

## FORMATION OF POLYMERIC COMPOSITE MATERIALS REINFORCED BY OIL FLAX FIBER

*In work the analysis of the previous researches of the mechanism for formation of polymeric composite materials with the use of natural fibers as fillers and the estimated mechanism of the reaction between linen fiber and a polymeric matrix in the course of formation of composites are made. The hypothesis of possible barriers for emergence of adhesion between fiber and a matrix when pressing composites and ways of their overcoming is developed. The aim of the work is to prove experimentally the possibility of the use of fibers of oil flax as a cellulose filler for formation of composites on the basis of phenol formaldehyde polymers, and also, to develop theoretically the mechanism of interaction of oil flax fiber cellulose with a polymeric matrix of phenol formaldehyde resin. The indicators of bending strength and toughness of phenoplast filled with fiber flax is even higher than those of the phenoplast based on cotton linters. Thus, it was found that the quality of the polymer composites is somewhat higher than the quality of composite materials with addition of cotton which are imported to Ukraine. The experimental results confirm the hypothesis stated in the theoretical part of the article that reduction of the mass fraction of pectin, lignin and waxes in linseed flax fibers, increases the adhesion in a polymer matrix during the formation of the composites. The mechanism proposed of oil flax cellulose fiber and phenol formaldehyde polymer interaction makes it possible to claim that to increase adhesion of oil flax cellulose with phenol formaldehyde resin it is necessary to unblock hydroxyl groups of flax cellulose, that is to exempt them from waxes and thus to increase hydrophilicity of flax fiber. Therefore, to receive polymeric composite materials with the use of oil flax fiber as filler, preliminary deep purification of flax fiber from waxes is necessary.*

*Key words: composites, phenol formaldehyde resin, flax cellulose, adhesion*

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## ФОРМУВАННЯ ПОЛІМЕРНИХ КОМПОЗИЦІЙНИХ МАТЕРІАЛІВ, АРМОВАНИХ ВОЛОКНОМ ЛЬОНУ ОЛІЙНОГО

*У роботі проведено аналіз попередніх досліджень щодо механізму формування полімерних композиційних матеріалів з використанням природних волокон у якості наповнювачів та висунутий передбачуваний механізм реакції між лляним волокном та полімерною матрицею в процесі формування композитів. Побудовано гіпотезу щодо можливих перепон для виникнення адгезії між волокном і матрицею під час пресування композитів і шляхів їх подолання. Поставлено завдання експериментально довести можливість використання волокон льону олійного як целюлозного наповнювача для формування композитів на основі фенол-формальдегідних полімерів, а також теоретично розробити механізм взаємодії целюлози волокна льону олійного з полімерною матрицею фенол-формальдегідних смол. Показники міцності при згинанні та ударної в'язкості фенопластів з наповнювачем з волокна льону олійного навіть вищі, ніж характеристики фенопластів на основі бавовняного лінту. Таким чином, встановлено, що якість отриманих полімерних композитів децю вища за якість композиційних матеріалів із додаванням бавовняного волокна, яке імпортується в Україну. Одержані експериментальні результати підтверджують гіпотезу, яку викладено в теоретичній частині даної статті про те, що завдяки зниженню масової частки пектину, лігніну та восків у складі лляного волокна підвищується адгезія лляного волокна до полімерної матриці в процесі формування композитів. Запропонований механізм взаємодії целюлозного волокна льону олійного та фенол-формальдегідного полімеру дає можливість стверджувати, що для підвищення адгезії целюлози льону олійного фенол-формальдегідною смолою, необхідно розблокувати гідроксильні групи лляної целюлози, тобто звільнити їх від восків і таким чином підвищити гідрофільність лляного волокна. Тому, для отримання полімерних композиційних матеріалів з використанням у якості наповнювача волокна льону олійного необхідно попереднє глибоке очищення волокна льону від восків.*

*Ключові слова: композити, фенол-формальдегідні смоли, лляна целюлоза, адгезія.*

### Problem statement.

The main materials which are used nowadays as fillers are glass, graphite aluminium, carbon, pine forest and beryllium. But when using natural fibrous fillers in composite polymeric materials, it is possible to reach safer production, more simple utilization and considerably lower raw materials purchase expenses. Therefore, recently it has become actual to use natural fibrous fillers in polymeric composite materials.

