Influence of dispersity of reinforcing polymer to the polymer-fiber composite materials’ rigidity

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Abstract
This research aims at validation of the technological approaches to the provision of penetrating the polymer binder into the structure of the filament carrier in order to construct a developed interfacial layer in the form of molecular brushes. Brush "bristles", enshrined by the outer end in the layer of the copolymer binder, can give elastic properties to the composite material obtained by duplicating the shell material with reinforced adhesive interlining materials.

As a large part of the interlining materials range comprises a mixture of polyester fiber with cotton or viscose, the problem of accessibility of textile liner web for reinforcing polymer is originally considered in relation to the cellulosic component, which has a developed system of pore spaces.

This work defines the technical possibility of regulating the elastic-deformation properties of the fused panels of garments by changing the degree of reinforcing polymer (RP) dispersion fineness, providing different terms for penetration into the structure of fiber material. To change the capacity of the RP to penetrate into the fiber structure a method of ultra-dispergation was used by the mechanical activation of hydrosols in a colloid mill. There is an experimental prove of the decisive role of the reinforcing polymer penetration into the pore spaces of the cellulose component of the interlining material for the formation the branched comb structure of interfacial layer, which provides a comprehensive improvement in the ability of materials to form the bulk shape of the garment and its preservation while distorting.

Keywords: Fusible interlining, elastic-deformation properties, a reinforcing polymer dispersion, mechanical activation, size of nanoparticles, pore structure of cellulose fiber.

1. Introduction
Currently, the problem of increasing the stiffness of the material for outerwear is being solved by duplicating it with fusible interlining material. In such a case the stiffness of the fused panels depends on the stiffness of each layer of the textile material, as well as on the stiffness of the glued bonding. The latter, in turn, depends on the type of glue, the adhesive dots size and frequency of their arrangement. In order to ensure the conditions of fused panels forming an improvement of textile bases aimed at increasing their formability, and as for the gluing adhesive coating – at reducing the size of the adhesive dots. This contributes to the production of sufficiently soft fused panels, which do not visually differ in appearance from the shell material, easily take the required shape during the wet-heat processing. In order to provide dimensional stability in the areas with a maximum distorting, it is ne-
necessary to use additional interlinings made of different kinds of materials. At the same time, as it is known from the course of theoretical mechanics, increasing the stiffness (EI) of a homogeneous elastic material can be achieved either by increasing its modulus of elasticity (E, Pa), or by increasing the axial moment of inertia of the parts (I, m⁴), which, in turn, is determined by the thickness [1]:

\[ I = bh^3/12, \]  

(1)

where \( b \) is the size of the part in the direction of the deformation, \( h \) – thickness of the part.

The traditional way of duplicating the shell material by a softer interlining material with a discretely distributed glue dots is aimed at increasing the stiffness by increasing its thickness. Wherein elasticity (E) of the fused panel often becomes lower than that of the shell material [1]. In the Article [2] we have set out the main principles of the innovative way of improving the fusible interlining materials by coating a textile web with reinforcing polymer dispersion (RP). Selection of the RP is carried out with the consideration of its ability to interact with the adhesive glue polymer (GP). The following conditions should be provided:

- the RP should penetrate into the material structure, while the GP should strictly be located on the material surface;
- polymerization of the RP and its reaction with GP should proceed only at the final stage of the wet-heat treatment (WHT) of the part, that is at a temperature above the melting point of the GP and above the temperature of the fusing the shell material with an interlining;
- reacting of the polymers should not impair the adhesive ability of the GP and the bond strength of the fused panels.

Using two types of polymers with different functional purpose allows to subsume the new type of interlining material as a polymer-fiber composite. The special properties of these materials are associated with the formation of interfacial layer on the "polymer - fiber" interphase, in particular organization of which the application of nano-scale molecular design methods plays a huge role [3].

Specific opportunities of the nano-structured organization of the interfacial layer can be achieved on the basis of modern advances in polymer chemistry of complex spatial architecture [4-10]. The macromolecular substances belonging to the group of multi-armed stars, dendrimers, are characterized by a high density of the polymer material in the volume unit, and thus they can be considered as new molecular objects approaching in properties to the particles [11]. Another trend is the formation of branched molecular structures in the form of brushes and comb polymers, and their structure of the macromolecules is determined by covalent attachment to the main chain side of the narrow disperse lateral radicals [12, 13]. The rigidity of the primary valences chain is determined by interaction of the lateral branches. Thus, the flexibility of the poly-\( \alpha \)-olefins ridge, poly alkyl methacrylates and poly alkyl acrylates is reduced in 3 - 4 times with increasing the numbers of monomeric units in the lateral branches from 1 to 10. Similarly, the equilibrium rigidity of the chemically bonded block co-polymers of polyimide and poly methyl methacrylates increases in ten times by comparison with the indicator of the initial aromatic polyamides [14].

