

EFFECT OF THE DRAWING PROCESS ON THE THERMAL STABILITY OF GELATINE-POLY-ACRYLONITRILE GRAFT COPOLYMER FIBRES

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Abstract

The thermal stability of gelatine-polyacrylonitrile graft copolymers fibres obtained under various conditions of deformation has been studied. The thermal properties of examined fibres depend on the synthetic component of the fibre forming material – polyacrylonitrile which appears in the form of grafted PAN chains and PAN homopolymer. It was stated that the highest thermal stability have those fibres which formation process included two stages of drawing with the use of deformation close to the maximal values, with the value of the total draw ratio amounting to 691%. It should be supposed that with such a drawing process, already in its first stage, are created advantageous conditions for the formation of paracrystalline regions to a larger extent and their orientation along the fibre axis.

Keywords: DSC, DTA, gelatine, gelatine-polyacrylonitrile graft copolymer fibres, polyacrylonitrile, thermal analysis, thermal properties, thermal stability, TG

Introduction

The chemical modification of gelatine by grafting makes it possible to utilise inexpensive technical gelatine, recovered from tanned leather wastes, to prepare a new fibre-forming material [1]. Fibres made from gelatine-polyacrylonitrile graft copolymer combine advantageous absorption properties of natural polymer with the properties of synthetic polymers such as strength required in textile processing and thermal stability.

It is possible to use the solution obtained directly from the synthesis of gelatine-polyacrylonitrile graft copolymer for fibre spinning provided that the grafting conditions are appropriately selected [2] as such a spinning solution should have a possibly high concentration of the fibre-forming material with a dynamic viscosity suitable for wet spinning on a conventional machine.

Rheological examinations of these copolymer solutions have shown that they are non-Newtonian fluids rarefied by shearing without flow limit showing a good sta-

bility for a long period of time [3]. The values of parameters n and K depend on the concentration of gelatine and the acrylonitrile to gelatine ratio in the reaction mixture. The determination of the effects of these factors on the porous fibre structure as well as on the absorption and strength properties of fibres made it possible to select optimal grafting conditions in respect of both the processability of solutions and the characteristics of the resultant fibres [4]. The major problem in the manufacture fibres from gelatine-polyacrylonitrile graft copolymer is the tendency towards protein macromolecule globulisation and related low strength properties of fibres. To develop conditions for spinning fibres from such a copolymer, it was first necessary to determine the relations between the basic process parameters such as the as-spun draw ratio, temperature and concentration of coagulating bath, total draw ratio and its distribution on the one hand, and the fibre porous structure as well as absorption and strength properties of the resultant fibres on the other hand [5]. Such studies were the basis for performing the optimisation process intended to obtain as high fibre strength as possible and to retain good absorption properties of fibres. The basic technological parameters in this case is the extent of deformation including the values of as-spun draw ratio, total draw ratio and an appropriate distribution of draw ratios in the two-stage drawing process. These values affect also the thermal properties of fibres. Thus, the aim of the present study was to determine the thermal stability of gelatine-polyacrylonitrile graft copolymer fibres obtained under various conditions of deformation.

Experimental

Fibre spinning conditions

Fibres were spun by the wet method from solution, using a laboratory spinning machine equipped so as to provide continuous control of the technological parameters and their stability at a required level. The spinning solution used consisted of gelatine-polyacrylonitrile graft copolymer in a 60% $ZnCl_2$ solution obtained directly in the grafting process (containing some amount of homopolymer). Fibres were spun with negative values of the as-spun draw ratio, using spinnerets with 500 orifices whose diameter was 0.08 mm each. Fibre solidification took place in a solvent containing bath at a low temperature.

The fibre drawing process was carried out in two stages: in hot water and in superheated steam. Two variants of drawing were used: A – draw ratios close to maximal values in both stages or B – an appropriate distribution of draw ratios in the first stage and draw ratio close to maximal value in the second stage. Detailed description of the fibre formation conditions and methods of measuring moisture absorption and strength of the fibres are given in paper [5].

Table 1 Results of the drawing process and properties of gelatine-polyacrylonitrile graft copolymer fibres

Sample symbol	Draw ratio in hot water/%	Draw ratio in steam/%	Total draw ratio/%	Fibre tenacity/cN/tex	Fibre elongation/%	Moisture adsorption at		Water retention/%
						100%	65%	
						RH of air/%		
44I	285	105	691	14.4	10.0	8.6	3.8	19.5
44II	148	302	898	11.6	5.4	9.5	3.8	30.0
45I	89	100	267	8.4	7.5	10.2	3.7	36.2

