processes of degradation and stabilization of the pitch-polymer matrix. To investigate the processes of degradation and stabilization of the pitch-polymer matrix, first of all, it is necessary to analyze the influence of stabilizers on its components: CTP and PVC.

At the same time, there are no similar studies in the literature concerning CTP. Therefore, this work was devoted to study the individual stabilizers effect on the process of thermo-oxidative degradation of CTP.

Material and methods

B-grade medium-temperature CTP and stabilizers, irganox 1010, calcium stearate, zinc stearate and melamine, were used in the study.

The characteristics of CTP were as follows: the softening point determined by «ring-rod» method is 83°C; the viscosity at 135°C is 10 Pa·s; the density is 1300 kg/m³. The group composition was as follows (%): α₁-fraction 8; α₂-fraction 27; β-fraction 34; γ-fraction 31. The Vicat softening temperature was 53°C.

Irganox 1010 (Fig. 1) is a spatially difficult

phenolic antioxidant for primary treatment and long-term thermal stabilization. The chemical name of irganox 1010 is pentaerythrite tetraoxy (3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate). Irganox 1010 is a white and loose powder; its molecular weight is 1178 g/mol; the melting range is 110–125°C; the density is 1150 kg/m³ (at 20°C); the volumetric density of powder is 530–630 kg/m³.

The structural formula of melamine (2,4,6-triamino-1,3,5-triazine, triamide of cyanuric acid) is shown in Fig. 2. Its molecular weight is 126.13; it is colorless crystals; the melting point is 354°C (with decomposition); the density is 1571 kg/m³.

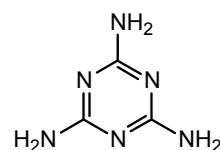


Fig. 2. The chemical formula of melamine

By a mechanism of action, irganox 1010 (further called as irganox) and melamine belong to the first type antioxidants, they act as hydrogen donors.

Calcium stearate ((C₁₇H₃₅-COO)₂Ca) is a white powder with the density of 1035 kg/m³ and the melting point of 170°C. Zinc stearate ((C₁₇H₃₅-COO)₂Zn) is a white amorphous powder; its melting point is 140°C.

Calcium stearate and zinc stearate are used as a stabilizer-acceptor of HCl for PVC.

The experimental procedure included preliminary dispersion and mixing of the CTP (5 g) and stabilizers (in the amount of 2% relative to the CTP) in the mill to get a homogeneous state and further heat treatment of the resulting mixture in a Binder M53 chamber at 150°C for 1 hour.

To assess the effectiveness of stabilizers, a change in the weight of materials was chosen as a criterion. The change in the weight of the samples

was determined in accordance with the requirements of GOST 12020, ISO 11358. Average arithmetic values of five parallel measurements were used as the results. The error in measuring the mass was 0.0002 g. The difference in values between parallel samples did not exceed 0.01%.

The changes in the structure of CTP before and after the addition of stabilizers during thermo-oxidation degradation were observed by Nicolet iZ10 Fourier Transform Infrared (FTIR) spectrometer using the CTP powder by collecting 64 scans at a resolution of 0.01 cm^{-1} in the range of $4500\text{--}500\text{ cm}^{-1}$. The limits of the permissible absolute error of the wave number scale were $\pm 0.5\text{ cm}^{-1}$.

Results and discussion

The weight losses of CTP without stabilizers and with stabilizers (irganox, melamine, calcium stearate, and zinc stearate) after aging in a Binder M53 chamber at $T=150^\circ\text{C}$ for 1 hour are presented in Table.

It is known that CTP is an extremely reactive material. When heating CTP in the presence of oxygen, there is an elimination of hydrogen and alkyl groups with the formation of radicals, which are further recombined with the formation of large molecules [3,11]. This is due to the low energy of the C–H bond in the multinuclear aromatic compounds. The free radical formed is stabilized by the interaction of a free electron with π -electrons of the aromatic ring. The densification of the initial CTP is a result of the recombination of free radicals formed [12]. The reaction proceeds through free radicals that are permanently formed by the action of oxygen [13]. Thus, the polycondensation process, oxidative dehydropolycondensation, occurs. In the thermal oxidation of CTP, the reactions of oxidative dehydrogenation of low-molecular hydrocarbons are dominated. This is accompanied by the formation of oxygen-containing compounds, in particular water [14].

