UDC 661.8

I. Krutko, V. Kaulin, K. Satsyuk (DonNTU)

TESTING OF MODIFIED COAL TAR PITCH AS POLYMER MATRIX IN COMPOSITE MATERIALS

Structural compositional polymeric materials are one of the most common materials of present time. The basis of polymeric matrix of these materials are different polymers. Production of polymers is a compound process that determines their high cost. Having regard to the high demand for polymeric composites the search of cheaper ones is very actual today.

Coal tar pitch is a unique product with a rich set of properties, among which are polymeric ones. Coal tar pitch is cheaper than classical polymers and it characterized by resistance to acids, alkalis, water, does not put on biodestruction under the influence of various microorganisms, has low thermal conductivity.

Modification of coal tar pitches provides a wide opportunity to adjust and change their properties. This opens a new direction - the use of coal tar pitch chemical potential for creating the disperse-filled compositional polymeric materials.

Past studies have shown the possibility of active influence on polymeric properties of coal tar pitch by modifying with chemical additives such as polyvinyl chloride and polymer of polyolefin line with intergrafted functional groups. The results of thermochemical and structural changes indicate that between coal tar pitch and modifiers the chemical and physico-chemical interaction takes place. Reactions of polymerization and polycondensation leads to the structuring of coal tar pitch, increasing the strength of structure, thermal stability.

The obtained pitch composite has relatively high mechanical properties and thermal stability. The obtained material for all parameters can be attributed to the hard-burning polymer composite what gives it a cogent advantage comparably to thermoplastic polymers.

Tests of modified coal tar pitch as a polymer matrix showed that it can successfully compete with classical polymers in order to create compositional materials.

Keywords: coal tar pitch, modification, polymeric matrix, filler, asbestos, mechanical properties, thermal stability, pitch composite.

Composite materials (CM) are heterophase systems [1], obtained from two or more components, where one component is a matrix in which another component (or other components) is distributed in a certain manner, and separated from the matrix by the line of demarcation.

Modern composites have not only a wide range of physical and mechanical properties, but also are capable to directional changes. The fact that the required functional properties of these materials are formed beforehand in the process of their creation, increases their prospectivity by varying the composition and structure in many times.

Structural compositional polymeric materials are one of the most common materials of present time. The basis of polymeric matrix of these materials are different polymers. Production of polymers is a compound process that determines their high cost. Having regard to the high demand for polymeric composites the search of cheaper ones is very actual today.

The properties of polymeric compositional materials (PCM) are determined by the properties of polymeric matrix, the nature of filler and interphase interaction between them.

Coal tar pitch is a unique product with a rich set of properties, among which are polymeric ones. Coal tar pitch is cheaper than classical polymers and it characterized by resistance to acids, alkalis, water, does not put on biodestruction under the influence of various microorganisms, has low thermal conductivity.

But, despite the great similarity with polymers [2], coal tar pitch cannot be considered as a classic macromolecular compound. To improve the polymeric properties of coal tar pitch it is necessary to modify it, i.e. to change the chemical composition and internal structure.

Past studies [3,4] have shown the possibility of active influence on polymeric properties of coal tar pitch by modifying with chemical additives such as polyvinyl chloride (PVC) and polymer of polyolefin line with intergrafted functional groups (PM-EV). The results of thermochemical and structural changes indicate that between coal tar pitch and modifiers the chemical and physico-chemical interaction takes place. Reactions of polymerization and polycondensation leads to the structuring of coal tar pitch, increasing the strength of structure, thermal stability. Due to the processes of structure formation physical and mechanical properties of coal tar pitch are improved, such as the maximum compression stress (σ), modulus of elasticity in compression (E), bending maximum stress (σ) and modulus of elasticity in bending (E) (Table 1).

