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The effect of hyperbranched polymers on the dyeing of polypropylene fibres

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Abstract

The incorporation of hyperbranched polymer into polypropylene prior to fibre spinning markedly enhanced the dyeability of polypropylene with C.I. Disperse Blue 56; the disperse dye displayed much greater substantivity towards the modified polypropylene than its unmodified counterpart. The observed enhancement of dye uptake can be attributed to the introduction of polar groups provided by the stearate-modified hyperbranched polymer. The finding that dye uptake on the modified fibre reached a maximum at 110 °C after reduction clearing suggests that "saturation" of the introduced polar groups had occurred. While the fastness of dyed fabrics made from polypropylene fibre which had been modified with 3% hyperbranched polymer, to five repeated wash fastness tests at 60 °C was very good, the fastness of the dyeings to light was poor. The incorporation of the hyperbranched polymer into the polypropylene prior had no effect on the physical properties of the fibre. © 2002 Published by Elsevier Science Ltd.

Keywords: Hyperbranched polymers; Modified polypropylene; Dyeing; Disperse dyes

1. Introduction

Polypropylene (PP) is a versatile and widely used polymer, enjoying applications as diverse as packaging, pipes, household appliances, textiles, automotive factors and films. The success of the polymer can be attributed to several intrinsic, advantageous properties, namely easy processability, low specific gravity, almost zero water adsorption, good chemical resistance, good anti-static character as well as wide availability and low cost. However, this success is also due to the use of stabilizers which overcome the inherently low thermal and UV stability of the polymer.

Only the isotactic configuration of the polymer is normally used to form textile fibres. Isotactic PP forms a two-phase structure comprising crystalline and non-crystalline material, the degree of crystallinity usually being in the range of 50–65%. PP is available in monofilament, multifilament and staple fibre, fibrillated yarn as well as non-woven fabric. It enjoys manifold applications, as exemplified by medical fabrics, industrial sewing threads, cordage, artificial turf, carpeting and geotextiles; little is used in apparel. Polypropylene fibre is undyeable because of its non-polar, aliphatic structure as well as its high crystallinity and

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high stereo-regularity (which are responsible for the good physical properties of the material) which limits the accessibility of dye molecules. Many attempts have been made over many decades to overcome this problem including [1,2]:

- the dyeing of unmodified fibre with hydrophobic dyes through the use of various accelerators, carriers, or fibre swelling agents;
- modification of the polymer by attaching dye-receptive monomers or functional groups to the polymer molecules via copolymerisation or grafting; and
- incorporating dye-receptive additives within the polymer prior to fibre spinning.

Although modified, dyeable PP fibres are commercially available, the vast majority of polypropylene fibre is mass coloured with pigments.

The purpose of the present work was to determine whether the dyeability of PP could be enhanced through the incorporation of *hyperbranched macromolecules* into the polymer prior to fibre spinning. Dendrimers and hyperbranched polymers (together also known as "dendritic polymers"—see Fig. 1) are characterised by a highly branched structure, a compact shape and a large number of (reactive) end groups. Due to these structural characteristics their properties largely deviate from normal, linear polymers, e.g. in their rheological behaviour and in the possibility to take up guest molecules by specific interactions with the macromoleule's interior. Numerous applications for dendritic polymers are currently under investigation; a recent review focussed on the combination of dyes with dendrimers or hyperbranched polymers [3].

Hyperbranched polymers are generally produced by polycondensation reactions. An example is the synthesis of hyperbranched polyesteramides [Hybrane (DSM New Business Development)] obtained from the reaction of cyclic anhydrides with diisopropanolamine [4]. By an appropriate choice of anhydride (or combination of anhydrides) and modifying end groups, the properties of the resulting polymers (e.g. solubility, compatibility, surface interactions and host/guest behaviour) can be varied over a wide range, which gives the possibility to tailor the product for a wide variety of applications [5]. An example is the product Hybrane PS 2550, which is built up from phthalic anhydride and diisopropanolamine, with 50% of the hydroxy end groups being esterified with stearic acid (Fig. 2) Due to the presence of the fatty acid alkyl chains, this product is compatible with polypropylene, while the presence of polar groups and aromatic rings will give interactions with appropriate dyes.

The aim of the work was to determine the dyeability of PP fibre which had been modified by the incorporation of 3% by mass of the hyperbranched polyesteramide; in addition, the effect of the incorporation of *Hybrane* on the physical properties of polypropylene fibre was assessed.