For today scientists around the world have achieved certain success in formation of composites with the use of natural cellulose fibers as fillers. In particular, it concerns the research of features of receiving polymeric composite materials with the use of natural fibers as fillers and studying of mechanisms of chemical reactions of fillers with polymeric matrixes in the course of formation of composites as described below.

### Recent research and publications analysis.

The scientist Hongsheng Luo of the Polytechnical University of Hong Kong received composites on the basis of nano-whiskers of cellulose and polyacrylic acid (PAA). The scheme of the chemical reaction of formation of polymer with the use of nano-whiskers of cellulose is given in Fig. 1.

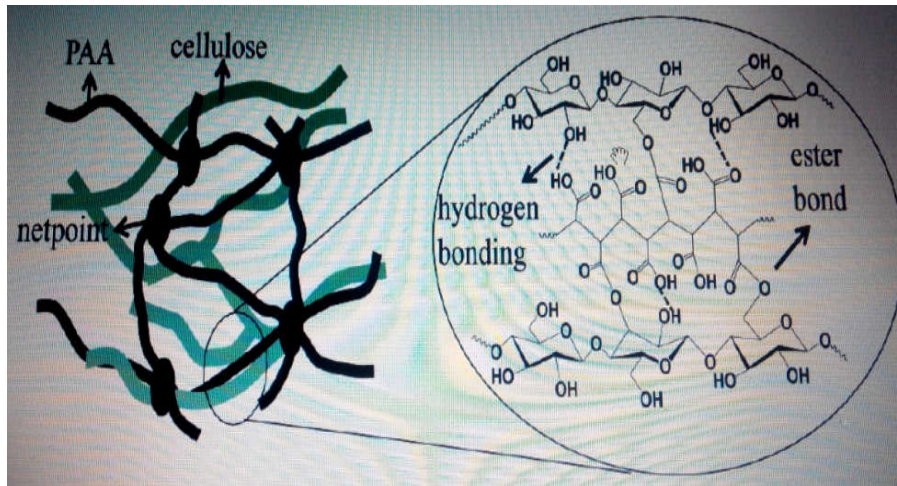


Fig. 1. The chemical reaction of formation of polymer with the use of nano-whiskers of cellulose and polyacrylic acid (PAA) [1]

The American scientists Jaewoong Lee, R. M. Broughton, S. D. Worley, T. S. Huang studied the mechanism of formation of intermolecular communications between the bleached cotton cellulose and m- aramid in the course of formation of a composite, which is shown in Fig. 2.

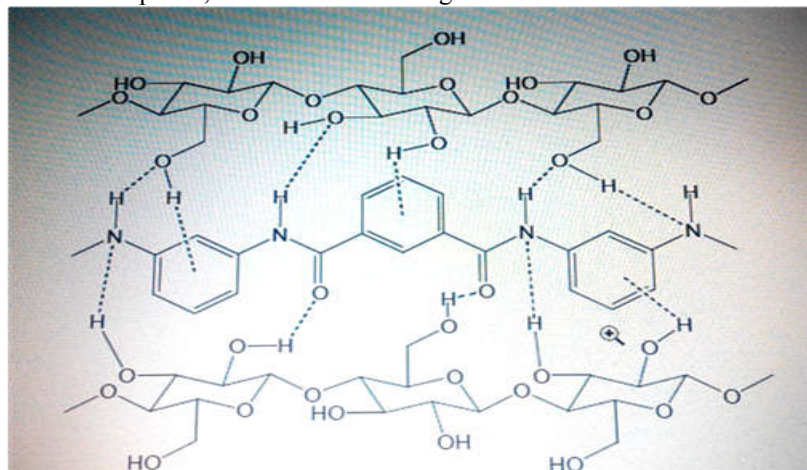


Fig. 2. Intermolecular communications between the cellulose and m-aramid [2]

