(REFEREED RESEARCH)

IMPORTANCE OF POLYMER SIZE RHEOLOGY FOR EFFICIENT SIZING OF COTTON WARP YARNS

PAMUK ÇÖZGÜ İPLİKLERİNİN VERİMLİ HAŞILLANMASI İÇİN POLİMER HAŞIL REOLOJİSİNİN ÖNEMİ

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ABSTRACT

This paper is about rheology of copolymer acryl amide and acrylic acid solution, as potential agent for warp sizing of cotton yarn as well as in the warp sizing process. The changes of rheology parameters of polymer size are analyzed depending upon concentration and temperature. Based on the results, it was determined that decrease of polymer size concentration conditions viscosity decrease. The temperature increase causes decrease of polymer solution viscosity for the same concentration. In addition, kinetic parameters at various temperatures were monitored, where i.e. activation energy of polymer size decreases with the decrease of its concentration. Higher polymer size concentration enables more deposit on the yarn. Based upon the results on polymer size features as well as on certain physical parameters of sized yarn, some rheology and kinetic parameters cause appropriate behaviour of polymer molecules in solution, which improves bonding and penetration ability into yarn, and then it directly influences on more efficient warp sizing.

Key Words: Polymer size, Rheology, Sizing, Cotton warp, Copolymer, Acryl amide, Acrylic acid.

ÖZET

Bu çalışma haşıllama prosesi ve pamuk çözgü ipliklerinin haşıllanmasında potansiyel etken madde olarak kopolimer akril amid ve akrilik asit çözeltilerinin reolojisi hakkındadır. Polimer haşılın reolojik parametrelerinin değişimi, konsantrasyon ve sıcaklığa bağlı olarak analiz edilmektedir. Sonuçlara göre, polimer haşıl konsantrasyonu azalmasının viskoziteyi düşürdüğü belirlenmiştir. Sıcaklıktaki artış aynı konsantrasyonda, polimer çözelti viskozitesinde düşüşe sebep olmaktadır. Ayrıca, farklı sıcaklıklardaki kinetik parametreler incelendiğinde, polimer haşıl aktivasyon enerjisinin konsantrasyon düşüşü ile birlikte azaldığı görülmektedir. Daha yüksek polimer haşıl konsantrasyonu iplikteki birikimi arttırmaktadır. Sonuçlara bakıldığında, bazı reoloji ve kinetik parametrelerinin çözeltideki polimer moleküllerinin uygun davranışına sebep olduğu, bağlanmayı arttırdığı, penetrasyonu geliştirdiği, dolayısıyla daha verimli çözgü haşıllanmasını etkilediği görülmüştür.

Anahtar Kelimeler: Polimer haşıl, Reoloji, Haşıllama, Pamuk çözgü, Kopolimer, Akril amid, Akrilik asit.

1. INTRODUCTION

The latest period in sizing process development is characterized by special attention directed towards the improvement of the process. The warp yarn woven on the fast looms must be well prepared. The number of interruptions, as well as lost time caused by the interruptions represent important research field, aiming to reduce the standstill time. Improvement of the phase is seen in introduction of new sizing agents along the appliance of new solution on the sizing machines, in order to achieve better warp yarn processing conditions. Using synthetic polymer size can significantly optimizes warp yarn features, which enables further increase of weaving mill efficiency (1, 2).

Warp sizing efficiency does not depend only upon adhesion between deposited size and warp yarn, but also upon ability to from a film, rheology features of size, physical chemical features of warp yarn as well as upon technology parameters of sizing machines. Besides, it is necessary to easily remove size after sizing from the raw fabrics (3, 4).

Rheology characteristics are closely connected with preparing the size. Concentration and viscosity of size have direct influence on warp sizing degree and its efficiency. Size behaviour under the determined constant structure depends upon intensity of mechanical action during the preparation (viscosity decreases when the number of rotation increases), viscosity (penetration of size is weaker when viscosity is higher, surface deposit is bigger and dusting is higher is the weaving mill) and alike. At low intensity, sizing degree is unsatisfactory and yarn hairiness is higher (5-7).

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Polyacrylic size agents are mainly used than other synthetic agents. Since it can apply more than 20 different monomers, acrylate polymers features can be regulated so that they match characteristics of various warp yarns. Technological characteristics of sizing with acrylate polymer agents depend upon product structure, i.e. upon macromolecule length (polymerization degree), arrangement of molecule mass and heterogeneity of monomer arrangement. Considering this, products of the same chemical composition can differ in behaviour during the preparation and appliance (8-10).

