

Receiving Properties Spectrum of Highly-Filled Polymers by Surface “Cementing”

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Abstract – As a result of theoretical research of experimental data a polymer highly-filled composite CDC (composite durable cement) with the gradient of physico-mechanical and antifriction properties changing in depth which together with high strength and durability has an impact resistant viscous core. It has been determined that combination of nylon with epoxiplastic laquer block copolymer (N+ELBC) and consequent surface “cementing” change significantly the materials surface morphology which influences its tribotechnical properties. One of the reasons for increased stability and fatigue durability of CDC oleagen at such surface treatment is rational usage of lubricant (plasticizer) in the friction zone. The article proves efficiency of introduction of multi-purpose fillers (Si, phenol, phenylisopropyl-phenylennediamine, sodium nitrate, blacklead) hindering fatigue-crack nucleation by inhibiting thermal decomposition of polymeric matrix and their extension thanks to additional stress relaxation in the outlet zone.

Keywords– polymer composite durable material; surface “cementing”; molecular chains sewing; oleagens; crystal phase.

I. INTRODUCTION

Our previous research has shown [1] that products or joints which are under simultaneous frictional and dynamic (impact) loads should have different in their thickness physico-mechanical and tribo-technical properties, as their surface and deep layers have different functions. In this regard the surface of the product should have high hardness and the deep layers (“the core”) should have high impact toughness. Introduction of

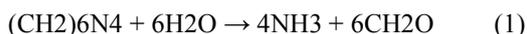
fibrous modifying agents increases material strength and its viscosity [2,3], but at the same time good properties are the same through all the volume and this method does not allow receiving the gradient of necessary working properties of the detail or joints in their depth. It has been determined that increased sliding properties and material durability, for example, Standard Atmosphere-1 (SA-1), can be received by high-degree of its filling and hardness increase [5, 6]. But a serious drawback of such material is low mechanical strength.

It is known [7] that if epoxy resin is used as a binding material high filler loading capacity of the composition is achieved (80-88 mass. %) by improving the connection of the filler with the matrix. Despite good adhesion to the fiber glass and good water resistance of epoxy resins, compositions based on them have insufficient impact strength due to frangibility and low cohesion strength of these resins. Essential from the point of view of thermal stabilization is taking place in the mixture of bonding resins: nylon with epoxiplastic laquer block copolymer (N+ELBC), both during processing and after producing parts from it, further chemical interaction of epoxy groups with amido groups of polyamide resins and phenolic hydroxyls ELBC under an elevated temperature (120-200°C) [7,12]. But this way of these resins mixture solidification simultaneously increases hardness and frangibility throughout the material [7] which is unacceptable for joints and structures.

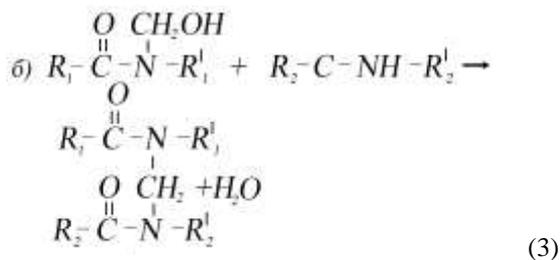
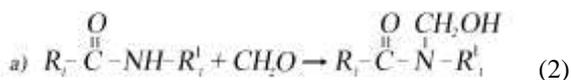
II. METHODS AND MATERIALS

In order to solve this problem a method has been suggested providing the process of cross linkages (hardening) of frictionally deformed surface layers and receive polymer frame with high surface hardness. This method is called “cementing”, and the material - oleagen CDC. This material based on the mixture N+ELBC contains powder cuprum, blacklead, lubricant № 158, glycyol alcohol. In case of diffusive saturation of the product based on N+ELBC with the hardening agent, in particular, hexamethilenthramin (hexamethylenetetramine), the latter can initiate the process of linking – conversion of linear macromolecular chains into the meshy one (spatial). Here the following reactions are possible.