Under the influence of temperature two complicated processes occur simultaneously in the CTP: destruction and polycondensation. Destruction with the formation of low-molecular substances is accompanied by weight loss of CTP when heated.

The analysis of the presented data (Table) showed that in all cases the stabilized CTP (CTP–S) lost weight when heated in the presence of air, i.e. destructive processes with the formation of low-molecular volatile compounds were observed.

The calculations have been performed according to the law of additivity (Table) to estimate the degree of interaction of components in CTP–S after heat treatment; the obtained results showed that all the stabilizing additives interact with the CTP components since actual weight losses differ from the calculated ones.

During the interaction of CTP with melamine, calcium and zinc stearates, the actual weight loss is less than the calculated one. The interaction of CTP with these stabilizers leads to diminishing the weight loss which is accompanied by the elimination of low-molecular compounds. In these cases, the condensation processes between the CTP and the stabilizer predominate.

In the case of CTP interaction with irganox, the actual weight loss is higher than that calculated by additivity law which may indicate that irganox, upon interaction with the CTP, initiates the degradation reactions with the formation of low-molecular compounds.

The functional groups variation of CTP with and without stabilizers was observed by Fourier transform infrared (FTIR) spectroscopy. It is known that there are the peaks at $3040\text{--}3050\text{ cm}^{-1}$ (i.e. the aromatic hydrogen-stretching vibration) and near 1600 cm^{-1} (i.e. the C=C skeleton stretching vibration) in CTP showing aromatic structures [15]. The peaks at $2700\text{--}2980\text{ cm}^{-1}$ and from 1480 to 1370 cm^{-1} are related to the aliphatic hydrogen stretching absorption in CH_2 and CH_3 structures [16]. The peaks at 2920 cm^{-1} and about 2860 cm^{-1} are characteristic of CH_2 -group, and the peak at about 2960 cm^{-1} is characteristic of the methyl CH_3 -group [3]. The absorption band at $1690\text{--}1730\text{ cm}^{-1}$ characterizes the vibrations of the carbonyl group C=O in the CTP [3,4].

A comparison of the FTIR spectra of the initial, heat-treated CTP and the CTP–S after thermal aging is presented in Fig. 3.

Effect of stabilizer additives on the weight loss of CTP

CTP	Composition, weight fraction				Actual weight loss, %	Deviation from additivity, %
	Irganox	Melamine	Zn stearate	Ca stearate		
100	0	0	0	0	1.33	–
100	2	0	0	0	1.72	+31
100	0	2	0	0	1.28	–2
100	0	0	2	0	1.25	–5
100	0	0	0	2	1.18	–15

As can be seen from the FTIR spectra, the peaks at 3045 and 1600 cm^{-1} show aromatic structures existing in initial CTP, heat-treated CTP and CTP-S.

An increase in the peak intensity of the band at 3045 cm^{-1} after heating CTP indicates an increase in the condensation degree of its aromatic systems.

The absence of the absorption band at 2957 cm^{-1} (i.e. corresponding to the stretching vibrations of CH_3 group) in the heat-treated CTP and the weakening of the bands peaks at 2920 and 2855 cm^{-1} (corresponding to the stretching vibrations of the aliphatic CH_2 group) indicate the elimination of these groups as a result of the effect of elevated temperatures. Heat-treated CTP has no peak at 1735 cm^{-1} which are characteristic of the stretching vibrations of carbonyl $\text{C}=\text{O}$.

