Optimising the production of combined filter/sorption composite materials

A.V. Genis, A.V. Kuznetsov, G.M. Il’yutkina, and L.V. Polyakov

Scientific Research Institute of Synthetic Fibre with Experimental Works (AO ‘VNIIISV’), Tver, Russia

SUMMARY

The main relationships governing the production of combined filter/sorption materials by plying-up with the application of adhesive melts have been studied. It has been established that the use of single-stage bonding technology makes it possible to improve the physical and physicomechanical properties of multilayer non-woven mats. The possibility of optimising the plying-up process by using multiple non-linear regression analysis has been demonstrated. Materials with service properties suitable for use in protective clothing have been obtained.

Recently, hybrid composite materials (HCMs) have been widely used. The processing and service properties of these materials can be broadened by combining in a single HCM fibre fillers of different nature, or by successive laying of the materials to form a mat of different alternating layers [1].

Among the varieties of HCMs are high-performance combined fibre materials possessing a broad combination of filter, sorption, and physicomechanical properties, based on processes of aerodynamic forming from melts and solutions, which ensure the production of innovative fibre materials from superfine fibres of 1–3 µm diameter and non-woven materials from polyacrylonitrile (PAN) and polyurethane (PU) consisting of fine fibres containing a finely disperse filler [2, 3].

A distinguishing feature of technology for the formation of a combined filter/sorption material (CFSM) is that the stage of layer combination is accompanied with bonding of the layers.

An effective means of solving this problem is to join individual layers of the material by plying-up of two or three layers.

The plying-up of materials using adhesive systems is a multifactor process. It consists in applying an adhesive to one or several sides of the surfaces to be bonded and subsequent joining of the plied-up materials using heat and compression created on special equipment. Bonding occurs by the action of forces of adhesion (the interaction of functional groups of the adhesive and the material), and also by the physical penetration of the adhesive melt into the base material (impregnation) [4].

It is important in practice to carry out in sequence the main stages of bonding, including the filling with adhesive of any unevennesses of the joined surfaces (substrates) being joined, which is accompanied by wetting, the occurrence of adhesion between the adhesive and the substrate, and the solidification of the adhesive, causing an increase in its cohesive strength. Whether this mechanism occurs and the necessary properties of the obtained CFSMs are obtained depends on the chemical nature of the adhesive, the nature of its distribution on the surface of the substrate, and the method and parameters of bonding.

Thus, when choosing the adhesive melt, prerequisites are that it has a softening point that is markedly lower than the temperature of thermal stability of the fibres of the substrate, that the adhesive has a wide range of melting, and also that adhesives based on copolymers with a high melt flow index (MFI) are used [5].

For the formed multilayer materials to retain the necessary air permeability, determining the hygiene properties and comfort of the end products, distribution
of the adhesive in dots on the surface of the substrate is most often used. Here, the adhesive layer is applied in dots by pouring and impressing using a doctor blade and a stencil \[4, 5\].

Additional improvement in the number of adhesive joints is achieved by using non-traditional methods of bonding, including primarily methods of plasmochemical treatment of the materials being bonded, and also IR radiation of the adhesive and substrate. With the latter method, softening of the adhesive is achieved without breaking down the structure of the fabric substrate. For this reason, IR irradiation of materials being thermally bonded is most often used in modern equipment furnished with high-speed IR heating elements. The heating method indicated makes it possible to shorten the heat treatment time of the materials, and also to prevent or reduce the creasing or deformation of the materials being joined. With this method of heating, the strength of the bonded materials increases roughly by 20–25%, and moreover there is a considerable saving in energy resources.

Note also that the choice of IR heating affects the chemical nature of the adhesive used, realising the method of physical (thermal) surface activation.

With the literature analysis conducted and the results of laboratory investigations conducted at AO ‘VNIISV’ taken into account, a scheme of single-stage plying-up with the application of a powder thermoadhesive melted by IR irradiation between the materials being bonded was chosen. Consequently, a trial unit was created for producing multilayer CFSMs of 2–5 layers, making it possible to obtain plied-up fabrics without heating of the second mat and thereby to reduce the thermoplastic compaction of the fibre polypropylene and carbon-filled constituent layers of the CFSMs, ensuring on the whole the air permeability required of it. A diagram of the unit is shown in Figure 1.