On the facilities of the LLC "Priluki-Plastmass" Priluki, Chernigov region, polymeric composite materials are received today by pressing of phenol formaldehyde resin and cotton lint which now is scarce import raw material, and therefore, has high cost. In this regard, the question of replacement it with its cheaper and available domestic raw material which is not worse than cotton in physic-mechanical properties is very actual. Consequently, the problem of ensuring broad industrial use of fibrous materials, which can make alternative to cotton, is extremely important. Meanwhile, Ukraine has its own raw natural material containing cellulose, which annually renews, it is oil flax. Due to unique properties of flax, demand for this raw material is actively increasing. In this regard, in recent years around the world, and in particular, in Ukraine, crops of this culture have been considerably increased. It is necessary to notice that fiber of oil flax can be high-quality raw material for receiving cellulose and cellulose semi-finished products, paper, yarn, and also textile materials [3]. Besides, today flax fiber is widely used abroad for reinforcing of composite materials [4]. But there is no such experience in Ukraine. Therefore, the aim of the work is to prove experimentally the possibility of the use of fibers of oil flax as a cellulose filler for formation of composites on the basis of phenol formaldehyde polymers, and also, to develop theoretically the mechanism of interaction of oil flax fiber cellulose with a polymeric matrix of phenol formaldehyde resin.

Theoretical part. We will consider the estimated mechanism of interaction of flax cellulose with a polymeric matrix. The first stage of the process of receiving polymeric composite materials on the basis of flax fiber cellulose and phenol formaldehyde resin is receiving phenol formaldehyde resin. The mechanism of chemical reaction of polycondensation is shown in Fig. 3:

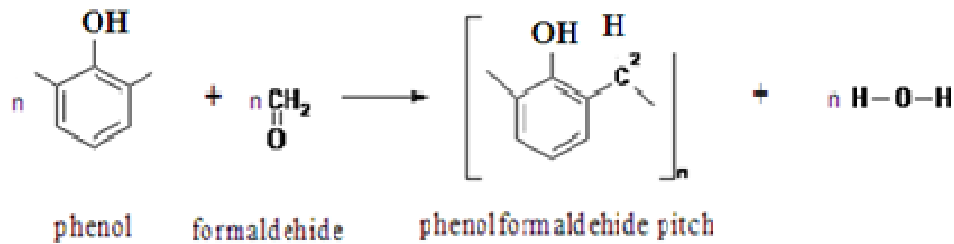


Fig. 3. The chemical reaction of the receiving of phenol formaldehyde resin

The second stage is a chemical reaction of the interaction of linen cellulose and phenol formaldehyde resin that is the formation of polymeric composite materials which may be run under the scheme given in Fig. 4:

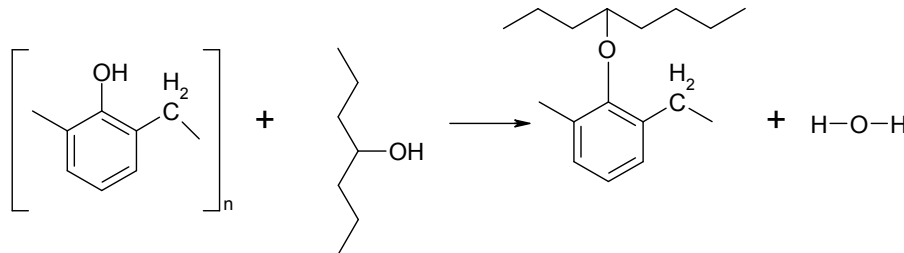


Fig. 4. The scheme of a chemical reaction of the interaction of linen cellulose and phenol formaldehyde resin

#### Materials and results

On the basis of preliminary theoretical and pilot studies on the facilities of LLC "Priluki-Plastmass" we made experimental samples of composite materials in which they used flax fiber received from stems of oil flax as filler. But in the course of receiving composites there was a stratifying of a polymeric matrix and fiber that is why there was no adhesion between fiber and the matrix. This negative phenomenon might have been caused by impurities in the flax fiber, including waxes which blocked active hydroxyl groups of cellulose. After all, it is known that wax in flax fiber composition causes its water repellence reducing reactionary ability of cellulose. In a result, such flax fiber has low wettability and therefore is unfit for pressing in composites. Thus the hypothesis was developed that preliminary purification of flax fiber from impurities, unlike with cotton fiber which almost doesn't contain them, is necessary for adhesion between flax fiber and a polymeric matrix when forming composites.

