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SIZING OF COTTON YARN WITH A COPOLYMER OF ACRYLAMIDE AND ACRYLIC ACID

Suzana Đorđević^{1,*} <u>ID</u>, Anita Tarbuk² <u>ID</u>, Nikola Stojanović³ <u>ID</u>, Tihana Dekanić² <u>ID</u>, Dragan Đorđević⁴ ID

¹Academy of Applied Studies Southern Serbia, Department of Technology and Art Studies Leskovac, Leskovac, Serbia

²University of Zagreb, Faculty of Textile Technology, Zagreb, Croatia

³Higher School of Communications, Belgrade, Serbia

⁴University of Niš, Faculty of Technology, Leskovac, Serbia

The aim of this study is the development of a new sizing agent for cotton warp yarn based on a copolymer of acrylamide and acrylic acid. Traditional sizing agents for warp yarns have the following limitations: environmental concerns, cost and resource intensity, recycling and recovery issues, performance limitations, health and safety risks. The research focuses on the application of different concentrations of the copolymer as a sizing agent for cotton varn, as well as the sizing process itself. It was found that a decrease in solution concentration causes a drop in viscosity, while an increase in temperature reduces the viscosity of the copolymer solution. The activation energy of flow (7.9-20.7 kJ/mol) for sizing was also monitored for different copolymer concentrations. Higher concentrations of copolymer sizing agents, as well as certain viscosities, allow for greater add-on percentages on cotton yarn (4-12%). The deposited copolymer causes shrinkage (from 0.4 to 1.5%) and changes in yarn fineness (from 2 to 12%), while the breaking strength increases after sizing (up to 19%) as well as elongation at break (up to 22%). The efficiency of sizing the cotton warp using the acrylamide-acrylic copolymer depends on the rheology of the sizing solution. The use of acrylamide and acrylic acid copolymers as a sizing agent for cotton yarns offers several advantages over traditional sizing agents: improved film-forming and adhesion, enhanced yarn strength and abrasion resistance, excellent water solubility and ease of removal, environmentally friendly, thermal and chemical stability, consistent quality and performance.

Keywords: copolymer, rheology, sizing, cotton yarn.

^{*} Author address: Suzana Đorđević, Academy of Applied Studies Southern Serbia, Department of Technology and Art Studies Leskovac Serbia, Partizanska 7, Leskovac, Serbia e-mail address: szn971@yahoo.com



INTRODUCTION

The use of high-speed looms alone does not guarantee the success of a weaving mill, which is measured by the quality of the woven fabrics and the weaving costs. Based on economic indicators, it has been proven that the significance of downtime is directly related to productivity. Therefore, the efficiency of high-performance weaving systems depends on the possibility of reducing downtime. This can be indirectly achieved by improving the quality of warp preparation for weaving, where the sizing phase plays a key role [1-3].

Warp sizing involves applying a protective adhesive coating (sizing agent) to warp yarns (the lengthwise yarns in a fabric) before weaving. This improves their strength, abrasion resistance, and reduces breakage during weaving [4].

The quality of sized warps, considering the dynamic stresses on the warp threads during weaving, must keep pace with the quality and speed of high-productivity looms. The complexity of the sizing process is reflected in numerous parameters related to the properties of the sizing paste, the characteristics of the yarns used, and the features of the sizing machine, which always represents a significant field of research aimed at obtaining the highest quality sized warps [5–7].

The efficiency of sizing directly depends on the adhesion between the applied sizing agent and the warp yarn or the ability to form a film. All of this is determined by the rheological properties of the sizing paste, the physicochemical properties of the yarn, as well as the technological parameters of the sizing machine. Additionally, there is always an essential requirement that the sizing agent can be easily removed from the greige fabric after weaving [8–10].

Synthetic polymers or copolymers are often used as sizing agents or thickener agents due to their properties: water solubility, film-forming ability, viscosity control, and adhesive properties [11].

For example, the advantages of a copolymer of acrylamide and acrylic acid would be as follows [12-14]:

- Water Solubility: These copolymers are highly water-soluble, making preparation and application straightforward. They can be easily removed from the yarn after weaving, facilitating desizing and reducing environmental impact.
- <u>Abrasion Resistance</u>: Yarns sized with acrylamide-acrylic acid copolymers exhibit excellent abrasion resistance, which is crucial for minimizing yarn breakage during weaving.
- Adaptability: The properties of acrylate-based sizing agents can be tailored by adjusting the polymer composition, molecular weight, and solution conditions, allowing customization for different yarn types and weaving requirements.

