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Characterisation of modified polypropylene fibres

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Due to excellent mechanical properties, high chemical stability and processability polypropylene fibres are mostly used in different technical fields. However, because of low surface energy, lack of reactive sites and sensitivity to photo or thermal oxidation the polymer properties are insufficient for some applications. Therefore several techniques for fibres modification are reported, e.g., plasma treatment, chemical modification etc.

To alter the chemical and physical properties hydrophobic polypropylene monofilament fibres were surface modified and the sulphonation with concentrated sulpuric acid was used. The sulfonation was performed at different conditions, e.g., different temperatures and varying period of time and a detailed study of treatment conditions influence on the fibre properties was carried out. The sulphur content on fibres was determined by mass spectroscopy. The sulfonic acid cation exchange polypropylene fibres were characterised in terms of elektrokinetic and mechanical properties. © *2003 Kluwer Academic Publishers*

1. Introduction

Man–made fibres exhibit good mechanical performance while the surface properties are mostly insufficient for several applications. Modification of fibre-forming polymers is a good way to prepare new products with improved properties [1]. Properties like wetting, dyeing, adhesion, friction, biocompatibility, etc., can be improved and controlled by means of surface modification [2–3]. Several techniques for surface modification are reported. Plasma and laser treatment are some of the most commonly used physical methods in modifying surface physical as well as chemical properties of materials [4].

1.1. Polypropylene

Polypropylene PP is beside polyesters one of the mostly used polymer for producing man–made fibres especially for technical applications. Polypropylene fibres have good mechanical properties and can withstand temperatures up to 140°C before melting at about 170°C. The polymer density is less then that of water, which allows them to float as ropes, nets, etc. Low costs, good chemical resistance to acid and alkaline environments has greatly influenced the high production quantity of this polymer type [5]. Due to its high hydrophobicity and chemical – non-reactivity for some purposes surface modifications are needed. By the modification ion exchange fibres can be obtained. Cation – active and anion – active fibres can be used in different application fields. To follow the modification efficiency various characterization techniques can be used. In our research cation – active PP fibres were prepared by the process of sulphonation [6] and the fibres were characterized by zeta potential measurements.

1.2. Zeta potential

Electrokinetic properties of sulphonated polypropylene fibres were determined to study the influence of different treatment conditions on sulphonating effect and efficiency of sulphonation.

The streaming potential method was used, as it has been shown to be the most appropriate technique to study electrokinetic properties i.e., the zeta potential (ζ – the potential which refers to the potential at some idealized plane of shear between the solid and liquid phases when any relative motion is induced between them) of fibres and filaments systems. The ζ was calculated from the streaming potential (U_s) data using the Smoluchowski equation [7]:

$$\zeta = \frac{U_s}{\Delta p} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{L}{Q} \cdot \frac{1}{R} \tag{1}$$

where: ζ, the zeta potential; U_s, the streaming potential; Δp, the hydrodynamic pressure difference across the plug; η, the liquid viscosity; ε, the liquid permittivity; ε_0, the permittivity of free space; L, the length of the plug; Q, the cross-sectional area of the plug; R, the electrical resistance across the plug. The term (L/Q), consists of two parameters neither of which can be easily measured. In the Fairbrother and Mastin (FM) approach the term (L/Q) is replaced by $(R_s \chi_s)$, where R_s is the electrical resistance of the plug when the measurement cell is filled with an electrolyte whose specific conductance, χ_s, is accurately known. Thus, Equation 1 becomes:

$$\zeta = \frac{U_s}{\Delta p} \cdot \frac{\eta}{\varepsilon \cdot \varepsilon_0} \cdot \frac{R_s \cdot \chi_s}{R} \tag{2}$$

Equation 2 is perfectly adequate for most practical systems.