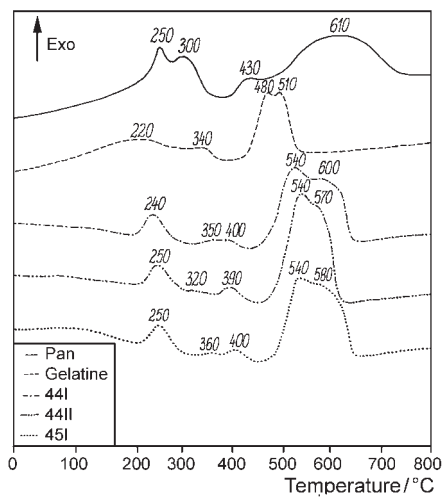


Fig. 1 DTA curves of fibres, polyacrylonitrile and gelatine in air atmosphere

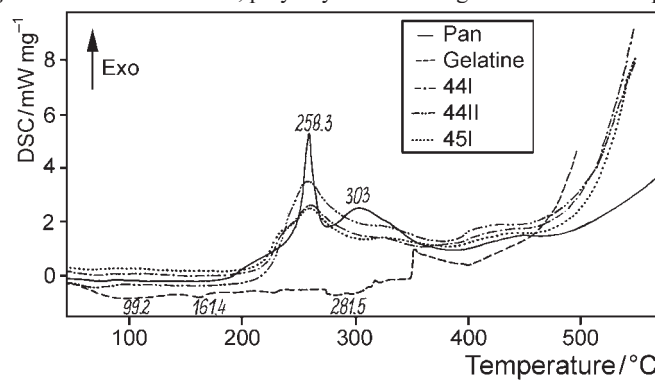


Fig. 2 DSC curves of fibres, polyacrylonitrile and gelatine in air atmosphere

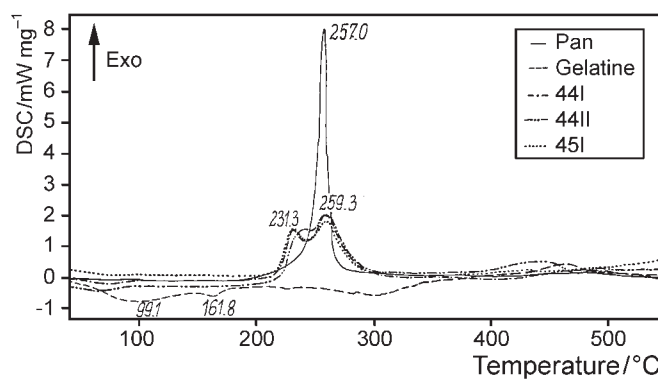


Fig. 3 DSC curves of fibres, polyacrylonitrile and gelatine in inert atmosphere

Subject of investigation

The selected fibres marked with symbols 44I, 44II and 45I, derived from optimisation series [5], were spun under the same conditions of solidification but with different total draw ratio values and draw ratio distribution. The solidification conditions of fibre 45I were intensified by decreasing the solvent content in the coagulating bath. Both stages of drawing were carried out with deformations close to their maximal values (Table 1). Gelatine and polyacrylonitrile were also subjected to the thermal analysis for comparison purposes.

Method of measurement

The thermal analysis of fibres was performed by means of derivatograph, differential scanning calorimetry (DSC) and thermogravimetry (TG), using Paulik–Paulik–Erdey system Derivatograph, a DSC 204 microcalorimeter and a thermobalance TG-209 of Netzsch.

The derivatographic analysis was carried out in the atmosphere of air, using weighed portions of 60 mg at a heating rate of $7.9^{\circ}\text{C min}^{-1}$ within the temperature range from 20 to 800°C . In the case of microcalorimetry and thermogravimetry, the measurements were carried out both in air and inert gas, using weighed portions of 6 mg at a heating rate of $10^{\circ}\text{C min}^{-1}$ within the temperature range from 30 to 700°C .

Results and discussion

From the thermogravimetric curves of gelatine it follows that its initial heating causes the evaporation of its moisture amounting to about 14% (Figs 1–5). This evaporation is clearly shown in the DSC curves obtained both in air and inert gas in the form of two endothermic transitions recorded at temperatures 100 and 160°C (Figs 2 and 3). At a temperature of 280°C , regardless of the atmosphere used in measurements, the thermal destruction of gelatine begins and is continued in two stages resulting in its complete decomposition (Figs 4 and 5).

The exothermic changes of polyacrylonitrile in air (Figs 1 and 2) at temperatures of 250 and 300°C are connected with thermo-oxidative processes and the cyclisation of nitrile groups [6], which is accompanied by sample mass loss amounting to 13% (Fig. 4). The cyclisation of polyacrylonitrile in the atmosphere of inert gas is manifested in the form of a strongly exothermic peak recorded at a temperature of 257°C , with the sample mass loss in these conditions amounting to 2.5%.