In order to develop this concept we carry out research on the justification of technological approaches to ensure penetration of the polymeric binder in the fibrous structure of the carrier. On this basis it is possible to obtain composite materials with a strong interfacial layer of copolymer binder in the form of molecular brushes that penetrate into the pore spaces of the textile component. Brush "bristles", enshrined by the outer end in the layer of the copolymer binder, give elastic properties to the material.

This work defines the technical possibility of regulating the elastic-deformation properties of the reinforcing interlining material (RFI) by changing the degree of reinforcing polymer dispersion fineness, providing different terms for penetration into the structure of fiber material. As a large part of the interlining materials range comprises a mixture of polyester fiber with cotton or viscose, the problem of accessibility of textile liner web for reinforcing polymer is originally considered in relation to the cellulosic component, which has a developed system of pore spaces. To change the capacity of the RP to
penetrate into the fiber structure a method of ultra-dispergation was used by the mechanical activation of hydrosole in a colloid mill [15, 16].

2. Materials and Methods
The objects of study were two types of fusible interlinings (FI1 and FI2) and two types of fiber materials for them (textile liner web). Characteristics of fusible interlinings are described in Table 1.

| Unit designation | Fiber material % | Type of textile liner web | Surface density, g/m² | Type of glue polymer covering | Quantity of glue dots, pcs./cm² | Fusing temperature, °C |
|------------------|------------------|---------------------------|-----------------------|-------------------------------|---------------------------------|------------------------|
| FI1              | viscose 70, polyester 30 | knitted                  | 65                    | irregular, spotting, polyamide | 76                              | 130-140                |
| FI2              | polyester 60 cotton 40 | knitted                  | 75                    | irregular, spotting, polyamide | 120                             | 130-140                |

As a reinforcing component, the perspective products of acrylate water dispersion DPA, DPA-1 and DPA-2, applied earlier in the work [2], were used. Information of the manufacturers about the basic properties of the products is shown in Table 2. The dynamic viscosity rate of the products allows their application on the textile liner web with the screen finishing method.

| Unit designation | Composition                      | Dry solids weight ratio, % | pH        | Dynamic viscosity, µ⋅10³, Pa-c | Mean particle size, r⋅10⁶, m |
|------------------|---------------------------------|----------------------------|-----------|-------------------------------|-----------------------------|
| DPA              | (met)acrylic monomers co-polymer | not less than 55           | 5-7       | 40                            | 0.1                         |
| DPA-1            | acrylic acid and styrol co-polymer, stabilized by anionic surfactants | 50                          | 7.5 – 8.5 | 100                           | 0.03 - 0.1                  |
| DPA-2            | acrylic acid, styrol and butyl acrylate co-polymer | not less than 48           | 7.5 – 8.5 | 300                           | 0.06 - 0.4                  |

Suit fabrics were used as shell materials. Information about the materials is shown in Table 3.

| Unit designation | Fiber material, % | Surface density, g/m² | Stiffness, (EI⋅10³, N·cm²) | Elasticity, % |
|------------------|-------------------|-----------------------|----------------------------|---------------|
|                  |                   |                       | warp | weft | warp | weft |
| SM1              | viscose-55, wool - 35, PET - 10 | 240 | 5.2 | 3.1 | 26.8 | 31.1 |
| SM2              | viscose-50, PET - 50 | 181 | 2.8 | 2.3 | 31.7 | 38.5 |
It is worth of noting that the lighter fabric KT2 with a lower level of rigidity has higher elasticity. Obviously, this is largely due to an increase in the ratio content of polyester fiber. Changing the particle sizes in the RP dispersions was performed using a method of mechanical activation in a colloid mill while varying rotor speed (n) and the duration of treatment (τ) in two modes: C – cycled formulation flow in close circuit, M – multiple treatment, intercooling after each pass up to ambient temperature. All treatment modes used in result comparison are presented in Table 4.

| No. Item | Treatment mode | n, min⁻¹ | τ, min | Temperature of the solution, °C at the entrance | Temperature of the solution, °C at the output |
|----------|----------------|----------|--------|-----------------------------------------------|-----------------------------------------------|
| 1        | C              | 1500     | 10     | 25                                            | 50 ± 5                                       |
| 2        | C              | 3000     | 5      | 25                                            | 75 ± 5                                       |
| 3        | M              | 2000     | 5      | 25                                            | 35 ± 2                                       |
| 4        | M              | 5000     | 3      | 25                                            | 40 ± 2                                       |