TABLE 1. Physico-mechanical properties of modified coal tar pitches

Composition (%)	σ compression, MPa	E compr, GPa	σ bending, MPa	E bend, GPa	T_S by Vick, ℃
Initial coal tar pitch	3	0,3	5	1,1	53
Thermo-treated pitch	3	0,3	5	1,1	60
Coal tar pitch, PM-EV (5)	16	1,3	4	2,1	60
Coal tar pitch, PVC (3)	18	1,8	7	2,4	69
Coal tar pitch, PVC (3), PM-EV (5)	21	2,2	9	3,8	69

As it seen from the table 1 the highest mechanical properties has coal tar pitch, modified by complex modifier PVC-PM-EV. Coal tar pitch, modified by PVC modifier has the worse, but also sufficiently high levels of mechanical strength. Thus modified coal tar pitch has better properties.

Modification of coal tar pitches provides a wide opportunity to adjust and change their properties. This opens a new direction - the use of coal tar pitch chemical potential for creating the disperse-filled compositional polymeric materials.

Increasing the technological and operational properties of pitch polymers can be achieved by introducing the filler into pitch polymeric matrix, i.e. the creation of compositional polymeric materials. Creating such materials considered in recent years as the main reserve of obtaining the new materials with improved properties.

When creating compositional materials the important factor is the nature of filler. Fillers can be powdery, laminar, fibrous and others. Introduction of filler is always accompanied by simultaneous improvement of one characteristics of filled material and decreasing others. Various fillers can regulate the technological properties of polymeric compositional materials in wide range.

Most interesting is the filler in the form of fibers, which have sufficiently high elastic strength characteristics.

Strength and inflexibility are the most important characteristics of any material.

It is known that fibrous fillers have high strength characteristics. In addition, at the interface matrix -fibrous filler there is a strong interphase interaction, due to the specific surface area, which is much greater than in the case of lamellar or spherical particles of the same mass. This leads to creation of extended interphase surfaces and developed interphase layers. Therefore the short-fibrous fillers are called reinforcing, because with similar content of dispersed and fibrous fillers the latest provede higher increase in strength of the composite.

To improve the strength characteristics of the PCM and the creation of chemically resistant and insulating materials asbestos is widely used due to high strength characteristics, thermal resistance and excellent chemical resistance.

Asbestos refers to a class of disperse fillers, mineral by origin, by the form - to a class of chrysotile fibrous fillers. Chemical composition of chrysotile asbestos is a strongly hydrated magnesium silicate with general formula $Mg_6[(OH)_4Si_2O_5]_2$.

As asbestos refers to inorganic silicates, it has thermo-, and atmospheric resistance and chemical inertness. Chrysotile asbestos is made up of layers of tetrahedron of silicon oxide and magnesium hydroxide, which consistently alternate.

The chrysotile asbestos is characterized by the following parameters [5]: destructive tensile stress 2,1 GPa, tensile modulus 160 GPa, density 2400-2600 kg/m^2, diameter of fibers 16-30 nm, specific surface area of 17-60 m^2/g, pH 10,3. One of the important advantage of asbestos fibers to other fibrous materials of inorganic origin is its high flexibility, and lack of large industrial equipment wear. Therefore, as a filler for testing of modified coal tar pitch as the polymeric matrix in pitch composites was selected the asbestos fiber.

In accordance with the practice of developing new materials for pilot plant was accumulated experimental batches of pitch compositional materials. The analysis of physico-mechanical, thermal and other characteristics obtained from pitch composites allowed to appreciate the ability to create the new compositional materials on the basis of modified coal tar pitch.

To obtain a pitch composite a medium temperature coal tar pitch was used: softening temperature 83℃ (using ring-hinge method), viscosity at 135℃ – 10 Pa·s, softening temperature by Vick - 53℃, content of α-fraction – 34,9%, β-faction – 34,1%, γ-fraction – 31,0%.

The process of filling the coal tar pitch with asbestos consists of several stages, each one is characterized by special conditions and requirements for its implementation. A base for getting a polymeric compositional materials is the process of mixing.