In water or moist environment hexamethylenetetramine dissolves into ammonia and formaldehyde:

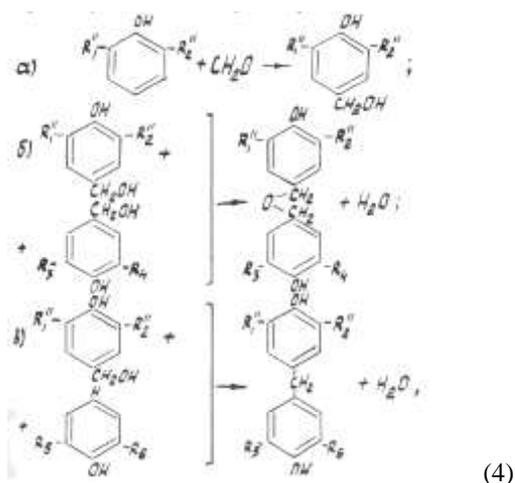


Further formaldehyde solution (formalin) reacts with nylon (capron) and ELBC. Reaction with nylon has two stages, where formaldehyde eliminating from its molecule one-by-one hydrogen atoms with loose binding, links chains laterally:



where: R_1, R_1^1, R_2, R_2^1 are polyamide residues.

Reaction of formaldehyde with ELBC has accompanying reactions:



where: $R_1'', R_1''; R_3, R_4; R_5, R_6$ are ELBC residuals.

“Cementing” (gel-fraction increase) of the surface layers (Fig. 1.) was done by sample(product) heat treatment in stages in the saturated hexamethilenthramin solution (hexamethylenetetramine) in glycyol alcohol at 120°C, 140°C, 160°C, 180°C and 200°C during 3 hours in each mode.

Degree of cure of the surface coating made from resinous composition was determined by the hardness as the most convenient criterion of indirect estimation of linking degree in network polymer (thermosetting material) [9].

III. RESULTS

Studying surface degree of cure in oleagens CDC we received firmness dependence (GOST 4670-67) of the material at depth 0.5 mm on thermal treatment temperature (Fig.2).

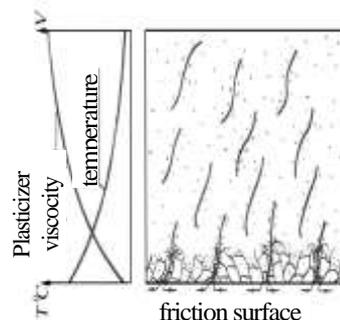


Fig. 1. Oleagens CDC structural scheme

Determination of hardness at the depth of 0.5 mm is necessary because at high temperatures (180°C and 200°C) there appeared dimples and other crater-shaped roughness on the sample surface which did not allow estimate real hardness of the surface layer.

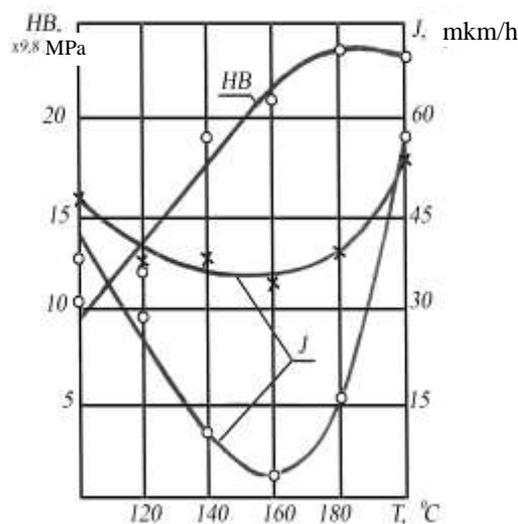


Fig. 2. Temperature effect during thermal treatment (T) on hardness (HB) and wear rate (J) of oleagens CDC during thermal treatment: -o- with a hardener and -x- without a hardener

It is possible that dimples on the surface are the result of cavitating outbreak of evaporating glycol alcohol. As the result the curve of changes in oleagens CDC hardness treated at 200°C, is maximum in volume at distance 0.5 mm from the sample surface (Fig.3.).