The process of reinforcing fusible interlining (RFI) sample preparation includes a set of sequentially implemented operations:
1) RFI production: samples of fusible interlining material were coated by reinforcing polymer dispersions by screen printing method with diamond-shaped indentation that have the specific material surface coverage value 0.55 and dried at ambient temperature;
2) Fused panel production: at the transmission-type thermo press Japsew SR-600 (China), at maximum speed and a temperature of 90°C;
3) Moist-heat treatment: vapour moisturization up to 20 – 30 % at a temperature of 140°C for 30 seconds.

Determination of particle size in the RP aqueous dispersion was performed by Dynamic Light Scattering method (DLS) [17-19]. To dilute preparations of acrylate dispersions (DPA) to a working concentration of 0.05 g/l and rinsing of glassware in accordance with the recommendations [20, 21] bidistilled water was used, subjected to further purification by ion exchange chromatography in order to eliminate the adverse effect of nanoscale impurities. To eliminate systematic errors of measurement the dosage of the objects under study was carried out with a disposable medical syringes, and measurements were performed in disposable Rotilabo-disposable cuvettes (company Carl Roth GmbH & Co.KG, Germany) on the instrument Zetasizer Nano ZS company Malvern Instruments Ltd. (England) with a computer program controlling the distribution of the dispersion particles. Standard setting of the device program requires selection of the proposed shape of the particles of the substances under study (in this case, spherical) and the introduction of setting parameters of the Refractive Index value of the dispersed phase \( \text{RI}_{dp} \) and of the dispersion medium \( \text{RI}_{DM} \) value of which can be determined by the net database [22]: \( \text{RI}_{DP} = 1.33; \text{RI}_{DM} = 1.48 \). The indicator stiffness of textile liner and fused panel was calculated in accordance with GOST RF 10550-93 using contactless console methodology with the device PT-2. The indicator molding ability characterizes the relative size of the material (panel) field which repeats the three-dimensional surface. It was conducted in accordance with patent RF №234347 ‘The method of measurement molding ability of textile liner’. Detailed description of the methods is presented in [2].

3. Results and Discussion
First of all, a change of RP state during process stages of garment forming was studied. In this regard, textile liner web FI1 without GP was used. Analyses of the samples was done after drying the material with applied polymer dispersion at a temperature of 25°C and after the stages imitating the technological processes of fusing and WHT. The results presented in Fig. 4 and 5, allow us to trace the relationship between the size of the particles in polymer dispersions hydrosols and the changes reached in their presence of the elastic-deformation properties of the textile web of the interlining material FI1.
The data in Fig. 1 reflects a fundamental difference in the characteristics of the dispersed phase state in DPA and DPA-1. For DPA (curve 1) a monomodal dependence of the particle size distribution (r) of the polymer dispersion in the range of 60 - 150 nm is obtained. The total volume of the dominant fractions (V) with a size of 99 - 127 nm is about 60%. The bimodal dependence of nano-size particles distribution with maximum points in the range 20 – 45 nm (V = 45 %) and 200 – 350 nm (V = 26 %) is characteristic for DPA-1 (curve 1*).

Fig. 2 demonstrates a difference in the change of reinforcing material stiffness in successive process stages by varying the volume of RP application.

As it is known, natural and man-made cellulosic fibers have a system of sub-microscopic pores in the microfibrillar structure and mezo-pore spaces between the elements of the supramolecular structure of fibers (fibrils). When dry their sizes are $1 - 2$ and $10 - 15$ nm respectively, and when soaking they increase up to $3 - 7$ and $25 - 35$ nm. Substances with the larger size cannot penetrate into the fiber structure and are deployed on the surface of the filament and its interfiber spaces.

It is fair to assume that both preparations in their current form are not able to penetrate into the submicroscopic pores of viscose fiber. Dispersion of DPA preparation can no penetrate even into the mezo-pore structure of the fibers. The preparation forms a film in interfiber zones and on the surface of the yarns. Polymerization of the preparation on the WHT stage (curve 4) increases the stiffness EI, which is progressive while the amount of applied polymer increases.

This type of spatial dislocation is characteristic for DPA-1 after drying (curve 1*) and lining (curve 2*). At that, at the stage of the WHT (curve 3*), due to humidification, the conditions for the swelling of the cellulose fibers and increase of the mesopores’ sizes in its supramolecular structure are created. This allows RP small fractions to penetrate into the fiber structure. Redistribution of the polymer component causes a reduction of sample stiffness relative to its level after drying and fusing.