The first stage is coal tar pitch pounding. It is necessary for improving the heat conduction when heated by increasing the surface area, and for convenience when mixed with particles of modifier and filler. As the coal tar pitch is a fragile substance under normal conditions, for its pounding most suitable conditions of shock and deteriorate loads that may have been implemented in hammer crusher.

The second stage of process is mixing the coal tar pitch with modifier (PVC and PM-EV) in a predetermined ratio. The task of dispersing mixing is to destroy aggregates and distribute component particles statistically evenly by volume. In addition, while coal tar pitch mixing with modifiers the mechano-chemical interaction can take place, by means of which strong bonds between particles of coal tar pitch and chemical additives are formed.

The next stage is mixing of obtained pitch polymeric mixture with filler - asbestos. Purpose of this process – to reduce the compositional heterogeneity of system, result - it becomes more homogeneous. While mixing the additional particles grinding is also takes place. Mixing was performed in a high-speed mixer.

As the coal tar pitch is in solid aggregate state under normal conditions, the next stage of process is heating. When heating the coal tar pitch moves from glassy to elastic-plastic, plastic-liquid and then to the visco-liquid state. Under the certain temperatures [3] the coal pitch approaching to non-newton liquid. This condition is characterized by the lowest pitch viscosity and can provide efficient mixing of mass, and hence a uniform distribution of particles in coal tar pitch, modifier and filler. These conditions allow to modify the coal tar pitch with maximum efficiency. In addition, the adhesion properties of coal tar pitch are improved, which is important for effective wetting of filler particles.

At the same time with heating the stirring was taken place. Efficient stirring the mixture of coal tar pitch and modifiers with asbestos is necessary to intensify the physical and chemical interactions between coal tar pitch and modifiers, wetting heat and mass transfer in the reactor and compliance the mixture homogeneity.

In the experimental apparatus (Fig. 1) mixing effect is provided by two screws, which are parallel in one chamber and rotate towards each other. Screw mixers are most effective for mixing of material with high viscosity. While rotating toward each other two screws are like roll mills, which grind material between them, besides presenting material along the screw. Displacement and grinding also take place in the interval between the screw and frame.

Scheme of experimental plant for compositional materials obtaining based on modified coal tar pitch is shown on Fig. 1.