Tests with a front friction and wear machine of oleagens CDC samples treated at different temperatures showed that at 160°C wear rate is minimal and are equal 3 km/h (TABLE 1, Fig. 2).

TABLE I. WEAR RATE OF OLEAGENS CDC SAMPLES TREATED AT DIFFERENT TEMPERATURES (p=9.8·10⁴Pa, V=0.5 m/s)

Temperature, °C	120	140	160	180	200
Wear rates, mkm/h	29	11	3	16	57

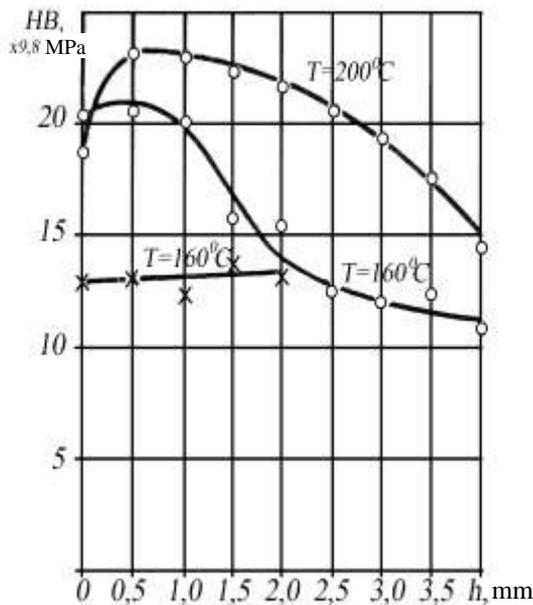


Fig. 3. Changes in oleagens CDC hardness in depth during heat treatment: -o- with a hardener, -x- - without a hardener

Fig.2. and Fig.3. show that in case of treating material without hexamethylenetetramine its surface hardness and wear resistance are significantly lower than after treating in hardening solution.

Oleagen CDC has been tested (p=49·10⁴Pa, V=0.5 m/s) with other oleagens (TABLE 11).

TABLE II. COMPARISON TEST RESULTS WITH A FRONT FRICTION AND WEAR MACHINE OF ANTIFRICTION MATERIALS IN "OLEAGENS" GROUP

Oleagens type	wear rate , mkm/h	friction coefficient	temperature in the friction zone, 0C
- D(C-1)	18	0.24	140
- KC-2	7	0.21	140
- UV-2	15	0.23	161
- KSPE	8	0.18	120
- CDC	3	0.14	102

Increase of antifriction properties and fatigue wear resistance of oleagens CDC and oleagens CDC and KSPE, is perhaps explained by the state of the sample friction surface and the counter body which are covered with a thin layer of the modified copper during friction. These layers are easily visible (Fig. 4: a) or via a microscope (b)).

At greater increase separate areas of CDC oleagens friction surface contain copper particles (Fig.5, a, b) covered with the mixture of N+ELBC. Electron-microscopic study proves that mixture of N with ELBC and further surface cementation change significantly the material surface morphology. If for oleagens not linked with "cementing" lubrication, migration into friction zone goes smoothly directly from inter-joint area, then for CDC oleagens cross linkages somewhat hinder plasticizer "migration" [10] (Fig.1.), as evidenced by absence of a wide net of inter-joint pores filled with plasticizer on the micro photos. In that case the most part of the plasticizer is "ducted" into the friction zone by surface of fibers perpendicular to the friction surface.