After crushing the linen raw materials were subjected to pulping in the laboratory pulping apparatus (Fig. 5.) by an oxidizing method at a temperature of 100 °C of 1 hour. Boiling compounding:

- hydrogen peroxide – 4,0 g/l;
- sodium hydroxide – 10,0 g/l;
- the calcined soda – 2,0 g/l;
- sodium silicate – 1,0 g/l;
- sodium tripolyphosphate – 1,0 g/l;
- penetrating agent – 0,3 g/l.

After pulping solution merges and washing begins: circulation by hot and cold water, processing by sulphuric acid (2 g/l), again washing with cold water and drying.



Fig. 5. Laboratory pulping apparatus

When pulping the main part of impurity passes into solution. But wax-like substances are hydrophobic hydrocarbons, esters of unsaturated acids and alcohols - remain in fiber and can be removed only with their emulsification. For these purposes we add surface-active substances to pulping solution - penetrating agent. At high

temperature wax melt ( $T_m = 600\text{ }^{\circ}\text{C}$ ), spread on a fiber surface, and the penetrating agent transfers them to a drop-like state and transfers to pulping solution in the form of an emulsion according to the following scheme (fig. 6).

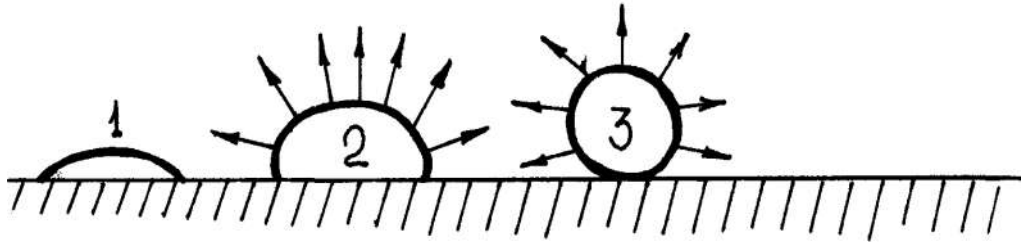


Fig. 6. Mechanism of emulsification of waxy impurity

Previously, using traditional techniques of the chemical analysis, they observed the content of main chemical components of the raw flax fiber and flax fiber after pulping process and wettability of flax fiber samples.

To determine the cellulose content, we used an accelerated method based on the conversion of cellulose to glucose by hydrolysis [5]. This method is based on oxidation of glucose received as the result of hydrolysis by iodine in an alkaline medium. The equation of the reaction is:



50 ml of filtrate containing hydrolyzed cellulose in the form of glucose was taken for titration. The experiment was repeated 5 times. The error of the experiment equaled 0,1 %. The content of the cellulose was calculated by the formula:

$$U = \frac{G_2 \times K}{G_F \times \frac{100 - K}{100}}, \quad (2)$$

where  $G_2$  - the mass of glucose in a fiber sample, g;

$G_F$  - initial mass of the fiber, g;

$K$  - ratio of the relative molecular mass of the elementary cellulose and glucose level.

One of the methods most frequently used in determination the content of lignin is hydraulic weighing that was also used in this work. This method is based on the fact that being exposed to vegetable fibers, freed prior from waxes, fats and resins with 72% sulphuric acid, lignin remains intact while all other components of the vegetable tissue change into solution. It makes it possible to separate lignin and determine its amount gravimetrically.

To determine the quantity of lignin there were selected 5 samples of 2 gram flax fiber that were crushed into fluff, weighed up to 0,001g accuracy and processed for 48 hours with 72% sulphuric acid. To achieve a better solution, the mixture was boiled for 2 hours, cooled and filtered afterwards.