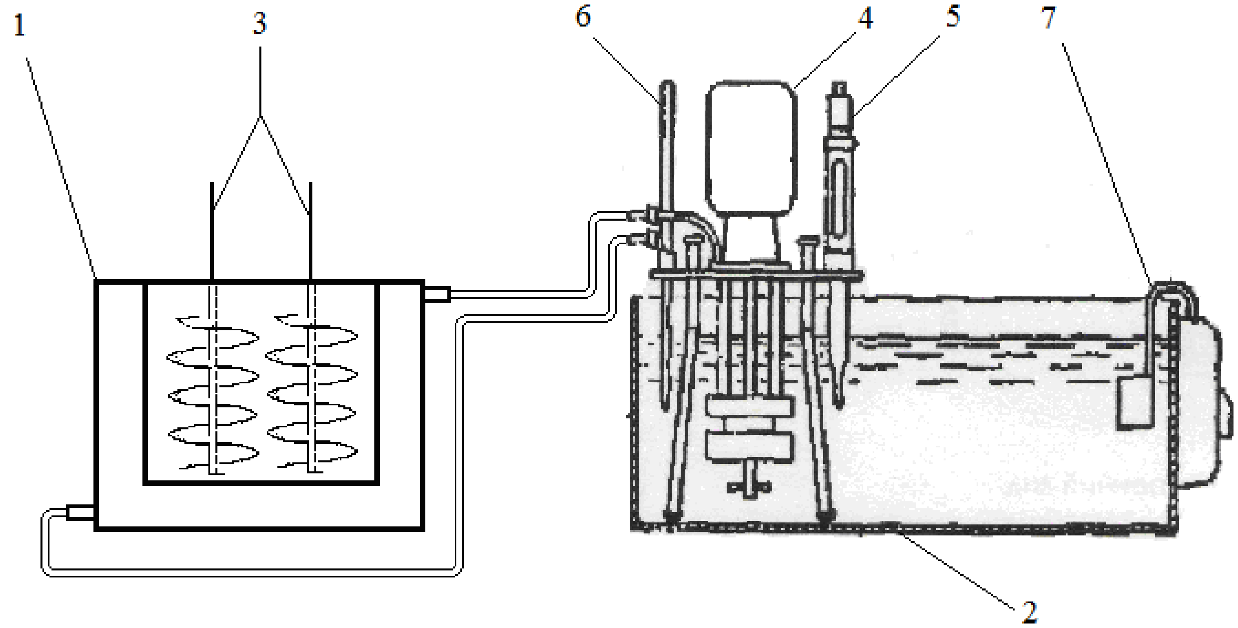

Figure 1. The scheme of experimental plant for compositional materials obtaining based on modified coal tar pitch

1 - jacketed reactor, 2 – thermostat, 3 - screw mixers, 4 - pump, 5 - contact thermometer, 6 - controlling mercury thermometer, 7 – electric heating element.

Experimental was the following.

Initial materials - coal tar pitch and modifier in specific experimental conditions ratio was stirred at 20-25℃ to externally smooth. Then the mixture under the same conditions thoroughly mixed with asbestos.

Then the resulting homogeneous mixture is loaded to the reactor, which is pre-heated to the desired temperature of experiment, and covered with lid. After a certain period of time (depending on the temperature of experiment) when the mixture is melted which is enough to include mixers and the right time of experiment is noted. After the allocated time, the mixers were turn off and obtained the pitch composite is unloaded.

In the laboratory conditions a series of experiments with different matrices and the same filler content (27%) at 170℃ and 15 minutes of stirring were conducted in the reactor.

According to state standard specification samples of pitch composites were produced and tested in accordance with state standard specification GOST 15088-83 on thermal stability by Vick.

On universal testing machine M500-50CT (Testometric, England) the maximum stress and modulus of elasticity in bending according to state standard specification GOST 4648-71 were determined.

Results are shown in Table 2.

Table 2. Properties of composites obtained from modified coal tar pitch

Number of exper.	Composition (%)	σ bending, MPa	E bending, GPa	Thermal stability by Vick, ℃
1	Coal tar pitch, asbestos (27)	31	5,5	77
2	Coal tar pitch, PVC (3), PM-EV(5), asbestos (27)	43	8,7	91

As it seen in Table 2, the pitch composite obtained from modified coal tar pitch (exp.2) has better mechanical and thermal properties compared with unmodified coal tar pitch. For mechanical and thermophysical parameters this pitch composite can be attributed to the materials of general engineering purposes.

In Table 3-4 the comparison of pitch composite obtained from modified coal tar pitch, and some unfilled and filled polymers with asbestos on mechanical properties and heat resistance is shown [5-9].

Presented with various literary sources data to the properties of polymers are significantly different and are informational in nature, because it is known that the mechanical and thermal properties of polymers and PCM are heavily dependent on many factors.

Table 3. Comparison of mechanical properties and thermal stability of pitch composites and unfilled polymers [6-8].

Material	Max. bending stress, MPa	Bending modulus, GPa	Thermal stability by Vick, ℃
Pitch composite	43	8,7	91
Polyethylene	12-17	0,12-0,26	80-12 0
Polystyrene	55-70	2,8-3,5	75-105
Polypropylene	56-70	0,7-1,9	140-155
Polyvinylchloride	80-120	3,0-4,0	75-80

Table 4. Comparison of mechanical properties and thermal stability of pitch composites and filled polymers [5.9].

Material	Filler, %	Max. bending stress, MPa	Bending modulus, GPa	Thermal stability by Vick, ℃
Pitch composite	Asbestos, 27	43	8,7	91
Polyethylene	Asbestos, 30	40	2,9	69
Polyethylene	Fiberglass, 30	33-56	1,1-2,4	-
Polystyrene	Asbestos, 40	51	4,1	90
Polypropylene	Asbestos, 27	89	6,8	86

Suitability of compositional material use for a particular purpose is determined by a combination of technological and operational properties. One of the most important characteristics of polymers and PCM is their flammability.