This study aims to correlate the results obtained from measuring the rheological characteristics of the copolymer solutions with those of the sized yarn, in order to achieve a more economical and efficient application of the new polymer preparation in the sizing process of cotton yarn. By optimizing the rheology of the acrylamide-acrylic acid copolymer, manufacturers can balance viscosity, film strength, and application



characteristics to improve cotton warp sizing efficiency. A copolymer with moderate viscosity, good shear-thinning behavior, and elastic yet tough film-forming properties is likely to perform best.

MATERIAL AND METHODS

In the experiment, a single-thread yarn (100% cotton) with a fineness of 28 tex was used as the substrate, while the chemicals included a previously prepared solution of a copolymer of acrylamide and acrylic acid.

This copolymer, with a molar mass of 113,000 g/mol, was a ready-made agent, previously prepared for various purposes.

Rheological measurements of the polymer sizing agent were carried out using a rotational viscometer Visco Basic Plus (Fungilab S.A. Spain).

Based on preliminary research, this copolymer solution behaves like a Newtonian fluid; the viscosity remains constant and does not depend on the rate or intensity of mixing, i.e. the rate of deformation.

The activation energy (Ea) is usually extracted from the Arrhenius equation using temperature-dependent viscosity data [15]:

$$\eta = A \cdot e^{Ea/RT} \tag{1}$$

Where:

η - dynamic viscosity (Pa·s).

Ea - activation energy (J/mol).

R - gas constant (8.314 J/mol·K).

T - absolute temperature (K).

A - pre-exponential factor.

Plotting $ln(\eta)$ vs. 1/T gives a straight line with slope Ea/R, from which Ea is calculated. Pure copolymer of acrylamide and acrylic acid, at various concentrations, served as the polymer sizing agent. The concentrations of the sizing agent ranged from 2 to 8%. Sizing of the cotton yarns was performed by padding (bath ratio 1:10) at room

temperature (22 °C), followed by drying, also at room temperature. Size Pick-up (%) is the percentage increase in weight of a yarn after applying a sizing agent, relative to its original dry weight [16]:

Size Pick-up (%) =
$$\frac{\text{Dry weight after sizing-Dry weight before sizing}}{\text{Dry weight before sizing}} \times 100$$
 (2)

The following parameters were tested: viscosity (SRPS ISO 6388), size pick-up, yarn shrinkage (ISO 18066), yarn fineness (SRPS EN ISO 2060), breaking strength, and elongation (SRPS EN ISO 13934-1).

RESULTS AND DISCUSSION

The rheology (flow behavior) of acrylamide-acrylic acid copolymer solutions significantly affects their performance as sizing agents for cotton warp yarns. Key rheological



parameters such as viscosity are influenced by both the concentration of the polymer solution and temperature. Lower polymer concentration and higher temperatures both reduce the viscosity of the sizing solution. This change in viscosity directly impacts the ability of the sizing agent to penetrate and coat the cotton yarns effectively.

Changes in the rheological parameters of the copolymer sizing agent with varying concentration and temperature of the copolymer solution are shown in Figure 1.

According to the results, it is noticeable that the viscosity decreases with a reduction in the concentration of the polymer sizing agents. The influence of the polymer solution temperature on viscosity is also evident, changing according to the Arrhenius equation. As expected, the viscosity of the polymer solution decreases with increasing temperature at the same concentration.

Viscosity values up to a concentration of 4% differ only slightly. For concentrations of 5% and higher, viscosity increases significantly and decreases more steeply with rising temperature. At a concentration of about 5 copolymer, the following occurs. Enough polymer chains are present to form a dense, partially crosslinked network, leading to increased intertwining and potential hydrogen bonding between acrylamide (-CONH₂) and acrylic acid (-COOH) units. Furthermore, the denser network structure resists molecular motion, increasing the energy barrier (activation energy) required for processes such as diffusion, swelling, or reaction. In contrast, below 5% copolymer concentration, the network is too loose or dilute, with fewer interactions between chains. Molecular mobility is higher, so the activation energy is lower. Above 5% copolymer concentration, the system may become too compact or saturated, reducing further structural development. Additional polymer chains may not significantly increase interactions, or may even create phase separation or saturation of the gel, reducing the energy requirements for movement. On the other hand, acrylic acid increases hydrophilicity, while acrylamide provides flexibility and the potential for hydrogen bonding. At 5% copolymer concentration, the equilibrium of these components likely results in maximum resistance to swelling, requiring more energy to activate diffusion or reaction processes (e.g., ion transport, hydrogel deswelling). When it comes to electrostatic and hydrogen bonding, acrylic acid provides carboxyl groups that can ionize, while acrylamide provides polar amide groups. At a copolymer concentration of 5%, the system can reach a maximum interaction density (e.g., hydrogen bonding, ion pairing), increasing viscosity or diffusion barriers, which again increases the activation energy. Also, in many copolymer-based systems, there is a critical concentration at which the system transitions from a sol to a gel or exhibits maximum resistance to external influences (e.g., diffusion, reaction). This gelatinization threshold often corresponds to the maximum activation energy, as the system is most physically constrained at that point.