Polyacrylate agents for sizing are applied as solutions of sodium and ammonium salt. As merchant products, they are in the form of powder, mostly as a mixture of acid form of copolymer with Na-carbonate or -hydroxide, which creates salts when heated. Water solutions of ammonium polyacrylate salts are mainly used for sizing of cellulose and polyester fibres. These polymer salts are less hydroscopic than relevant sodium salts, and their flaw is smaller thermic stability and unpleasant ammonium smell. Ability of polyacrylate to form a film is exceptional, and adhesion depends upon relative air humidity so the strength of the formed film can be decreased rapidly at high air humidity. Special aptitude of polyacrylate usage is that they can be used as secondary agent in the mixture with starch. This warp sizing mass does not show imperfections, which are seen when only native starch is applied. Polyacrylate presence compensates viscosity change, which enables higher efficiency of sizing, provides high thermic stability, eliminates or drastically decreases starch degradation, eliminates the need for enzymatic desizing at choosing appropriate starch combination and decreases dusting in weaving mill (11, 12).

Along other synthetic sizing agents, water soluble polyester resin has appeared recently, and it is applied in sizing of polyester yarn. Sizing agents based on polyester are formed by step-growth polymerisation of ethyl glycol or diethyl glycol with isophthalic acid. Solubility in water is achieved by building in of sulphate isophthalic acid, which has characteristic sulphur group.

Molecule mass of the agents is in the area of 4000 to 5000, which makes only 10 % of molecule mass of other polymers used for sizing. Water solutions have low viscosity so they cannot be used for sizing of yarn made from short fibres, and sizing degree of polyester yarn is between 5 and 15 %. These agents have not found wider industrial application; they are most efficient at sizing of smooth polyester yarn (13-15).

This paper, based on the certain rheology features of polymer size, tries to define the best receipt and predict effects of cotton yarn sizing, i.e. to connect rheology and sizing yarn parameters, and discovers the effect, efficiency and possibility to apply potentially new polymer sizing agent.

2. MATERIAL AND METHOD

As substratum in the experiment was used single yarn (100 % cotton), 30 tex, and as potential agent for sizing, copolymer of acryl amide and acryl acid (8 %) - CAA. Copolymer of molecule mass 35.000 g/mol was finished agent (prepared agent) for various purposes, among other things for sizing as well.

Rheology measurements of polymer size were conducted using rotational viscometer *Visco Basic Plus* (Fungilab). Concentrations of polymer size were from 15.4 ÷100 percentage. 100 % polymer size is regarded as starting size without any dilute containing 8 % of copolymer, while other concentrations were obtained by diluting the original solution.

When setting the rheology parameters, sizing of cotton yarns was conducted by padding (bath ratio 1:10) on cold (20 ^{0}C), and then it was dried.

Desizing was conducted in the presence of wetting and washing agents of non-ionic type – *Kieralon CSA,* (BASF) on 50 ^{0}C for 30 minutes (bath ratio 1:100). Wetting agent concentration was constant; it was 2 g /l. Abundant washing out of all samples with warm, and then cold water follows next and drying at the end.

The following parameters were examined: viscosity (ISO 6388), sizing degree (based upon changes in mass), desizing degree (based upon changes in mass), breaking strength and extension (ISO 5081) and surface morphology (optical microscope - *Ceti*, scanning electron microscope - SEM, *Jeol JMC 5300,* with previous vapour deposition with gold for 4 minutes).

3. RESULTS AND DISCUSSION

3.1. Rheological Study

Changes of rheology parameters CAA size with variation of concentration and temperature of copolymer solution are showed in Table 1 and Fig. 1.

According to the results from mentioned table and figure, viscosity decreases when concentration of CAA size decreases. Influence of CAA solution temperature is evident, for the same concentration, which is expected. In addition, when concentration increases, viscosity of CAA solution increases for the chosen temperature. Viscosity values differ in small proportions up to size concentration of 46 %, and viscosity is much higher for concentration higher from 60 % and it slopes when temperature grows, Fig. 1.