The results of the thermal analysis obtained in the atmosphere of air and inert gas show that the fibres made of gelatine-polyacrylonitrile graft copolymer, regardless of the extent of their total draw ratios, are subject to changes within the temperature range corresponding to that of polyacrylonitrile (Figs 1–3). The cyclisation process of polyacrylonitrile macromolecules being in the composition of the fibres under investigation proceeds in two stages (Fig. 3). This allows to assume that the cyclisa-

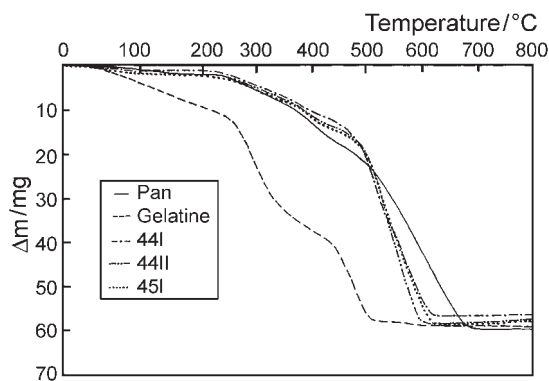


Fig. 4 TG curves of fibres, polyacrylonitrile and gelatine in air atmosphere

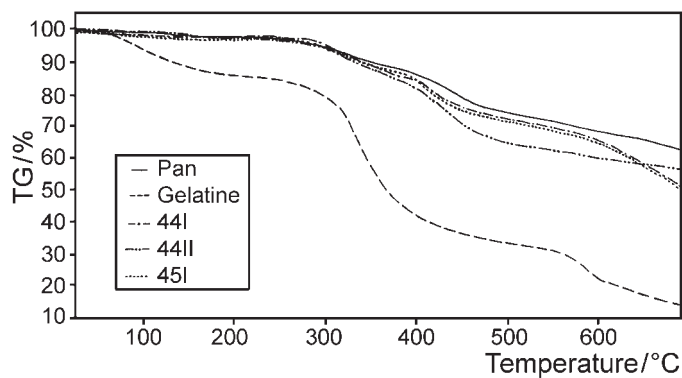


Fig. 5 TG curves of fibres, polyacrylonitrile and gelatine in inert atmosphere

tion processes of cyano groups in the PAN macromolecules in the form of grafted chains on gelatine and those of homopolymer proceed in various temperature ranges.

Table 2 Thermal stability indices of fibres, polyacrylonitrile and gelatine

Sample	Thermal stability indices			
	In air atmosphere		In inert atmosphere	
	T_5	T_{50}	T_5	T_{50}
44I	280	530	300	*
44II	260	530	280	*
45I	240	530	280	*
PAN	270	560	300	*
Gelatine	200	360	280	370

T_5 , T_{50} – temperature of 5 and 50% mass loss of the sample [8]

*the sample heated to temperature of 700°C do not show 50% of mass loss

From the thermogravimetric curves it follows that thermal stability induces T_5 and T_{50} of the examined fibres and those of PAN are similar and considerably higher than the thermal stability of gelatine (Table 2). Among the examined fibres, the highest thermal stability is shown by fibres marked with symbol 44I, the total draw ratio of which is 691%. These fibres are also characterised by the best strength properties (Table 1). Thus, it may be assumed that both the thermal stability and strength properties of the analysed fibres are connected with the changes in the supermolecular structure of their material. In the spinning solution, gelatine macromolecules with grafted PAN chains in the lyotropic solvent, $ZnCl_2$, assume the form of disaggregated coils. In the fibre formation process during solidification, especially during the drawing stage, the coiled gelatine macromolecules change their spatial configuration and the grafted chains change their position in the direction of drawing forces. The coiled chains are then flattened and secondary bonds can be formed between CN groups of the grafted PAN chains. These bonds can be also formed between the ungrafted chains of PAN homopolymer which are parallelised due to the applied stress. In such a system, a paracrystalline structure, characteristic of polyacrylonitrile, is formed by both the grafted PAN chains and the macromolecules of PAN homopolymer. The presence of paracrystalline regions in fibres made of the same material but spun in different conditions and from a solution with different composition has been found in paper [7].

The character of the formed structure depends on the extent of deformation applied as well as on the thermal conditions of fibre drawing which affect the system mobility and capability to crystallise. Thus, the thermal properties of fibres depend not only on the number and length of grafted chains but also on the conditions of deformation processes which consequently affect quantitatively the formation of secondary bonds and the extent of grafted chains inter-linkage and combination with the linear macromolecules of PAN homopolymer. These conditions affect also the formation of paracrystalline regions responsible for the thermal stability of the fibre-forming material.

The results of our studies show that the highest thermal stability have those fibres which formation process included two stages of drawing with the use of deformations close to the maximal values, with the value of the total draw ratio amounting to 691%. One should expect that with such a drawing process, already in its first stage, are created advantageous conditions for the formation of paracrystalline regions to a larger extent and their orientation along the fibre axis. Such a structure also ensures that the resultant fibres have good strength properties and somewhat lower absorption properties (Table 1).

Conclusions

1. The thermal properties of gelatine-polyacrylonitrile graft copolymer fibres depend on the synthetic component of the fibre-forming material – polyacrylonitrile which appears in the form of grafted PAN chains and PAN homopolymer.

2. Under specified solidification conditions the thermal stability of these fibres depends on the fibre structure being affected by the value of total draw ratio and the distribution of deformations in the two-stage drawing process.

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