2. Methods

2.1. Preparation of the samples

Polypropylene monofilament fibres were sulphonated by immersing in a 2% methanol solution at 20°C for 30 min, followed by drying [8, 9]. Subsequently, the monofilament was immersed in fuming acid at different temperatures (20–90°C) over different times (5–120 min), followed by washing in water and drying. After treatment a membrane was prepared by partial melting of the treated filaments. The films were washed in a 1% solution of nonionic washing agent until constant conductivity was reached.

2.2. Analytical methods

Sulphonation efficiency was followed by electrokinetic properties determination. The influence of different treatment conditions, i.e., different treatment temperature and treatment period was investigated. An Electrokinetic Analyzer EKA, A. Paar KG was used for streaming potential measurements. Each point on the graphs represents the mean value of at least 5 measurements.

For the calculations Equation 2 was used. The surface conductance has not been taken into consideration. Potential measurements of fibres were always performed in the fibre cell using 0.001 n KCl as electrolyte solution. The pH of the electrolyte solution was always varied in an identical way. It was first adjusted to pH 10 using 0.1 n NaOH and afterwards decreased step-wise with 0.1 n HCl. The zeta potential values mentioned here are always those obtained at the constant part of the zeta potential – pH function in the alkaline region at pH = 9.

Stress – strain curves were obtained on the dynamometer Statigraph S Textechno (DIN 53857, ISO 5018).

3. Results

The zeta potential as a function of pH of sulphonated polypropylene membranes is presented in Figs 1 and 2. PP membranes were treated at temperature 20°C for different times (5, 15, 60 and 120 minutes). Fig. 1 shows the rising of the zeta potential plateau with increasing time. The isoelectric point of treated samples shifts with increasing treatment time towards neutral region.

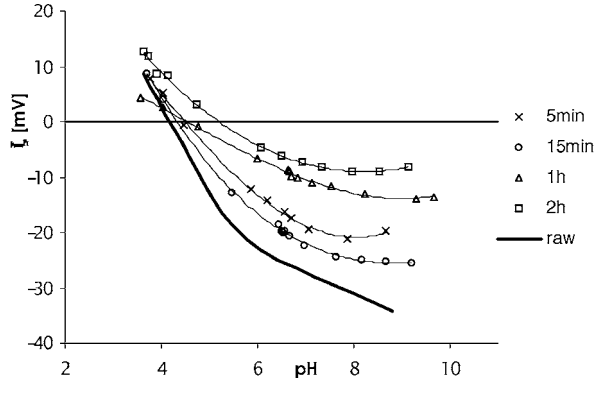

Figure 1 Zeta potential of modified PP as a function of pH: Influence of treatment time on isoelectric point.

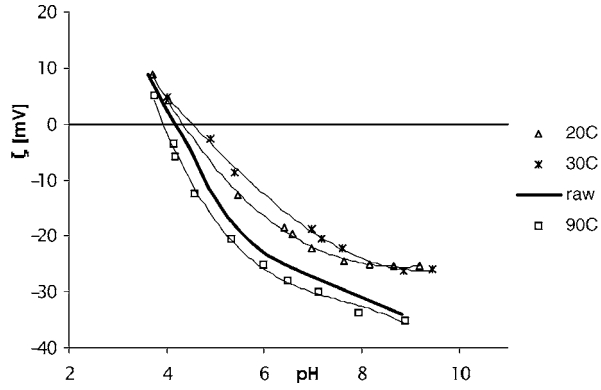

Figure 2 Zeta potential of modified PP as a function of pH: Influence of treatment temperature on isoelectric point.

PP membranes were treated for 15 min at different temperatures (20, 30 and 90°C). Fig. 2 shows the reduction of zeta potential plateau at high treated temperature (90°C) under the curve of untreated PP membrane. The samples treated at low temperature show the same tendency as samples shown in Fig. 1.