A comparison of the FTIR spectra of CTP with and without irganox (2% relative to CTP) after heat treatment (Fig. 3) showed that the difference consists

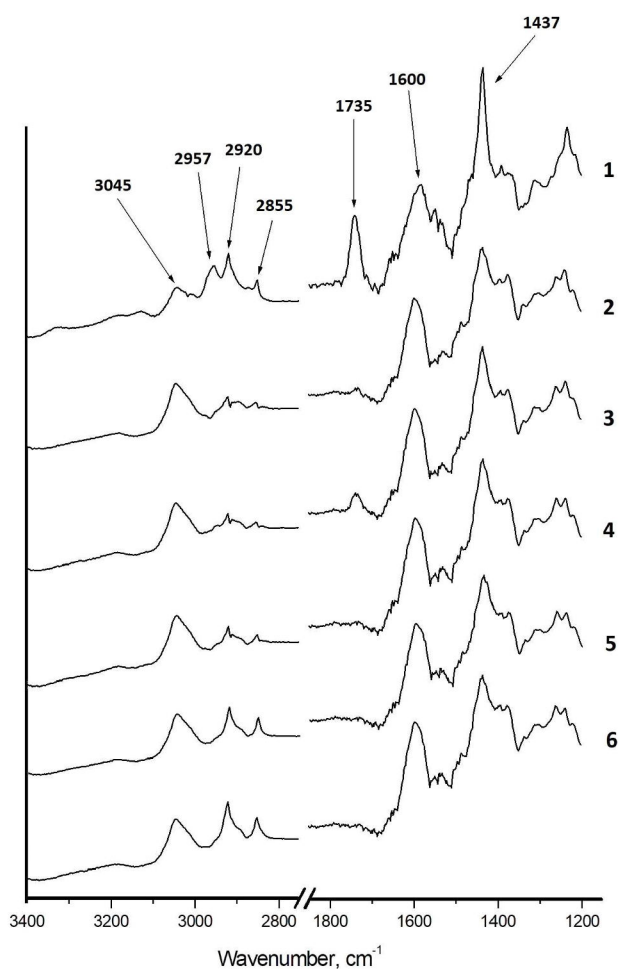


Fig. 3. FTIR spectra of initial CTP (1), heat-treated CTP (2) and CTP-S stabilized by 2% of the following additives: irganox (3), melamine (4), calcium stearate (5), zinc stearate (6).
T=150°C, 1 hour

only in the appearance of a weak peak at 1735 cm^{-1} (the stretching vibrations of $\text{C}=\text{O}$ carbonyl) in the CTP stabilized by irganox (CTP-I). The appearance of carbonyl groups in the heat treated CTP-I is most likely due to the presence of this group both in irganox and in the products of its interaction with CTP components.

Based on the analysis of the data obtained, the interaction of irganox with CTP can be represented as follows. When the CTP is heated, radicals are formed as a result of the elimination of hydrogen and alkyl groups [3,11]. It can be assumed that the resulting free radicals of the CTP react with radicals of irganox to form large size multinuclear molecules. Multinuclear aromatic compounds eliminate substituents and hydrogen easier due to low binding energy at the periphery of the molecules. And the more the compound is condensed, the easier it is to separate the side groups [12]. For this reason, it is easier to eliminate the aliphatic groups, presented in the composition of irganox, from the products of its interaction with CTP, and the losses of CTP substituents in the form of volatile compounds are intensified.

The FTIR spectra of the CTP and the CTP stabilized by melamine (2% relative to CTP) after thermal oxidative exposure are almost identical (Fig. 3). The weak interaction between the CTP and melamine is also indicated by a slight deviation from additivity (-2%).

Melamine, as a hydrogen donor, can not only interact with free radicals of the CTP, but also attach functional groups eliminated from the CTP (in particular, carboxy-containing) by the amino group. The addition of melamine to CTP leads to a slight deceleration of destructive processes accompanied by the formation of low-molecular compounds.

The gravimetric method and the calculation by additivity law showed that the weight losses of CTP after heating both with calcium stearate and with zinc stearate decreased (Table).