Table 1. Rheology parameters of CAA size at various concentration at 20 ^{0}C

CAA size concentration (%)	Viscosity η (Pa·s)
100	0.9527
92.3	0.6725
76.9	0.5587
61.5	0.3140
46.2	0.1710
30.7	0.0910
15.4	0.0540

Viscosity can be regarded as energy dissipation measure. Mechanic energy is wasted on demolition of system structure (mechanism by which it is degraded into heat). Curves of flow show particular structures at the flow. Appearance of Newton viscosity can be interpreted as the consequence of structural changes caused by shearing on the layers during the flow (6, 7).

Based on the presented results and preliminary research it can be said that the CAA solution behaves as Newton fluid and values *Ea* can be determined from the equation $\eta = A \cdot e^{Ea/RT}$. After logarithming and drawing of graphical dependence $\ln\eta = f\left(\frac{1}{T}\right)$, based upon segment (ln A) and slope (Ea/R), it is easy to calculate the parameters, invariable A and activation energy, Fig. 2 and Table 2. Activation energy has the highest value at CAA size concentration of 61.5 % and it is 341.5 J/mol. Activation energy decreases when CAA size concentration drops, followed by decrease of viscosity.

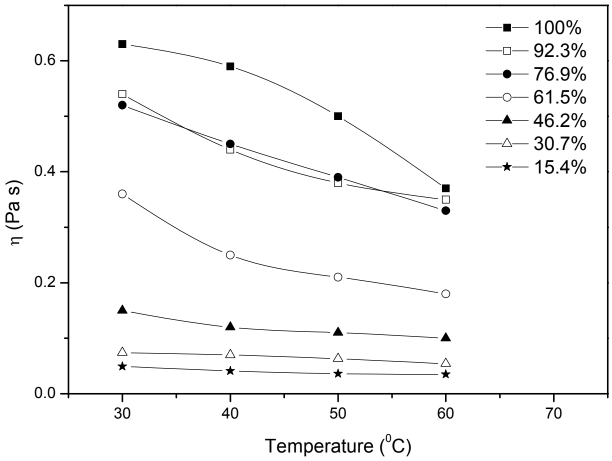

Figure 1. Correlation of CAA size viscosity and temperature

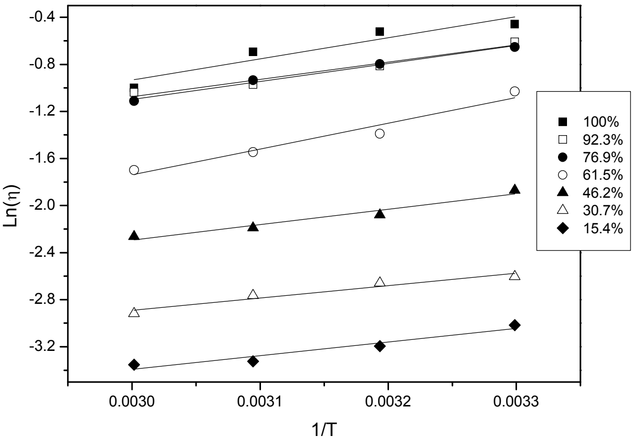

Figure 2. CAA size viscosity in temperature function

Table 2. CAA size kinetic parameters of various concentrations

Size concentration (%)	Activation energy Ea (J/mol)	Constant A (J/mol)
100	240.2	0.25
92.3	218.0	0.23
76.9	217.2	0.22
61.5	341.5	0.09
46.2	198.1	0.07
30.7	145.9	0.04
15.4	174.9	0.02

3.2. Sizing Study

Table 3 contains parameter values, which indicate the yarn processing effects with CAA size: change of mass, length and fineness.

Based upon the data from Table 3 and rheology parameters given in the previously analysed tables and charts, the influence of CAA size viscosity on efficiency of sizing process can be observed. Higher CAA size concentration enables more deposit on the yarns.

What features will sizing mass have, depends upon viscosity. Surface deposit is higher when viscosity increases, in contrast to low viscosity that simultaneously represents smaller deposit on the surface but probably more balanced and higher in the inner part, which represents additionally necessary process of sizing.

High CAA size viscosity disables penetration of the mass into the yarn, and the mass will probably stay on the yarn surface in higher percentage.

During the reaction of CAA size water solution, swelling of yarn fibres appears, which should be manifested as shrinking, but this does not happen, i.e. yarn extension appears according to the results from the Table 3. Extension values vary depending upon size concentration, reaching the highest value of 1.37 %. The most influential is CAA size of higher viscosity and explanation should be sought in the depositing process when CAA size is mechanically intruded into inner part of the yarn (padding), by conglutinating fibres at volume. Higher values of fineness of sized yarn mean that this parameter decreases making the yarn rougher. The descend is in proportion with CAA size deposit and it is in connection with appliance of yarn mass.