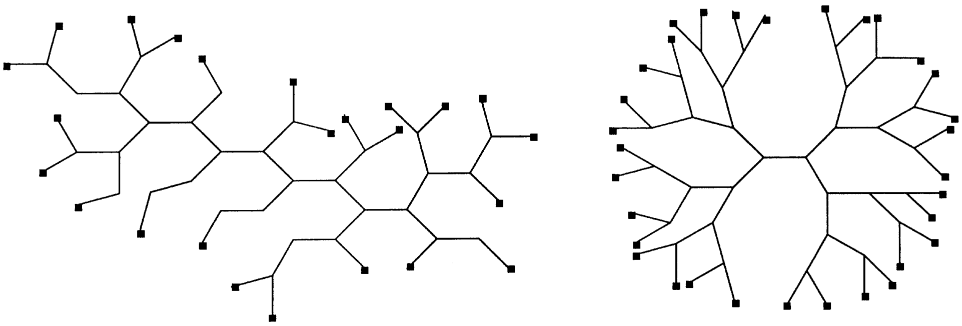

Fig. 1. (a) Hyperbranched; (b) dendrimer.

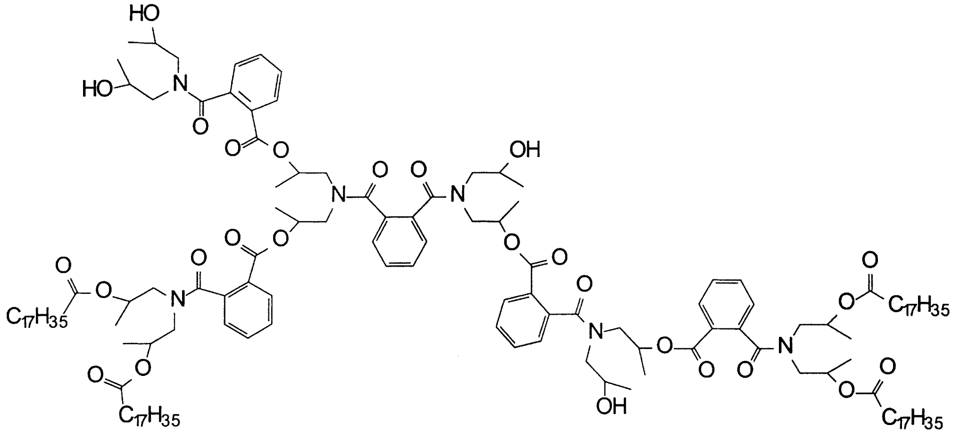

Fig. 2. Hybrane PS2550 (partially stearate-modified; Mn = 2500).

2. Experimental

2.1. Blending

The composition of the polypropylene blend was:

- polypropylene powder: Stamylan P 110E30SF (DSM New Business Development);
- hyperbranched polymer: Hybrane PS2550 (DSM) 3% by mass;
- UV stabiliser: Chimassorb 944 (Ciba-Geigy); 0.1% by mass; and
- thermal stabiliser: Irgafos 168 (Ciba-Geigy); 0.05% by mass.

The blended powder was extruded using an MP2030 (APV) co-rotating, twin-screw extruder with a screw diameter of 19 mm and a length:diameter ratio of 40:1. The polymer had a melt flow index of 26 dg min^{-1} at 230 °C and 21.6 N.

2.2. Melt spinning

Pellets prepared using the twin-screw extruder were spun using a Fournè-Bonn spinning machine equipped with a 12 hole, 500 mm spinneret pack, using Vystat PF38 (Vickers) spin finish. The resulting yarns were of 378.2 dtex in the case of the 3% Hybrane PS 2550 modification and 485.3 dtex for the unmodified polymer.

2.3. Drawing

The fibres were drawn in a Dienes drawframe using a top roller temperature of 100 °C, a hot plate temperature of 125 °C, a draw ratio of 5.5:1 and a drawing speed of 52 m min^{-1}. The resulting yarns were of 78.5 dtex (13.08 dpf) in the case of the 3% hyperbranched modified fibre and 78.4 dtex (13.06 dpf) for the unmodified fibre.

2.4. Knitting

Knitting was carried out on a TMW sampling machine using a knitting gauge diameter of 17 cm and a total of 168 needles (5.5 needles cm^{-1}).

2.5. Scouring

The knitwear was scoured before dyeing at 98 °C for 30 min in an open beaker in a solution (distilled water) comprising 2 g l^{-1} Ultravon EL (Ciba-Geigy) and 2 g l^{-1} Na_2CO_3. The scoured material was rinsed thoroughly in tap water and allowed to dry in the open air.