Flammability of compositional materials based on modified and unmodified coal tar pitch was determined in accordance with state standard specification 12.1.044 "Fire safety of substances and materials".

Flammability of the sample was determined:

- by kinetic methods - descending mass of material (Δm), time of reaching the maximum temperature T_{max},, time of self-combustion T_s;

- by temperature characteristics - maximum temperature increment $\Delta t_{max} = (t_{max} - 200)$, the maximum temperature t_{max};

- by concentration - the so-called oxygen index (OI), which is the minimum molar concentration of oxygen in the gas mixture of oxygen-nitrogen, in which in this environment an independent sample burning of polymer is supported.

Studies on flammability showed that the compositional material based on non-modified coal tar pitch relates to combustible materials (Δm=35%; Δt_{max}=565℃, t_{max}=765℃, T_{max}=205 s, T_s=130 s, OI = 29%).

Compositional material, the matrix of which was the coal tar pitch, modified by PVC and PM-EV, for all parameters can be attributed to the hard-burning polymer composite (Δm=2,5%; Δt_{max}= 0, t_{max}= 200℃, T_{max}=300 s, T_s= 0-2 s, OI = 42,6%).

Tests of modified coal tar pitch as a polymer matrix showed that it can successfully compete with classical polymers in order to create compositional materials. The obtained pitch composite has relatively high mechanical properties and thermal stability. Polyethylene, polypropylene, polystyrene and others are flammable plastics with oxygen index OI=17-18%, except for PVC OI=49% (OI of pitch composite is 42,6%). The fact that pitch composite refers to the hard-burning material gives it a cogent advantage comparably to thermoplastic polymers.

References

1. Власов С.В. Основы технологии переработки пластмасс: Учебник для вузов. / С.В. Власов, Л.Б. Кандырин, В.Н. Кулезнев. – М.: Мир, 2006. – 600 с.

2. Крутько І.Г. Теоретичні передумови використання кам'яновугільного піку як полімерного матеріалу / І.Г. Крутько, В.Ю. Каулін // Наукові праці ДонНТУ. Серія: Хімія і хімічна технологія. – 2010. - №15 (163). – С.126-130.

3. Крутько І.Г. Реологічні дослідження модифікованих кам'яновугільних пеків / І.Г. Крутько, В.Ю. Каулін, К.О. Сацюк // Наукові праці ДонНТУ. Серія: Хімія і хімічна технологія. – 2011. - №16 (184). – С.150-158.

4. Крутько І.Г. Термічний аналіз модифікованих кам’яновугільних пеків / І.Г. Крутько, В.Ю. Каулін, К.О. Сацюк // Наукові праці ДонНТУ. Серія: Хімія і хімічна технологія. – 2012. - №19 (199). – С.133-138.
5. Наполнители для полимерных композиционных материалов. Справочное пособие. – М.: Химия, 1981. – 736 с.
6. Технические свойства полимерных материалов: Учеб.-справ. пособие./ В.К. Крыжановский, В.В. Бурлов, А.Д. Паниматченко, Ю.В. Крыжановская. – 2-е изд., испр. и доп. – СПб: Профессия, 2005. – 248 с.
7. Энциклопедия полимеров. М.: Советская энциклопедия, 1972. – 1224 с.
8. Шрейбер Г.К. Конструкционные материалы в нефтяной, нефтехимической и газовой промышленности. / Г.К. Шрейбер, С.М. Перлин, Б.Ф. Шибряев. – М.: Машиностроение, 1969, 396 с.
9. Кербер М.Л. Полимерные композиционные материалы/ М.Л. Кербер, В.М. Виноградов, Г.С. Головкин и др. – СПб.: Профессия, 2008. – 560 с.