The formation of CFSMs occurs as a result of initial uncoiling of the underlayer from reel 1; the given material is then fed to assembly 2 for dot application of adhesive powder by means of a specially coated feed shaft rotating at a speed of 60–120 rev/min. The underlayer of the material with the dot-applied adhesive then passes through a heating chamber with IR irradiation to melt the adhesive (3). By the time the underlayer (polypropylene non-woven material) leaves the heating chamber (3), a second, covering layer (carbon-filled non-woven material) is fed from reel 4. The formed two-layer material passes through squeeze rolls (5) and enters the receiver 6.

In the case of the manufacture of a three-layer material, two-layer material is fed from the upper uncoiling reel 4 and bonded to the single-layer material fed from uncoiling reel 1, which acts, for example, as an additional sorption layer.

Subsequent use of the equipment created achieved the goal of establishing the relationship between the physicomechanical and service properties of the CFSMs, which determine their application in items for protecting the skin and respiratory organs, and the principal parameters of bonding.

Besides sorption and protective properties, investigated earlier \[2, 3\], CFSMs must possess the required characteristics during service and wear of the end products, including air permeability, ply separation resistance, and tear strength of the multilayer materials.

The indicated physicomechanical and service properties of CFSMs were determined by standard procedures \[6\]. The air permeability, \( Q \), was found according to GOST 12088-77 on an FF-12 instrument (Metrimpex) with a pressure gradient \( D P = 50 \) Pa. The air permeability is characterised by the amount of air passing through one square metre of a specimen of the material per second with an established pressure difference on the two sides of the test specimen and is calculated by means of the formula:

\[
Q = (\nu/s) \cdot \tau
\]

(1)

where \( \nu \) is the volume of air passing through the specimen, \( dm^3 \), \( s \) is the tested area of the article, m\(^2\), and \( \tau \) is the duration of the test, s.

In the present study we calculated the index of the residual (retained) coefficient of air permeability, \( \Delta Q \), determined by means of the formula:

\[
\Delta Q = Q_2/Q_1 \cdot 100\%
\]

(2)

where \( Q_2 \) is the air permeability after pressing, \( dm^3/(m^2 \cdot s) \), and \( Q_1 \) is the air permeability of the initial layers, \( dm^3/(m^2 \cdot s) \).

The ply separation resistance \[6\] was determined according to GOST 15902.3-79 on an RM-3 tensile testing machine with a clamp length of 100 mm and a ply separation rate of 30 cm/min on specimens of materials measuring 15 × 200 mm, with preliminary
manual separation of a section of the test specimen of 75 mm length.

The tear strength was determined according to GOST 15902.3-79 on an Instron tensile testing machine with a clamp speed of 50 mm/min on 70 × 200 mm specimens that had been notched prior to this over a length of 120 mm to ensure the subsequent delivery of two lugs of 35 mm width in the clamps of the tensile testing machine.

In accordance with classical adhesion theory [7], the main process parameters influencing the properties of the adhesive joints are temperature, pressure, the duration of contact of the adhesive and substrate during heating and compression, and the properties of the adhesive, taking into account the surface relief of the substrate.

Note that the study of the degree of influence of the parameters of bonding on changes in the indicated properties of the CFSMs was preceded by the selection of the formulation of the adhesive melt, its grain size distribution, and the nature and amount of applied adhesive.

Practical tests of different adhesive melts [5] showed that to produce CFSMs based on ultrafine polypropylene and carbon-filled non-woven materials, developed at AO ‘VNIISV’, it is expedient to use the powder adhesive melts widely employed in industry under the trade name ‘Eva’ or ‘Sevilen’, which comprise statistical copolymers of ethylene and vinyl acetate possessing a low melting temperature (75–90°C). The MFI of these polymers varies from 0.6 to 500 g/10 min.

Under conditions of IR irradiation, with the adhesive melt consisting of the amorphous copolymer ‘Sevilen’, which possesses a wide melting temperature range and increased adhesion to the materials being bonded, it is possible to soften the powder adhesive, conducting bonding without breaking down the structure of the constituents of the non-woven mats.

On the trial unit (Figure 1), ‘Sevilen’ powder adhesive was applied to the surface of the substrate by the uneven dot method with an average plying-up temperature of 103°C. The influence of the fineness and amount of applied adhesive was assessed from the reduction in the air permeability of the two-layer substrate formed. It was established that the natural fractional composition of ‘Sevilen’ adhesive should contain an optimum granule size of 250–500 µm. This is due to the fact that coarse particles possess a smaller specific surface with an equal amount of applied adhesive, guaranteeing, after calendering, the greatest values of index ΔQ of the material, lying in the range 75–85%, on account of the minimal thermal compaction that occurs.