The viscosity of acrylamide and acrylic acid copolymer solutions decreases as the solution temperature increases. This inverse relationship is a typical behavior for polymer solutions, including poly(acrylic acid-co-acrylamide), and is attributed to increased thermal motion of polymer chains at higher temperatures, which reduces intermolecular interactions and facilitates easier flow. Additionally, the complex ionic and nonionic hydrophilic groups in these copolymers mean that temperature effects can also influence molecular conformation and aggregation, further impacting viscosity [14].



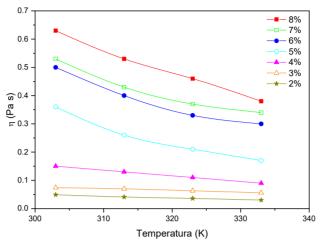


Figure 1. Dependence of the viscosity of the polymer sizing agent on temperature

Figure 2 shows the plot of $Ln(\eta)$ versus 1/T. Based on the curves, the activation energy of flow of the copolymer solution and the pre-exponential factor were determined. The coefficient of determination for the curves ranges from 0.970 to 0.995.

The activation energy of flow reflects how sensitive a fluid's viscosity is to changes in temperature. Ea for aqueous solutions of poly(acrylamide-co-acrylic acid) reflects how sensitive the viscosity is to temperature changes. It is a key rheological parameter, especially important for various industrial applications, but also for sizing yarn [17, 18].

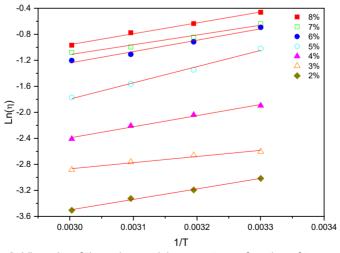


Figure 2. Viscosity of the polymer sizing agent as a function of temperature



According to Table 1, the activation energy has the highest value at a concentration of 5%, amounting to 20.72 kJ/mol, while the lowest value (7.86 kJ/mol) was recorded at a concentration of 3%.

Higher temperatures reduce the activation energy barrier for polymer chain movement, resulting in lower viscosity and easier flow.

Activation energy values for acrylamide-acrylic acid copolymer flow depend on the copolymer composition, molecular weight, and solution conditions (such as pH and ionic strength), but the general trend is that increasing temperature lowers the effective energy barrier for flow.

The copolymer's ionic nature (due to acrylic acid units) means that temperature effects may be more pronounced compared to non-ionic polymers, as increased thermal energy can help overcome electrostatic interactions that hinder chain mobility [18].

The activation energy for the sizing process decreases with lower polymer concentration, indicating that less energy is required for the sizing agent to interact with the yarn at lower concentrations. However, this may also reduce the effectiveness of the size layer.

Table 1. Kinetic parameters of polymeric sizing agent at different concentrations

Concentration of sizing agent (%)	Activation energy (kJ/mol)	Pre-exponential factor (×10 ⁻⁶ kJ/mol)
8	13.89	2.55
7	12.49	3.62
6	14.53	1.53
5	20.72	0.09
4	14.22	0.54
3	7.86	3.34
2	13.43	0.24

Table 2 presents the values of parameters indicating the effect of treatment with the polymer sizing agent: mass change, length change, and fineness change.

The copolymer's rheology affects how well it spreads and adheres to cotton. Optimal viscosity ensures sufficient hydrogen bonding between the -OH groups of cotton and the -COOH/-CONH₂ groups of PAM-co-PAA, as well as uniform coverage without excessive add-on. The groups in the copolymer are very polar and capable of forming multiple hydrogen bonds, while the hydroxyl groups are hydrophilic and readily form hydrogen bonds. The interaction between PAM-co-PAA and cellulose yarn (usually cotton) in yarn sizing involves a mix of physical adsorption, hydrogen bonding, and potentially ionic interactions, but not covalent bonds under standard conditions. Furthermore, electrostatic interactions are possible if PAA is ionized (-COO⁻) and reacts with cationic impurities or additives on the yarn. There are also van der Waals forces due to non-specific physical adsorption, as well as mechanical anchoring, when the copolymer physically entangles itself in the microfibrils/surface pores of the fibers.