While it is necessary for the size to have satisfactory degree of viscosity during the sizing, it is acquired that deposited size mass is easily removed during desizing in order to save energy and ease the following processes (finishing processes).

3.3. Desizing Study

The desizing process results are showed in the Table 4 and they all carry (-) sign regarding it is about value decrease of all examined parameters in relation to the previous processes. If the values of mass, length and fineness change are compared after desizing, it can be seen that certain regularities exist, depending upon the concentrations of deposited CAA size, i.e. their rheology. The higher CAA size concentration, the more exposed mass change is during desizing. Therefore, at higher CAA size concentrations thicker polymer film is created, mainly on the surface, which is easier removed when washed in warm water. The higher concentration produces higher viscosity, conditioned by certain structure of macromolecules, which are more or less capable to penetrate into yarn and adsorb themselves for the fibres. In addition, at lower CAA size concentrations, length change is more evident (shrinkage) during desizing, pointing out those with more significant change. Shrinkage happens during desizing, mainly returning the yarn its length as before sizing. The same thing happens with fineness, where the greatest changes happen at depositing of larger amounts of CAA size on the yarn surface.

As seen in the Table 4, in most cases slight mass change after desizing in relation to sizing process was seen. That is to say, fewer amounts are taken off the yarn than it is deposited. The reasons for this should be sought in behaviour of polymer molecules regarding the rheology parameters. CAA size is easier and in greater extend deposited on the yarn surface, partly inside, at cold processing, which is harder to remove by washing because polymer can interweave if certain conditions are fulfilled. Regarding this, one should not neglect possible migration of size from volume into surface layers during drying.

The quality of sizing yarn, among other indicators, can be described with breaking strength and elongation at break, Table 5, because the aim of sizing is, among other things, to increase the strength of warp threads, to a degree that will satisfy the weaving process in a sense of higher tear resistance during working on the loom. Sizing with CAA size with higher concentrations - higher viscosity will condition higher tear resistance. However, since it is not the case, it is evident that it has to be conditioned, among other things, mainly by kinetic flexibility of macromolecules, i.e. by dispersion of polymer macromolecules along the fibre on the inside and outside of the yarn. When CAA size viscosity decreases, ability to attach for the yarn fibres decreases, at concentrations of 46.2 % or below, the processing cannot be satisfied when these indicators are concerned and they are not showed in Table 5. CAA size processing in concentration of 61.5 % is pointed out with highest values for breaking strength and elongation, which is connected with copolymer macromolecules form at given conditions, viscosity and kinetic flow energy.

Table 3. Influence of cold sizing on the change of some examined yarns features

Size concentration (%)	Change of mass (%)	Change of length (%)	Change of fineness (%)
100	15.14	1.37	11.92
92.3	11.68	1.36	9.54
76.9	10.14	1.08	10.98
61.5	8.05	0.90	8.88
46.2	5.29	0.65	4.48
30.7	4.28	0.43	3.89
15.4	2.09	0.29	1.20

Table 4. Effect results of the desizing cotton yarns

Size concentration (%)	Change of mass (%)	Change of length (%)	Change of fineness (%)
100	-13.56	-1.45	-10.29
92.3	-8.50	-1.22	-9.55
76.9	-6.85	-0.92	-10.36
61.5	-4.25	-0.95	-7.23
46.2	-2.57	-0.58	-4.08
30.7	-1.82	-0.40	-2.95
15.4	-1.04	-0.22	-1.10

Table 5. Breaking strength and elongation of sized/desized yarns

Size concentration (%)	Breaking strength (N)	Elongation at break (%)
0	3.7	19.0
100	4.4/4.1	22.0/19.5
92.3	4.1/3.9	22.0/20.0
76.9	4.2/4.0	19.5/19.0
61.5	4.4/4.0	23.0/19.5

Values for breaking strength of desized yarn are smaller in comparison with processed yarn, under the same conditions in relation to size concentration and processing temperature, which is expected since the desizing process mainly, removes polymer binder entirely. According to the results, values for breaking strength are similar to the values for the yarn before sizing, which are actually good effects of desizing.