The quantity of lignin was calculated in percentage as to the mass of absolutely dry fiber with up to 0,01 g accuracy by the formula:

$$L = \frac{G_L}{G_F} \times 100, \quad (3)$$

where  $G_L$  - the mass of the lignin, g;

$G_F$  - the mass of the fiber, g.

It is worth considering the method of determining pectin substances in which pectin substances are determined by iodometric method that substantially speeds the analysis. This very method was used in the work [5]. To determine the quantity of pectin there were selected 5 samples of 2 gram fiber that were weighed up to 0,001g accuracy and then washed on a filter with hot water and treated with ammonium citrate for 2 hours while boiling. After processing, the solution was filtered, and the filtrate was used to determine the quantity of pectin. To do that the filtrate was added with a solution of sodium hydroxide, acetic acid and copper sulfate for sedimentation of copper salt of the polygalacturonic acid. The residue received was filtered and used to determine the quantity of copper by titration with the solution of the polygalacturonic acid.

The quantity of pectin was calculated in percentage by the formula:

$$P = \frac{V_R \times E_c \times K}{G_F} \times 100 \quad (4)$$

$V_R$  - amount of hyposulfite, ml;

$E_c$  - equivalent of the copper

$K$  - coefficient of conversion of certain amount of copper into the calcium salt of the polygalacturonic acid.

The quantity of wax-like substances was determined by extraction of benzene [6]. Purified, crushed and

kept at certain humidity, fibrous material was treated with dried and distilled benzene for 6-8 hours. The amount of wax-like substances was determined as to absolutely dry fiber.

$$W = \frac{M_2}{M_1} \times 100 \quad (5)$$

where  $M_1$  – the mass of the flax fiber before processing, g;  
 $M_2$  – the mass of the flax fiber after processing, g.

Determination of wettability was carried out in accordance with ISO 7213-81. "Cellulose. Sampling for tests". To do the analysis, 15 g of air-dry cellulose of an average sample was taken, weighed with no more than 0,1 g error, formed a sample of the aluminium cylinder size which had been made before according to a sketch. The cellulose was put into the cylinder, weighed before, and compressed up to the internal mark 50 mm. The dust dropped during formation of the cylinder was picked up and put into the cylinder along with cellulose. A crystallization cup was filled with distilled water of  $20 \pm 0,5^\circ\text{C}$  hot up to the level no lower than 20mm from the edge. Then the aluminium cylinder was placed inside to the level of the lower external low mark of the cylinder. In 30 seconds the aluminium cylinder with moistened mass was removed from the water and weighed with no more than 0,1 g error.

Wettability ( $X_2$ ) was calculated in grams by the formula:

$$X_2 = m_1 - (m_2 + m), \quad (6)$$

where  $m$  – the mass of air-dry cellulose, g;  
 $m_1$  – the mass of cylinder with cellulose after determination, g;  
 $m_2$  – the mass of empty cylinder, g.

Determination of the mass fraction of ash is carried out in accordance with ISO 1762-74 "Cellulose. Method of Determining the Ash Content" [7]. To carry out the experiment, 5 g of air-dry cellulose was weighed with no more than 0.01 g error. A crucible was heated at the temperature  $575 \pm 25^\circ\text{C}$  in a muffle furnace for 15 min, then cooled in a desiccator for 45 min, then weighed with accuracy up to the fourth decimal figure. The sample was placed into that crucible and roasted at a small fire of a gas burner up to complete carbonization, and then the crucible was placed into a muffle furnace and fried until complete combustion of the carbon.

After roasting, as evidenced by the absence of black particles, the crucible along with the content was cooled and weighed to the accuracy of four decimal figures.

Ash content in percent relative to the weight of the sample was calculated by the formula:

$$X_4 = \frac{m_1 \times 100}{m \times (100 - W)} \times 100, \quad (7)$$

where  $m$  – the mass of air-dry cellulose, g;  
 $m_1$  – the mass of ash, g;  
 $W$  – the humidity of cellulose, %.