Higher viscosity (from higher polymer concentration) allows for greater deposition of the sizing agent on the yarn (Size Pick-up), improving the bonding between the polymer and cotton fibers. This enhances the protective film formed on the yarn surface, leading to



better abrasion resistance and reduced yarn hairiness during weaving. As temperature increases, the viscosity of the polymer solution decreases, which can affect the uniformity and amount of size pick-up on the yarn. Optimal temperature and concentration conditions must be maintained to ensure efficient sizing.

The numerical values of the fineness (%) of yarn - a measure of the yarn's mass per unit length (tex) - increase after sizing, as the yarn absorbs the sizing material. This apparent change is due to an increase in weight and sometimes a slight swelling effect. The increase is proportional to size pick-up, since the size film adds mass to the yarn. Higher copolymer concentrations result in heavier coatings, thus increasing the yarn's linear density. This change affects weaving performance and must be controlled to prevent issues like stiffness or poor fabric handle.

When yarn is treated with a sizing solution that includes 2% to 8% copolymer of acrylamide and acrylic acid, its length can slightly decrease because of moisture absorption, tension relaxation, shrinkage from drying, or film formation on the surface. As the copolymer concentration increases, the yarn tends to shrink more. This is because higher copolymer levels form a thicker film that tightens the yarn, causing a slight reduction in length during drying. Additionally, the ionic nature of acrylic acid leads to increased moisture absorption, which contributes to temporary swelling followed by shrinkage.

Table 2. The influence of sizing on the change of certain yarn properties

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Concentration of	Size Pick-up	Change in yarn length	Change in yarn fineness		
sizing agent (%)	(%)	(shrinkage) (%)	(deterioration) (%)		
8	12	1.5	12		
7	11	1.2	10		
6	9	1.2	8		
5	8	0.9	6		
4	7	0.8	4		
3	6	0.5	3		
2	4	0.4	2		

Table 3 presents the values of the mechanical properties of cotton yarn after sizing with the new sizing agent, a copolymer of acrylamide and acrylic acid. Generally, the treatments of the yarn with copolymer sizing agents at higher concentrations, and thus higher viscosities, result in increased breaking strength. Exceptions are largely influenced by the kinetic flexibility of the macromolecules, i.e., the distribution of polymer macromolecules along the fibers on the surface and inside the yarn. With a decrease in the viscosity of the polymer sizing agents, the ability to bind to the yarn fibers also decreases, and at concentrations of 4% or lower, the treatments cannot meet the required standards for these parameters.

In essence, sizing cotton yarn with a copolymer of acrylamide and acrylic acid improves its breaking strength and elongation due to the film-forming and lubricating properties of the polymer. The increase is generally proportional to the concentration of the copolymer up to an optimal point (around 7%), beyond which gains may plateau or slightly decline due to excess stiffness or brittleness.

Breaking strength increases due to fiber bonding and reduced hairiness, which leads to better force distribution. At the same time, elongation improves because of smoother



fiber interaction and the flexibility provided by the copolymer. However, if the concentration of the sizing agent is further increased (>8%), it could result in a decrease in yield or even slight declines if the yarn becomes too stiff or brittle.

Table 3. Breaking strength and elongation of sized yarn

Concentration of sizing agent (%)	Breaking Strength (N)	Elongation (%)
-	4.7	11.0
8	5.4	13.5
7	5.6	12.0
6	5.4	12.8
5	5.2	12.3
4	5.1	12.0
3	5.0	12.0
2	4.9	11.8

A precisely defined viscosity of the solution, along with a precisely defined activation energy of flow, is necessary so that during the impregnation of the yarn-that is, practically during the polymer flow-adequate stresses (tangential, normal) develop as a function of the shear rate. This ultimately leads to the most favorable arrangement and distribution of the polymer sizing agent molecules inside and on the surface of the yarn, as well as binding to the fiber surface.

The viscosity of the polymer sizing agent at a concentration of 7% and an activation energy of 12.49 kJ/mol results in the most favorable sizing outcomes, i.e., it will ensure the most suitable add-on of the sizing agent, breaking strength, and elongation.