As can be seen from the obtained FTIR spectra, the zinc stearate and calcium stearate, interacting with CTP components, reduce the condensation of the system (the weakening of the intensity of the peak at 3045 cm^{-1} characterizing the stretching vibrations of the aromatic CH bond), forming methylene bridges between the aromatic rings (the appearance of the stretching vibrations of the peaks of aliphatic group CH_2 at 2920 and 2855 cm^{-1}). The reduction in the condensation of aromatic CTP systems under the action of calcium stearate and zinc stearate can inhibit the detachment of various substituents and the formation of low-molecular

weight volatile compounds which results in the reduction in weight loss.

Conclusions

The process of thermo-oxidative degradation of CTP was considered. It was shown that two complicated processes occur simultaneously in the CTP under the influence of enhanced temperature: the destruction and polycondensation, i.e. the process of thermal dehydropolycondensation. The destruction with the formation of low-molecular substances is accompanied by the weight loss of CTP when heated.

Based on the data of gravimetric and FTIR spectral analysis, it was established that individual stabilizers (irganox, melamine, calcium and zinc stearates) in the amount of 2% interact with CTP when heated in the presence of air. Melamine, calcium stearate and zinc stearate decelerate destructive processes in the CTP (in contrast to irganox) which is accompanied by the formation of low-molecular compounds.

Irganox interacting with CTP initiates the degradation reactions with the formation of volatile compounds. The reason can be the formation of large size multi-nuclear aromatic molecules, from which peripheral aliphatic groups are easily detached due to low binding energy. This is confirmed by a significant deviation of the weight loss from additivity.

Zinc stearate or calcium stearate interacting with CTP components diminish the condensation of the system, forming methylene bridges between the aromatic rings. Due to the decrease in the condensation of aromatic CTP systems, the processes of the detachment of various substituents and the formation of low molecular weight volatile compounds are inhibited, which results in the reduction in weight loss.

The obtained results should be taken into account when developing a complex stabilizer for basic stabilization of the pitch-composite.

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ВПЛИВ ПРИРОДИ СТАБІЛІЗАТОРА НА ПРОЦЕС ДЕГРАДАЦІЇ КАМ'ЯНОВУГІЛЬНОГО ПЕКУ

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Вивчено вплив стабілізаторів на термоокислювальну деградацію основного компоненту (кам'яновугільного пеку) нового матеріалу – пекокомполімеру. На основі даних гравіметричного та ІЧ-спектрального аналізу встановлено, що індивідуальні стабілізатори (ірганокс, меламін, стеарат кальцію та стеарат цинку) у кількості 2% взаємодіють з кам'яновугільним пеком при температурі 150°C у присутності повітря. Меламін, стеарат кальцію та стеарат цинку уповільнюють (на відміну від ірганоксу) в пеку деструктивні процеси, які супроводжуються утворенням низькомолекулярних сполук. Показано, що ірганокс при взаємодії з пеком ініціює реакції деструкції з утворенням летких сполук. Показано, що стеарат цинку або стеарат кальцію, взаємодіючи з компонентами пеку, знижують конденсованість системи, утворюючи метиленові містки між ароматичними кільцями. Завдяки зменшенню конденсованості ароматичних систем пеку гальмуються процеси утворення низькомолекулярних летких сполук та зменшується втрата маси в присутності стеаратів кальцію та цинку. Отримані результати досліджень необхідно буде враховувати при розробці комплексного стабілізатора для базової стабілізації пекокомполімеру.

Ключові слова: кам'яновугільний пек; термоокислювальна деградація; ірганокс; меламін; стеарат кальцію; стеарат цинку; ІЧ-спектроскопія.

THE INFLUENCE OF THE NATURE OF STABILIZER ON THE DEGRADATION OF COAL TAR PITCH

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Keywords: coal tar pitch; thermo-oxidative degradation; irganox; melamine; calcium stearate; zinc stearate; FTIR spectroscopy.

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