The application of a surplus amount of adhesive to the surface of the substrate, leading to an increase in the air resistance on account of an increase in the area of the air-permeable adhesive joints and additional heat compaction during formation of the end product by plying-up, is likewise accompanied with a drop in ΔQ.

To assess the influence of the surface consumption of adhesive on the air permeability of the fibrous carbon-filled material (FCM), digital photographs of the surface of the FCM with applied adhesive powder were taken. The photos were processed in an ImageJ 1.48d image processing system, after which the number of particles, the diameter of the particles, and the proportion of the surface occupied by the adhesive were calculated (Figure 2, Table 1).

From an analysis of the data obtained in Table 1, the optimum surface consumption of adhesive powder was found to be in the range 4–8 g/m², ensuring an admissible air permeability Q for CFSMs with the simultaneous retention of the required protective properties of these materials [2] and sufficient physicomechanical properties.

The indicated principal parameters of bonding, including the bonding temperature, t_b, the pressure (compressive force), P, and the pressing time, t_p, have different effects on the properties of the adhesive joints. The influence of temperature t_b is due to the rheological nature of spread of the adhesive over the surface of the materials being joined. Increase in temperature t_b leads to a reduction in the viscosity, η, of the adhesive, and to accelerated transition into the viscous flow state. It is to be expected that, with t_b lower than the melting temperature of the adhesive, additional increase in pressure P and in the duration of contact t_p will not lead to any softening of the adhesive.

The main consequence of the compressive force, P, is an increase in the contact area between the adhesive and the substrates being joined, which ensures an improvement in the physicomechanical properties. In
practice, the resulting action of parameters \( t_b \) and \( P \) is effective. However, an excessive increase in \( t_b \) and \( P \) in the process of plying-up causes flattening of the adhesive dots, which, increasing in diameter, become at the same time brittle on account of the intensifying processes of mechanochemical breakdown of the adhesive melt. Here, the total content of adhesive on the surface of the substrates decreases owing to its undesirable penetration onto the face side of the materials being joined. On the whole, it is to be expected that an increase in bonding strength should be accompanied with an improvement in the hygiene properties of CFSMs.

The influence of the duration of pressing is governed by the mentioned rheological factors. The effect of parameter \( \tau_b \) is equivalent to the effect of \( t_b \). Both parameters are related to the ability of the adhesive melt to spread on the surface of the substrate and to fill microdefects of the latter.

Taking into account the assumptions made, with a fixed surface consumption of ‘Sevilen’ adhesive powder of 5 g/m², mats of multifunctional CFSMs were formed by the plying-up of the initial constituent materials with \( t_b \) varying from 90 to 130°C, \( P \) varying from 80 to 160 g/cm², and the feed rate \( v_n \) of the CFSM for plying-up varying from 0.85 to 6.0 m/min, corresponding to a time \( \tau_b \) ranging from 35 to 5 s.

For the CFSMs obtained, the values of \( \Delta Q \), the ply separation resistance \( P_s \) and the tear strength \( P_t \) were determined. To begin with, the relationship between \( \tau_b \) and temperature \( t_b \) was established. At low feed rates \( v_n = 0.85 \) m/min, a long exposure time to temperature is observed, leading to additional shrinkage of the component carbon-filled non-woven mat based on PAN and PU (FCM), which is indicated by distortion of the FCM mat. The dependence has the form:

\[
\tau_b = 3.39 \cdot 10^4 \cdot e^{-0.07t_b} \tag{3}
\]

From Equation (3) it follows that an increase in \( \tau_b \) from 90 to 130°C is equivalent to a reduction in \( t_b \) from 35 to 5 s.

In the specified range of reduction in rate \( v_n \), with increase in \( t_b \) and \( P \) there is a perceptible reduction in \( \Delta Q \). The typical dependence \( \Delta Q = f(t_b, P) \) is presented in Figure 3, from which it follows that, when \( t_b > 110°C \) and \( P > 120 \) g/cm², the reduction in index \( \Delta Q \) slows down appreciably. To obtain higher values of \( \Delta Q \), it is necessary to carry out the plying-up process where possible with low \( t_b \) and moderate \( P \) values ensuring adequate characteristics \( P_s \) and \( P_t \).