Certain values of viscosity, i.e. activation energy, determine yarn sizing ability, by influencing on the mass, breaking strength, tear elongation, which causes certain behaviour of polymer molecules in the solution and ability to bond and penetrate into yarn.

It is necessary to define exact solution viscosity with exactly defined activation energy of flow, during the yarn impregnation, in the solution, i.e. adequate efforts will appear during the flow of polymers (tangential, normal) in function of shear speed, which all lead to the most suitable position and allocation of CAA size molecules into yarn and its surface and bonding for fibre surface.

3.4. Surface Morphology Study

Fig. 3 shows photographs of cotton fibres - yarn in the regime of various sizing processes gained by optical microscope. Raw sample of yarn has incoherent and cleaner surface, with the fibres partly scattered around the basic structure. At CAA size of 61.5 % concentration processing, a bit calmer surface with fibres bonded around basic yarn structure is noticeable. The similar phenomenon is noticed at processing with size of 92.3 % concentration. The higher CAA size viscosity, therefore higher size amount lead to higher agglutination of spurted fibres around yarn axis, higher adhesion fro fibres making this textile material suitable for smooth weaving process.

Actions on the surface after yarn sizing can be supported with SEM micrographs, Fig. 5, 6, where the existence of polymer conglomerates on the fibres are seen in relation to the raw sample, Fig. 4, where common embossed structure due to higher number of characteristic furrows and grooves are recorded. Magnification up to several thousand times are enough to identify existing polymer creations, of discrete nature, which, when connecting and surrounding the fibres, represent strong support for yarn in the cases of strong mechanical strains during weaving. Fig. 6 particularly strikes, where the highest concentration of CAA size with the highest viscosity surrounds the fibres, thus merging them.

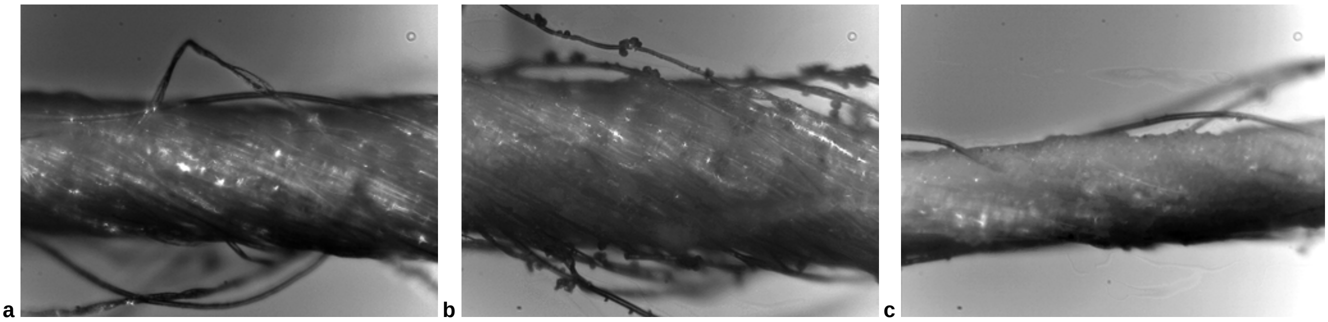

Figure 3. The look of raw cotton yarn (a), sized cotton yarn with concentration of 61.5% (b) and 92.3% (c)