Obtaining such result is determined by the ideal conditions of the experiment in the absence of GP, which is capable to unite a disparate polymer formation, migrated into the pores of the fiber. At the presence of the adhesive coating on the interlining an increase in stiffness of the RFI after the WHT was revealed. The effect grows with increasing of migration ability of RP dispersion. As the proof of this effect the results of experiments with carrying out mechanical activation of polyacrylate dispersions solutions that provide varying degrees of RP ultra dispersion can be viewed.
Fig. 3 and 4, through the examples of one of the most promising options for reinforcing polymer dispersion DPA-2, shows the effect of mechanical activation in the change of the hydrosol colloidal state and the change of the stiffness level of RFI1 by varying the amount of applied modifying component. Comparing the curves with the same notation implies that the ratio redistribution between the fractions with a particle size of 30 nm (curves 1 and 2) does not influence to the changes of the material stiffness. Mode 3 provides 80% split the dispersed phase of the pore spaces sizes of the cellulose fibers, which results in increased the gain of index EI in 2 - 2.5 times as compared with the application of an inactivated dispersion DPA-2. A further reduction in the size of the dominant factions to 9 nm (mode 4), although does not make any fundamental changes in the properties of the interlining material, but it certainly helps to increase the completeness of the transfer the RP into the interfibrillar structure of fibrous material.

**Figure 3.** The influence of conditions of the reinforcing polymer dispersion DPA-2 ultra dispergating process to the change of the volume distribution of the dispersed phase by particle size 
1 - without mechanical activation; 2-5 – modes of mechanical activation 1-4 (see Table 4)

**Figure 4.** The influence of conditions of the reinforcing polymer dispersion DPA-2 ultra dispergating process to the changes of stiffness of the RFI1: 1 - without mechanical activation; 2-5 – modes of mechanical activation 1-4 (see Table 4)

The results, received for the mode 4 (curve 5), are especially interesting. About 45% of the relative volume of the dispersed phase are fractions with a size less than 3.5 nm, and under the conditions of WHT they can penetrate into submicroscopic pores of the microfibrillar structure of viscose fibers. As a consequence the amount of increase of the RFI stiffness (ΔEI) respect to the reference point in 6-8 times exceed the increase in comparison with the growth dynamics of the inactivated form of preparation for DPA-2.

Evaluation of the impact of the dispersion degree of RP on the properties of composite material formed during the formation of fused panels, is conducted on the example of two types of suit fabrics, and two types of the FI reinforced by DPA-2. Characteristics of shell materials and FI are given in Table 1 and 3.

Table 5 shows the results of studies of the properties of fused panels received by fusing suit fabrics with FI and RFI. Molding ability of the samples was measured immediately after the fusing, stiffness and elasticity - after wet-heat treatment.

The data in Table 5 reflect the presence of the changes that are consistent with the changes of RFI indicators presented in Fig. 4 and 6.
Table 5. Influence of conditions of the DPA-2 ultra dispergating process on the deformation properties of suit fabrics fused with FI and reinforced interlining materials (RFI)

| Material       | Mode of mechanical activation DPA-2 | Molding ability, %  | Stiffness, (EI-10^3, N·cm²) | Elasticity, % |
|----------------|-------------------------------------|----------------------|------------------------------|--------------|
|                |                                     | warp     | weft    | warp     | weft     | warp     | weft     |
| SM1            | -                                   | 30.3     | 36.1    | 5.2      | 3.1      | 26.8     | 31.1     |
| SM1+FI1        | -                                   | 27.1     | 29.9    | 11.4     | 12.5     | 58.2     | 62.7     |
| SM1+RFI1       | 1                                   | 25.2     | 272     | 13.0     | 14.1     | 59.1     | 63.4     |
| SM1+FI2        | 3                                   | 26.3     | 28.0    | 15.3     | 17.4     | 66.8     | 71.7     |
| SM1+RFI2       | 5                                   | 26.7     | 29.3    | 18.5     | 21.8     | 71.3     | 74.1     |
| SM2            | 3                                   | 26.3     | 28.2    | 16.9     | 18.5     | 64.0     | 66.3     |
| SM2+FI1        | 5                                   | 23.6     | 26.0    | 18.5     | 20.7     | 65.7     | 68.3     |
| SM2+RFI1       | 3                                   | 24.6     | 26.8    | 22.3     | 23.8     | 71.6     | 75.2     |
| SM2+RFI2       | 5                                   | 26.0     | 27.7    | 26.9     | 27.1     | 73.7     | 77.4     |
|                | -                                   | 35.0     | 63.5    | 2.8      | 2.3      | 31.7     | 38.5     |
|                | 1                                   | 53.0     | 35.3    | 9.1      | 11.6     | 60.6     | 64.4     |
|                | 3                                   | 26.0     | 29.9    | 10.6     | 13.7     | 61.7     | 64.9     |
|                | 5                                   | 27.7     | 31.3    | 13.8     | 15.2     | 67.5     | 72.9     |
|                | 3                                   | 29.1     | 32.6    | 17.3     | 21.0     | 76.0     | 77.1     |

*) Numeration of the modes of the mechanical activation of the RP hydrosole corresponds to those on Fig. 5.

