Stefan Połowiński

Technical University of Łódź
Department of Physical Chemistry of Polymers
ul. Żeromskiego 116, 90 543 Łódź, Poland

Stiffening Agents Made from Poly(Itaconic Acid)

Abstract
As a result of the matrix polymerisation of itaconic acid, a product was obtained that was then used as a stiffener for cotton woven fabrics. It has been found that such fabrics impregnated with poly(itaconic acid) show considerable stiffness and have an attractive "sateen" handle. The stiffening effect is not stable, and declines during an intensive washing process.

Key words: *stiffening agents, cotton fabrics, poly(itaconic acid).*

Introduction

Nearly a hundred years ago (in 1908), Eschalier proposed an improvement of the properties of cellulose textiles by cross-linking with formaldehyde. Since then, numerous preparations and textile treatment methods have been used to improve fabric properties [1]. Various technologies and agents have been developed for specific finishes. Depending on the properties desired, filling, stiffening, weighting, lustering, softening, hygroscopic and other agents are available.

In the case of stiffening agents, in addition to starch, the most commonly used compounds include urea-formaldehyde or melamine-formaldehyde resins, as well as cross-linking agents such as N,N-dimethyurea, derivatives of cyclic amines and epichlorohydrin [2]. Some of these compounds, when applied onto fibres and during the use of those fabrics, emit highly toxic substances, for instance carcinogenic formaldehyde. Therefore, intensive research is being carried out to replace those toxic products, especially formaldehyde resins, with other compounds more suitable to impart the appropriate properties to woven fabrics. Recently, poly(itaconic acid) and copolymers of maleic acid have been proposed as cross-linking agents for cellulose to increase fabric stiffness [3,4].

Both maleic and itaconic acids polymerise with great difficulty. In a conventional polymerisation of itaconic acid initiated with AIBN, a 50% yield of the process is reached after about 150 h at a temperature of 60°C [5], and after 720 h at 20°C.

A characteristic feature of matrix polymerisation as a relatively new method of radical polymerisation is that the polymeric matrix used in the system accelerates this process [6]. This method has not as yet been used to polymerise itaconic acid. On the other hand, numerous studies have dealt with the matrix polymerisation of methacrylic or acrylic acid [7, 8], using poly(ethylene glycol), among other things, as a matrix. As is already known, polyacids form complexes with polyglycols, and so the polymerisation results in a complex of polyacid with polyglycol.

The aim of the present study was to prepare poly(itaconic acid) by matrix polymerisation, and to use the resultant product for finishing cotton fabrics to increase their stiffness.

Experimental

Synthesis of poly(itaconic acid)

Materials used
Itaconic acid (Koch-Light Lab. Ltd, England); ammonium persulphate (pure for analysis - FOCh, Poland); AIBN crystallised from ethanol; poly(ethylene glycol) 300 (Loba, Vienna, Austria) (PEG 300); poly(ethylene glycol) 6000 (Fluka Ag, Switzerland) (PEG 6000).

Poly(itaconic acid) was synthesised in accordance with the following procedures:
A. 25 g of itaconic acid was dissolved in 150 ml of PEG 300. After dissolution (at about 50°C), 0.5 g of AIBN was added and left at room temperature for 48 h. Anhydrous acetone was added to a 2 ml sample of the solution to precipitate the polymer, which was then filtered off, dried and weighed, obtaining 0.1185 g of PIA, i.e. about 41.5% of the polymer. The whole was dissolved in 500 ml of distilled water and used for fabric padding.
B. 25 g of itaconic acid and 8.46 g of PEG 6000 was dissolved in 100 ml of dioxane, and after dissolution 0.5 g of AIBN was added. The solution was heated for 8 h at a temperature of 50°C and then left for 48 h at room temperature. Anhydrous acetone was added to a 1 ml sample to precipitate the polymer, obtaining 0.1383 g of PIA, i.e. 73.57%. The whole was dissolved in 500 ml of distilled water and used for fabric padding.
C. 25 g of itaconic acid and 8.5 g of PEG 6000 was dissolved in 56 ml of water and 1 ml of ammonium persulphate solution (1g/50 ml water) was added and left for 48 h at room temperature. Then, another 1 ml of ammonium persulphate solution was added. After 24 h, 5 ml of ammonium persulphate solution was added and heated for 5 h at 50°C. The solution was completely homogeneous. After another 24 h, anhydrous acetone was added to a 1 ml sample in order to precipitate about 96% of PIA.
D. 25 g of itaconic acid and 8.5 g of PEG 6000 was dissolved in denaturated ethyl alcohol and made up to 100 ml. After dissolution (by warming), 0.5 g of AIBN was added and the whole was heated at 70°C for 13 h. The yield was about 10%.
E. 25 g of itaconic acid and 8.5 g of PEG 6000 was dissolved in 40 ml of water, and after dissolution 1 g of ammonium persulphate was added. The whole was heated at 70°C for 6 h and diluted with water to 100 ml. The yield was 77.6%.