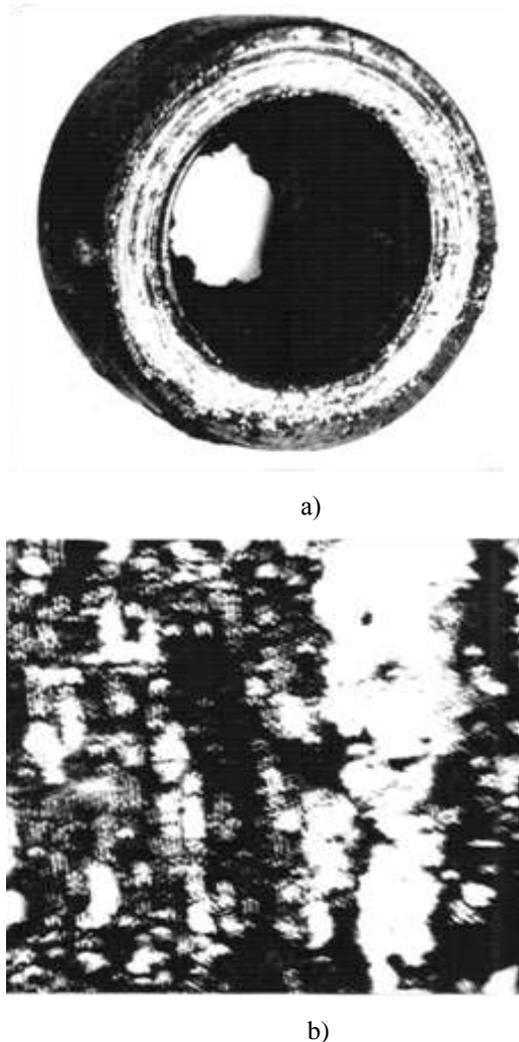


Fig. 4. Friction surface of CDC oleagens sample (a) and the counter body microphotograph (b) – x18

IV. CONCLUSION

So, “cementing” of the polymer surface compound increases its fatigue wear resistance and keeps high impact resistance capability of its deep layers. Besides, heat treatment allows removing strain and increase dimensional stability of parts and samples from oleagens CDC. This circumstance allows suggesting that one of the reasons for increased stability of antifriction properties and fatigue wear resistance of CDC oleagens in case of surface “cementing” is rational application of lubrication (plasticizer) in the friction zone.

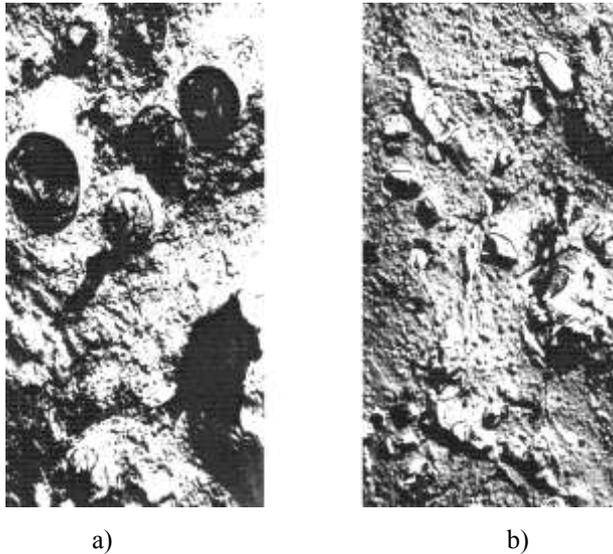


Fig. 5. Electron microphotographs of oleagen CDC friction surface (x5000)

Undertaken studies, including microscopic analysis of oleagens antifriction materials, show that there is a logical binding between the fatigue wear resistance and the morphology of the surface material, which allows controlling its tribo-technical properties. The efficiency has been proven of introducing purposeful fillers (Si, phenol, phenyl-isopropyl-

phenylenediamine, sodium nitrate, blacklead) hindering fatigue-crack nucleation by inhibiting thermal decomposition of polymeric matrix and their extension thanks to additional stress relaxation in the top zone (fibrous glass, graphite fiber, Si powders and blacklead) [3]. Material surface “cementing” has a significant positive effect on fatigue wear resistance and increases the compound hardness and crystallic phase whose percentage in oleagens CDC is greater than of other antifriction oleagens and is 42.8%.

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