By the example of the fused panels with SM1 and unmodified fusible interlining FI1 it is seen that the increase in the rigidity and elasticity of the material is accompanied by a deterioration of its molding ability. The use FI1 reinforced by the DPA-2 without its preliminary mechanical activation (mode 1) increases the indicators deviation in the same directions, while the most significant shift is observed in the reduction of the molding ability. This result objectively reflects the consequences of the surface distribution of the RP in the interfiber spaces of the textile carrier without penetration into the pore structure of the fiber. The results of applying FI1 reinforced by DPA-2 after its mechanical activation in the mode 3 reflect the efficiency of formation of the interfacial layer of the composite including meso-pore spaces of the interlining material. An additional increase in rigidity in 1.5 - 2 times exceeds the result for the process with non-activated RP. The increase in the growth rate of the index of elasticity relative to the level of unmodified fusible interlining reaches 10 times and is accompanied by a double loss reduction of molding ability. Increase of the formation range of the interfacial layer of the composite material due to the submicroscopic pore spaces of FI viscose component is provided by the reinforcement with the DPA-2 after its mechanical activation in mode 4. As a result, compared to the level of non-activated RP, increases of stiffness growth rates are achieved in 5-6 times and elasticity in 15-18 times, and the molding ability is practically not reduced. This process variant of forming the fused panels has advantages by the totality of indicators in comparison with the traditionally used technique of replacing FI1, for example, FI2 with higher surface density and the content of polyester fiber (see Table 1). Thus, despite the originally increased level of FI2 elastic-deformation properties, effectiveness of its reinforcing by ultradispersed RP is preserved in the same high ratios.

Similar patterns of change in the technological properties of the fused panels are observed also in the transition to a lightweight range of suit fabrics. In particular, the set of results obtained for polyesters-polyester viscose fabric SM2 shows maximum amplitude gains in the stiffness and elasticity of the package which are achieved without impairing their molding ability.

4. Conclusions
The research results have a great importance for creation of scientific and technological reserve and for developing the methods of producing composite polymer-fiber materials with adjustable elastic-deformation properties and new high-tech range of cellulose-containing interlining materials for gar-
ment production. The basis of the development is the principle of formation the branched structure of the interfacial layer of the composite material by joining to the macromolecules of thermoplastic polyamide adhesive side radicals of the thermosetting acrylate component additionally introduced into the system. It was experimentally established that the reinforcing effect of the interlining material and the fused panels for garments, formed with their assistance, is achieved if there is a penetration of polyacrylate dispersion into the fiber structure of the textile carrier. A set of researches is executed dedicated to the study of the nanoparticle sizes distribution in the hydrolysis of the reinforcing polymer by dynamic light scattering method, the dimensional changes of product characteristics as a result of mechanical activation in a colloid mill and evaluation of the relationship status of the change in the reinforcing polymer status with indicators of elastic-deformation properties of the interlining materials and fused panels. It is shown that the use of polyacrylate dispersion with a particle size larger than 40 nm causes the surface dislocation of the preparation without the penetration into the pore structure of the fiber. Such modifications of the interlining material ensures the increased density of the fused panels only for 10 - 15%. In this case the elasticity of FI increases only slightly, but the molding ability of fused panels before the wet heat treatment is reduced in 1.1 - 1.12 times. The presence in the reinforcing polymer dispersion particles with size less than 30 nm causes their penetration into the mesopore spaces of the cellulose part of the interlining material. It is reflected in a further increase of the fused panels’ rigidity up to 2 times, elasticity up to 10 times and is accompanied by a two-fold reduction in losses of molding ability. Application of the RP ultra-dispersed forms containing fraction with particle size less than 3.5 nm, allows to form the interphase layer of the composite with submicroscopic pores of the cellulose fibers. In this case, compared to the level of non-activated reinforcing polymer, increases of stiffness growth rates are achieved in 5-6 times and elasticity in 15-18 times, and the molding ability is practically not reduced.

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