CONCLUSION

In production conditions, inappropriate add-ons of sizing material are very often applied for warp sizing, with these amounts determined based on empirical indicators. Insufficient add-on of sizing material on the warp leads to an increased number of warp yarn breaks due to its inadequate strength and higher hairiness. Conversely, if excessive amounts of sizing material are applied to the warp, the stiffness of the yarn increases, which is unfavorable for the weaving process and results in unnecessary consumption of sizing agents.

By careful selection of the procedure, i.e., the active agent, as well as optimal selection of the temperature-time regime based on rheological indicators, it is possible to achieve an appropriate bath composition and treatment method aimed at obtaining uniform sizing and subsequent desizing.

The efficiency of cotton warp sizing using acrylamide-acrylic acid copolymer agents is highly dependent on the rheological properties of the sizing solution. Proper adjustment of concentration and temperature optimizes viscosity, which in turn enhances penetration, bonding, and the protective qualities of the size layer. These factors collectively lead to improved weaving performance and easier removal of the sizing agent in subsequent processing steps.

The positive environmental aspects of using this copolymer in starching cotton yarn are as follows: water solubility and low volatility, potential for biodegradation, and application in environmental protection technologies (wastewater treatment, soil moisture retention



in agriculture, or in slow-release fertilizers or agrochemical carriers). Environmental concerns regarding the use of copolymers include: the toxicity of the monomer acrylamide, persistence, or potential microplastics. To mitigate environmental concerns, researchers are exploring: bio-based monomers (e.g., itaconic acid instead of acrylic acid), blending with biodegradable polymers such as starch, cellulose, or chitosan, and there are also green synthesis methods.

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SKROBLJENJE PAMUČNE PREĐE KOPOLIMEROM OD AKRIL AMIDA I AKRILNE KISELINE

Suzana Đorđević¹ <u>ID</u>, Anita Tarbuk² <u>ID</u>, Nikola Stojanović³ <u>ID</u>, Tihana Dekanić² <u>ID</u>, Dragan Đorđević⁴ <u>ID</u>

¹Akademija strukovnih studija Južna Srbija, Odsek za tehnološko-umetničke studije Leskovac, Srbija

²Univerzitet u Zagrebu, Tekstilno-tehnološki fakultet, Zagreb, Hrvatska 3Visoka škola za komunikacije, Beograd 4Univerzitet u Nišu, Tehnološki fakultet, Leskovac, Srbija

Cilj ovog rada je formiranje novog sredstva za skrobljenje pamučne osnove od kopolimera akrilamida i akrilne kiseline. Tradicionalna sredstva za skrobljenje osnove imaju sledeća ograničenja: ekološke problemi, troškovi i intenzitet korišćenja resursa, probleme sa reciklažom i ponovnom upotrebom, ograničenja u performansama, zdravstveni i bezbednosni rizici. Istraživanje se bavi primenom različitih koncentracija kopolimera, kao agensa za skrobljenje pamučne pređe, kao i samim procesom skroblienia. Utvrđeno je da smanjenie koncentracije rastvora uslovljava pad viskoziteta dok sa rastom temperature opada viskozitet rastvora kopolimera. Praćena je i energija aktivacije tečenja sredstva (7,9-20,7 kJ/mol) za skrobljenje za različite koncentracije kopolimera. Veća koncentracija kopolimernih sredstava za skrobljenje kao i određeni viskozitet dozvoljavaju više nanosa na pamučnoj pređi (4-12%). Određene vrednosti viskoziteta, odnosno energije aktivacije tečenja, uzrokuju odgovarajuće ponašanje polimernih molekula u rastvoru a onda veću ili manju sposobnost vezivanja za pamučnu pređu. Deponovani kopolimer uzrokuje skupljanje (od 0,4 do 1,5%) i promenu finoće pređe (od 2 do 12%), dok jačina na kidanje raste posle skrobljenja (maksimalno za 19%) kao i izduženje do kidanja (maksimalno za 22%). Efikasnost skrobljenja pamučne osnove upotrebom akrilamid-akrilnog kopolimera zavisi od reologije rastvora za skrobljenje. Upotreba kopolimera akrilamida i akrilne kiseline kao sredstva za skrobljenje pamučne pređe pruža više prednosti u odnosu na tradicionalna sredstva za skrobljenje: poboljšano formiranje filma i adhezije, povećana čvrstoća pređe i otpornost na habanje, odlična rastvorljivost u vodi i lako uklanjanje, ekološka prihvatljivost, termička i hemijska stabilnost, kao i konzistentan kvalitet i performanse.

Ključne reči: kopolimer, reologija, skrobljenje, pamučna pređa.