Figures 4 and 5 present the dependences \( P_s = f(t_b, P) \) for different plying-up rates. As a result, the optimum temperature range (115–120°C) ensuring the best bonding conditions with reduction in \( v_n \) from 3 to 0.85 m/min was established. The fall in ply separation resistance \( P_s \) above \( t_b = 120°C \) is due to breakdown of the supermolecular structure of the adhesive melt. A distinctive feature of the behaviour of tear strength \( P_t \) is observed when the plying-up rate is changed from 0.85 to 6.0 m/min (Figures 6a to e). It was noted that, with increase in \( v_n \) from 4 to 6 m/min, \( P_t \) increases monotonically, but with reduction in \( v_n \) from 3 to 0.85 m/min there is an appreciable fall in \( P_t \).

![Figure 3. The experimentally determined dependence of the residual air permeability \( \Delta Q \) on temperature \( t_b \) with a plying-up rate \( v_n = 6.0 \) m/min and different pressures: 1 – 80 g/cm²; 2 – 100 g/cm²; 3 – 120 g/cm²; 4 – 140 g/cm²; 5 – 160 g/cm²](image-url)
This is primarily due to the fact that, with increase in the exposure time to temperature, not only does the degradation of the adhesive occur but also partial breakdown owing to the shrinkage that occurs and to the structure of the substrate mats that is created during aerodynamic forming. This, above all, concerns the adhesive joints between the fibres in the non-woven materials forming the constituent layers of the CFSMs.

Although at the first stage of the investigations the dependence of the service properties of the CFSMs on individual parameters of bonding \((t_b, P, \nu_n)\) was shown, the influence of these parameters upon each other was not fully taken into account. Therefore, to analyse the relationship between the plying-up parameters \((t_b, P, \nu_n)\), the mechanical and physical properties \((P_s, P_t, \Delta Q)\) of the CFSMs, and also to determine the process parameters most affecting the final characteristics of the indicated material, the method of multiple regression was used. Its overall purpose was to determine the quantitative relationships between several independent variables and a dependent variable. The file of initial data consisted of 125 values for each parameter of bonding.

### Table 2. The results of multiple non-linear regression analysis of the initial data

<table>
<thead>
<tr>
<th>Dependent variables</th>
<th>(\beta_{t_b})</th>
<th>(\beta_P)</th>
<th>(\beta_{\nu_n})</th>
<th>R</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta Q)</td>
<td>0.22</td>
<td>-0.63</td>
<td>-0.62</td>
<td>0.93</td>
<td>0.87</td>
</tr>
<tr>
<td>(P_s)</td>
<td>-0.46</td>
<td>0.65</td>
<td>0.51</td>
<td>0.98</td>
<td>0.96</td>
</tr>
<tr>
<td>(P_t)</td>
<td>-0.32</td>
<td>0.46</td>
<td>0.44</td>
<td>0.93</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Figure 4. The experimentally determined dependence of the ply separation resistance \(P_s\) on temperature \(t_b\) with a plying-up rate \(\nu_n = 6.0\) m/min and different pressures: 1 – 80 g/cm²; 2 – 100 g/cm²; 3 – 120 g/cm²; 4 – 140 g/cm²; 5 – 160 g/cm²

Figure 5. The experimentally determined dependence of the ply separation resistance \(P_s\) on temperature \(t_b\) with a plying-up rate \(\nu_n = 0.85\) m/min and different pressures: 1 – 80 g/cm²; 2 – 100 g/cm²; 3 – 120 g/cm²; 4 – 140 g/cm²; 5 – 160 g/cm²

Figure 6. The experimentally determined dependence of tear strength \(P_t\) on temperature \(t_b\) with a plying-up rate \(\nu_n\) of (a) 6.0 m/min, (b) 3.0 m/min, and (c) 0.85 m/min and different pressures: 1 – 80 g/cm²; 2 – 100 g/cm²; 3 – 120 g/cm²; 4 – 140 g/cm²; 5 – 160 g/cm²
In analysis of the linear model of multiple regression, data indicating its insufficient goodness of fit were obtained. Therefore, to make the model more accurate, additional non-linear terms were introduced into the equations. By multiple non-linear regression analysis, Equations (4) to (6) were determined, relating the indicated parameters of plying-up to the listed characteristics of the CFSMs:

\[
\Delta Q = 5.72 \cdot \ln v_n - 2.31 \cdot 10^{-5} \cdot t_b \cdot 1.46 \cdot 10^{-6} \cdot P^2 + 108.33
\]