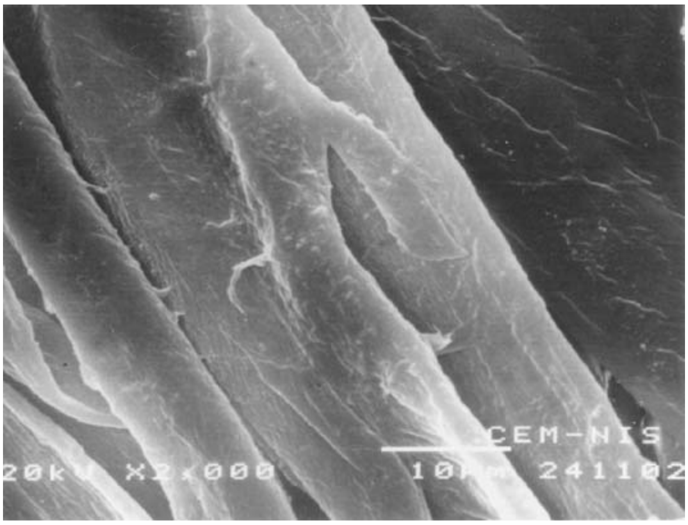

Figure 4. Micrograph of fibre surface in raw cotton yarn

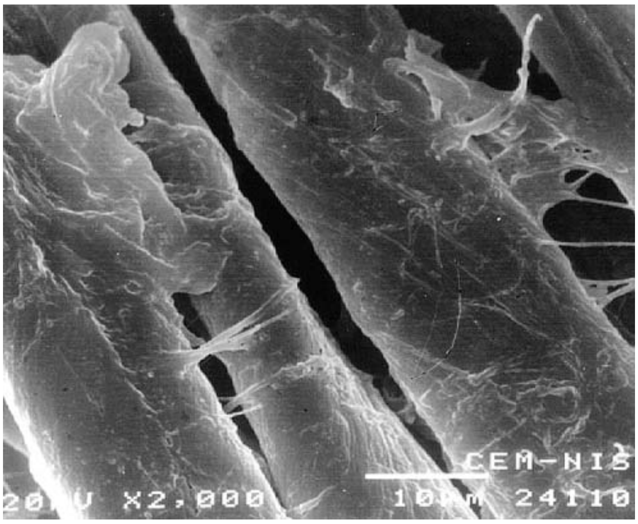

Figure 5. Micrograph of fibre surface in sized cotton yarn (61.5 %)

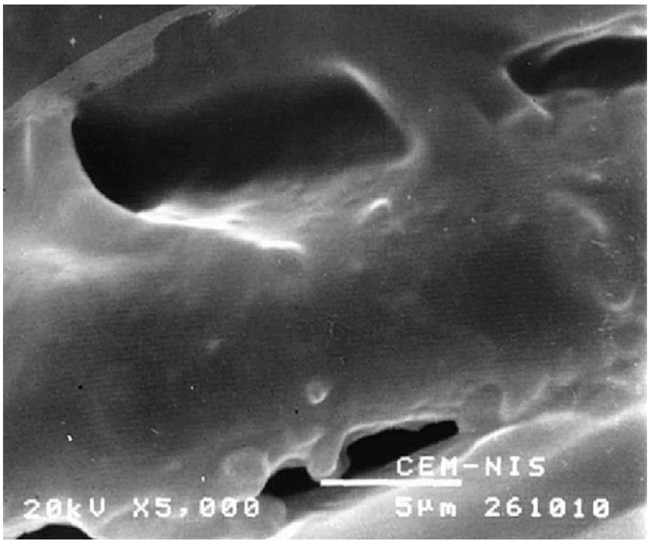

Figure 6. Micrograph of fibre surface in sized cotton yarn (100 %)

4. CONCLUSION

Inappropriate deposits of size defined upon some experience indicators are applied very often for thread sizing in production conditions. This causes increase of breaks of warp threads, because basic conditions regarding sufficient strength and appropriate hairiness are not fulfilled. Opposite to this, if too large deposits of size are applied, yarn roughness is increased, which is not sufficient for waving process and it is necessary to spend sizing agents, along negative influence on cloth production efficiency. For these reasons, it is necessary to define optimal and appropriate deposits of size on the yarn, at which the waving will be done with the maximum usage.

During desizing of cotton yarn, CAA size dissolves in water with elimination from the fibres, i.e. yarn. It is assumed that the yarn will behave in the similar way after the weaving, i.e. the desizing process of fabric, made from the yarn sized in this way, will be done efficiently. With carefully chosen procedure, i.e. active agent, and optimally chosen temperature time regime, based upon rheology indicators, appropriate structure of sizing bath and processing procedure can be reached, in order to achieve monotonous sizing and desizing.

Examined rheology parameters are directly connected with the choice of optimal receipt for sizing. Concentration, flow energy and viscosity of CAA size have immediate influence on sizing degree and desizing.

Conducted microscopic examinations have showed that the appliance of optical, particularly electronic microscope can provide satisfactory photographs, on which surface morphology of the fibres can be adequately perceived and analyzed.

CAA size viscosity of 0.314 Pas (61.5 %) and activation energy of 341.5 J/mol lead to the most suitable sizing results, based upon presented results, i.e. the most suitable size deposit, breaking strength and elongation to break will appear.

Additional research, using different procedures or various processing conditions and new additives can contribute to improvement of processing effects such as the process acceleration and simplification of the process.

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