The low tempertaure treatment (20°C) causes an increase of hydophilicity, expressed by the reduction of the negative ZP in the alkaline region and a shift of the isoelectric point from pH = 4 to pH = 6. The increased hydrophilicity is caused by a small degree of sulphonation perhaps only at the fibres' surface due to a reduced accessability of the fibers' bulk at this temperture. The resulting small number of sulphonic groups aquire cations from the liquid phase and this causes the shift of the isoelectric point towards the neutral region. The similar effect is observed using a treatment at elevated temperature (30°C).

At 90°C the fibre material becomes more accessible and a higher sulphonation level is obtained. The dissociated sulphonic groups are only partially saturated by cations and this causes the shift of the isoelectric point towards the acid region.

Acording to the different treatment temperature the melting point of the sulphonated polypropylene, treated at higher temperatures rises in comparison with the untreated fibres. Different behaviour of the surface and the bulk of the fibres during the heating is observed at high temperature sulphonated fibres.

The mechanical properties are presented in Figs 3 and 4.

Fibres treated at different temperatures and times show very small reduction of mechanical properties. Treatment at low temperature (20°C) indicates small distinctions of mechanical properties according to the heterogeneity of the material. High temperature sulphonating causes insignificant reduction of breaking strength and elongation.

To follow the efficiency of the sulphonation the sulphur content on the fibres was determined by mass

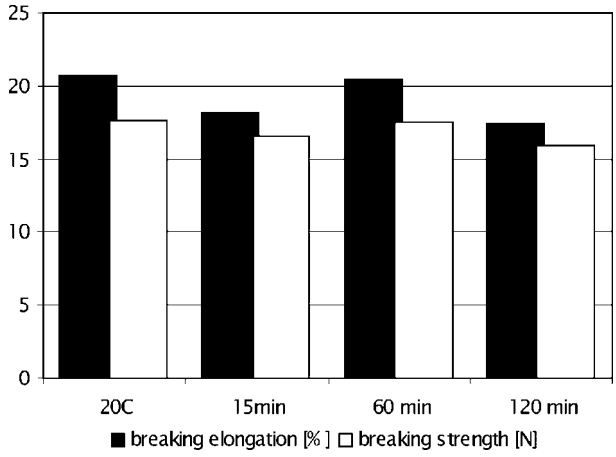

Figure 3 Breaking elongation and breaking strength of sulphonated polypropylene treated at 20°C for different times.

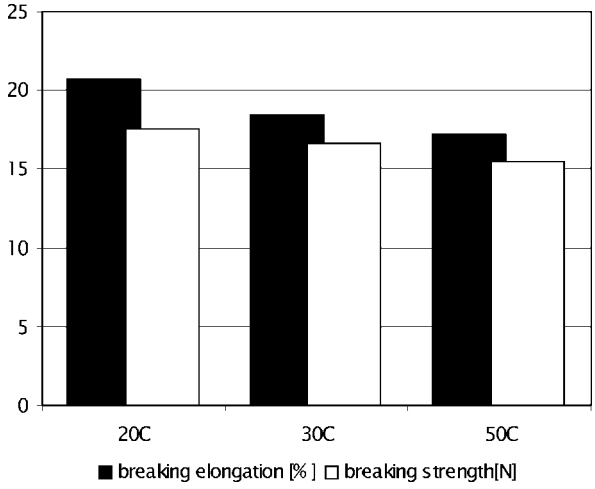

Figure 4 Breaking elongation and breaking strength of sulphonated polypropylene at different temperatures for 15 min.

spectroscopy. The results show the higher values of sulphur at fibres treated at higher temperature for longer period of time (436 mgS/kg) than raw material (45 mgS/kg).

4. Conclusions

The purpose of this research was mainly to determine the efficiency of sulphonation and to direct further researching according to the required mechanical and physical properties of material. The resulting determinations of mass spectroscopy and electokinetical properties show the required efficiency at high temperature treatment (90°C). According to small reduction of mechanical properties of polypropylene fibres, treated at high temperature, contributes satisfying results.

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