### Results and discussion

The experimental results of the analysis of the chemical composition of the raw flax fibers and fibers after boiling are shown in Table 1.

Table 1

**Chemical composition of flax fiber**

|            | Cellulose, % | Pectin, % | Lignin, % | Ash, % | Waxes, % |
|------------|--------------|-----------|-----------|--------|----------|
| Flax fiber | 81,79        | 7,74      | 5,96      | 1,48   | 3,03     |
| Flax fiber | 98,22        | 0,40      | 0,320     | 1,06   | -        |

By results of researches it is established that after pulping process wax is completely removed, the content of cellulose in flax fiber is increased by 16,43% in comparison with the raw fiber, the mass fraction of pectin is decreased by 7,34%, and a lignin – by 5,64%, also, during pulping process some decrease in the content of ashes was observed. Wettability of flax fiber after pulping made 105,43 g, and the raw fiber - 1,28 g, thus this indicator grew almost by 10 times. So the fiber of flax received after pulping process has a high content of cellulose and a high rate of wettability that is a powerful factor for formation of a polymeric composite.

To confirm the feasibility of replacing imported cotton with boiled linseed fibers in the manufacture of composites in facilities of "Priluki Plastics", after boiling flax fiber was later used to form the composite in the conditions of the said above enterprise.

Production of composites was the following: selected single samples were stirred and an average sample weighing no less than 1 kg was chosen. The average sample was placed in a clean, dry, moisture-proof package. A label indicating the batch number and the date of sampling was placed inside the package. Test specimens were prepared by compression molding. The main components for press materials were: resin, fibrous filler, hardener or resin curing agent, oils and others. Samples in the form of fiber bars were pressed in one place folding mold form.

As the result of these works, experimental samples of composite materials with the use of flax fiber were received. In the composites obtained, there were discovered the following physical and mechanical properties: strength in bending and impact strength.

Impact test was conducted in accordance with ST SEV 1491-79 "Method of Determining of Impact Strength by Sharpy" [8]. Determination was carried out at the pendulum speed  $2.9 \text{ m/s} \pm 10\%$ . The experiment was repeated five times.

Determination of the bending stress at fracture was carried out in accordance with ISO 178:2010 "Plastics. Test Method for Static Bending" [9] on bars measuring  $80 \times (10 \pm 0,5) \times (4 \pm 0,2) \text{ mm}$  at the temperature of  $23 \text{ }^\circ\text{C}$  and 50% relative humidity.

Physic-mechanical properties of cotton-based phenoplast and boiled flax fibers are shown in Table 2.

Table 2

**Physico-mechanical characteristics of cotton-based phenoplast and boiled flax fibers**

| Type of fillers   | Physico-mechanical characteristics of phenoplasts with different fillers |                                    |
|-------------------|--|------------------------------------|
|                   | Bending stress at fracture, MPa  | Impact strength, kJ/m <sup>2</sup> |
| Boiled flax fiber | 30,1   | 10,0                               |
| Cotton linter     | 30,0   | 9,0                                |

The table shows that the indicators of bending strength and toughness of phenoplast filled with fiber flax is even higher than those of the phenoplast based on cotton linters. Thus, it was found that the quality of the polymer composites is somewhat higher than the quality of composite materials with addition of cotton which are imported to Ukraine.

The experimental results confirm the hypothesis stated in the theoretical part of the article that reduction of the mass fraction of pectin, lignin and waxes in linseed flax fibers, increases the adhesion in a polymer matrix during the formation of the composites.

**Conclusions.** The mechanism proposed of oil flax cellulose fiber and phenol formaldehyde polymer interaction makes it possible to claim that to increase adhesion of oil flax cellulose with phenol formaldehyde resin it is necessary to unblock hydroxyl groups of flax cellulose, that is to exempt them from waxes and thus to increase hydrophilicity of flax fiber. Therefore, to receive polymeric composite materials with the use of oil flax fiber as filler, preliminary deep purification of flax fiber from waxes is necessary.

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