Based on the above syntheses, it was found that the polymerisation of itaconic acid in the presence of ethanol (sample D) takes place with a very low yield, and

only samples A, B, C and E were selected for further examination. At room temperature, the process (synthesis C) proceeds very slowly and requires an additional quantity of the initiator. Despite the high yield, the process is inconvenient from a practical point of view.

The best conditions for synthesis seem to exist in procedure E because of the rather short time of the reaction and the satisfactory yield. In addition to poly(itaconic acid), the product obtained also contained poly(ethylene glycol) which was not removed from the mixture used for padding.

Padding procedure

The padding of cotton woven fabric with a surface weight of 1.4 g/dcm^2 was carried out in a laboratory Ernest Benz padding machine with a roller load of 45 kG per 1 cm of roller length, at a speed of 2 m/min. Each fabric sample was padded three times, and then dried in an Ernest Benz drier at a speed of 0.5 m/min at a temperature of 100°C, followed by reheating (setting) at the same rate at 150°C.

Hand washing with soap

Fabric samples were immersed in a beaker containing 500 ml of water, 10 g of Na_2CO_3 and 5 g of soap at 60°C for 10 min. During the next 30 min, the whole content was sporadically stirred. Then, the samples were rinsed four times with distilled water and dried.

Washing in a washing machine

Fabric samples were washed in a domestic washing machine at a temperature of 40°C for 30 min, using Vizir washing powder (10g /L), and then rinsed three times with water. Samples C and E were additionally treated with calcium salt solution. They were immersed for 10 min in a solution containing 60 g/L of $CaCl_2$, rinsed in distilled water and dried.

Determination of flexural rigidity

The unitary flexural rigidity was determined by the constant deflection angle method [9]. The measurement consists in finding the length of a sample strip (L) hanging down to contact a surface positioned at an angle of 40°30'. The average bending length c=L/2 calculated from 5 measurements was used to calculate the unitary flexural rigidity G according to the following formula:

Table 1. Flexural rigidity, mN·m.

Sample	Before washing	After hand washing with soap	After washing in washing machine	Treated with CaCl$_2$ and washed with soap
0	0.019	-	0.007	-
A	0.036	0.022	0.010	-
B	0.165	0.026	0.006	-
C	0.452	0.050	0.009	0.201
E	0.413	0.053	0.009	0.287

Table 2. Results of measurements of opening angle.

Sample	Before washing, deg.	After hand washing with soap, deg.	After washing in washing machine, deg.	Treated with CaCl$_2$ and washed with soap, deg.
0	30.3	-	43.0	-
A	40.0	37.7	45.2	-
B	30.4	37.8	44.4	-
C	23.8	35.9	47.8	31.2
E	20.3	39.4	49.4	25.9

$$G = m_F \cdot c^3 \cdot g \cdot 10^{-9}, mN \cdot m$$

where:
m_F - the fabric surface weight,
g - the acceleration of gravity (9.806 m/s),
c - the average bending length.

The results of calculation are listed in Table 1, which shows that a very high rigidity was obtained when using concentrated solutions of C and E products; on the other hand, considerably lower figures are obtained when compounds A and B were used. The rigidity is considerably decreased after washing with soap, and effectively declines after intensive washing in a washing machine. The samples additionally treated with calcium salt maintain a higher rigidity even after washing with soap.

Crease resistance

The crease resistance of the woven fabrics under examination was determined according to Polish standard PN-63/P-04737. The results were calculated in the form of an average angle of sample arms opening in per cent in relation to 180°. The results obtained are given in Table 2.

As is seen from Table 2, the fabric samples impregnated with a diluted solution of PIA (A and B) show a rather insignificant stiffness that declines after washing. On the other hand, the samples impregnated with concentrated solutions (C and E) show considerable stiffness as well as an attractive "sateen" handle. This stiffness is considerably decreased after washing in a soap solution, and totally disappears after washing in a washing machine. The stiffness effect can be made slightly more resistant to washing with soap by additional treatment with a calcium salt solution.

■ **Conclusions**

Polymerisation of itaconic acid in the presence of poly(ethylene glycol) proceeds faster than polymerisation in conventional conditions. The product obtained can be used as a stiffening agent, similar to a new type of proposed cross-linked agents for cellulose which does not emit toxic substances. The stiffness effect is rather high, but the effect decreases after washing. The addition of divalent ions slightly improves the effect. However, at present the method can be used only for products not intended to be washed.

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