(4)

\[
P_s = -18.95 \cdot \ln v_n + 3.40 \cdot 10^{-5} \cdot t_b + 1.86 \cdot 10^{-3} \cdot P^2 - 4.19
\]

(5)

\[
P_t = -6.92 \cdot 10^{-2} \cdot \ln v_n + 6.55 \cdot 10^{-8} \cdot t_b + 8.09 \cdot 10^{-6} \cdot P^2 + 0.62
\]

(6)

The combined effect of all the independent variables \(v_n, t_b, P\) on the dependent variables \(P_s, P_t, \Delta Q\) in the multiple non-linear regression model was assessed using the coefficient of determination \(R^2\) and the multiple correlation coefficient \(R\), analysis of which indicates that the model explains a large part of the variability of the corresponding variables [8]. The relationships between the variables according to the Chaddock scale can be estimated as extremely high \((0.9 < R < 1.0)\). The coefficients of determination and the correlation coefficients for regression Equations (4) to (6) are given in Table 2.

On the basis of experimental data and calculated data obtained using regression Equations (4) to (6), graphs of the change in the service characteristics of CFSMs as a function of the plying-up parameters were plotted (Figures 7 to 9). These graphs demonstrate a good correlation between the calculated and the experimental data, and thus the possibility of applying the regression equations to estimate the service characteristics of CFSMs as a function of the plying-up parameters, and also to select the plying-up regime in order to produce CFSMs with the required properties.

However, it is worth noting that the accuracy of calculations of the characteristics of CFSMs by means of regression Equations (4) to (6) decreases significantly in the case of simultaneously high \(t_b\) and \(t_b\) values. As noted earlier, this is due to the fact that, with prolonged exposure to high temperatures, degradation of the adhesive and breakdown of the structure of the substrate mat occur, accompanied with a considerable reduction in \(P_s\) and \(P_t\) (Figures 5 and 6c). These processes are beyond the scope of the regression model, and therefore, when selecting the plying-up parameters \(v_n, t_b, P\) to produce CFSMs with the required properties \(P_s, P_t, \Delta Q\), it is necessary to apply Equation (3) in calculations, which makes it possible to select the optimum \(v_n, t_b\) values for \(t_b\).

An important role in assessing the influence of the independent variables is played by the coefficients of the regression model in Equations (4) to (6). However, in non-linear equations using them, it is not possible directly to compare the independent variables in terms of their degree of influence on a dependent variable on...
account of the difference in the units of measurement and the different degrees of variability. To eliminate these differences, beta-coefficients (standardised regression coefficients) (Table 2) are used in interpreting the model, calculated by means of the formula [8]:

$$\beta_j = a_j \cdot \sigma_{xj} / \sigma_y$$ (7)

where $\beta_j$ corresponds to part of the magnitude of the rms deviation ($\sigma_y$) of a dependent variable ($y$) with variation in an independent variable ($x_j$) by the magnitude of its own rms deviation ($\sigma_{xj}$) with constant values of the remaining independent variables.

The quantitative contributions of the independent variables $t_b$, $P$, and $v_n$ to change in the service properties of the CFSM were established using the $\beta$-coefficients indicated in Table 2.

From the results of regression analysis (Table 2) it follows that the greatest influence on $\Delta Q$, $P_s$, and $P_t$ is rendered by the bonding temperature ($t_b$) and clamping pressure ($P$) in the process of plying-up, and here the dependence $\Delta Q = f(t_b, P)$ is inversely proportional, while the dependences $P_s = f(t_b, P)$ and $P_t = f(t_b, P)$ are directly proportional.

At the same time it must be stressed that, to retain the required values of air permeability with the magnitudes of $\Delta Q$ varying from 75 to 90%, the production of CFSMs must be carried out with a feed rate of the material for plying-up in the range 2–3 m/min, with comparatively low values of $t_b$ from 95 to 105°C at a moderate pressure of 100–120 g/cm², ensuring admissible mechanical properties of the CFSMs.

Thus, the mathematical models created for predicting the main service characteristics of CFSMs confirmed the soundness of the established relationships when implementing plying-up technology once the degree of influence of each component in the given process has been determined.

REFERENCES