2.6. Dyeing

The dyeability of the modified PP was examined using C.I. Disperse Blue 56 (I), a commercial sample of which was kindly supplied by DyStar UK. Dyeings (1% omf) were produced using a Roaches Pyrotec S laboratory scale dyeing

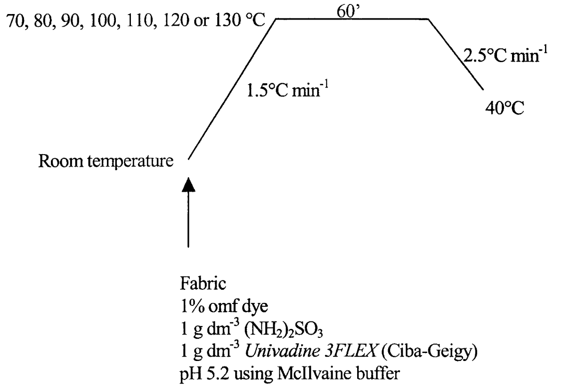

Fig. 3. Dyeing method.

machine equipped with infrared heating, in stainless steel dyepots of 300 cm^3 capacity; the dyeing method is shown in Fig. 3. At the end of dyeing the dyed samples were rinsed in tap water and reduction cleared using the method shown in Fig. 4. At the end of aftertreatment, the samples were rinsed in cold tap water and dried in the open air.

2.7. Colour measurement

This was carried out using an X-Rite bench top spectrophotometer coupled to a PC, using a 10° standard observer, D_{65} illuminant with both specular and UV components included. The colour strength of the dyeings was expressed as the *f*(*k*) value shown in Eq. (1) where $\bar{x}_{10\lambda}$, $\bar{y}_{10\lambda}$, $\bar{z}_{10\lambda}$ are the colour matching functions for the 10° standard observer at each wavelength [6].

$$f(k) = \sum_{400}^{700} (K/S)_\lambda (\bar{x}_{10\lambda} + \bar{y}_{10\lambda} + \bar{z}_{10\lambda}) \qquad (1)$$

2.8. Measurement of dyebath exhaustion

An aliquot of the cool (room temperature) residual dyebath was diluted using acetone and the absorbance measured at the λ_{max} of the dye using a Perkin-Elmer Lambda 9 UV/visible spectrophotometer using a silica cell of 1 cm path length. The extent of dyebath exhaustion was calculated by reference to a calibration curve.

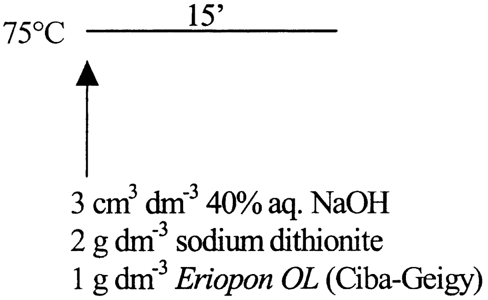

Fig. 4. Reduction clearing.

2.9. Fastness assessment

The dyed samples were subjected to the ISO C06C03 wash testing procedure and the ISO B02/1 light fastness testing method [7]. In addition samples of undyed, unmodified PP fabrics as well as undyed, modified fabrics were subjected to the ISO B02/1 light fastness test.

2.10. Tensile strength measurement

The tensile properties of both the modified and unmodified yarns were determined using a Statimat M (Textechno).

3. Results and discussion

The decision to incorporate 3% by mass of the hyperbranched polyesteramide was made in the light of preliminary investigations by DSM on the processability of Hybrane-modified PP. In terms of the effect of modification on the physical properties of the fibre, it was found (Fig. 5) that the tensile character of the polypropylene fibre was little affected by the incorporation of the hyperbranched polyesteramide. Some problems were experienced during knitting because of the low elasticity of the fibre, yarn rupture occurred as a result of the strong and brittle nature of the fibre, even when the knitting machine was run at the slowest speed possible. However, fibre breakage during knitting was overcome by releasing tension from the feed rollers.

Fig. 6 shows the colour strength [*f*(*k*) at λ_{max}] achieved as a function of dyeing temperature, for

1% omf dyeings of unmodified polypropylene knitted fabric before and after reduction clearing. It is clear that although the unmodified fibre was dyed to a pale depth, the majority of this was removed by the reduction clearing process. These two findings were expected in view of the well known low substantivity of disperse dyes towards unmodified PP. Fig. 7 shows the colour strength achieved at each of the seven dyeing temperatures used for PP fibre which had been modified with 3% hyperbranched polymer, both before and after reduction clearing. It is evident that reduction clearing removed a large proportion of the dye which had been adsorbed, as found in the case of the dyed, unmodified PP. However, a comparison of Figs. 6 and 7 reveal that the modified polypropylene displayed much greater substantivity for the disperse dye. The difference in the extent of dye uptake onto unmodified and modified substrates after reduction clearing is clearly shown by Fig. 8 from which it is evident that the incorporation of the hyperbranched polymer into the PP prior to spinning markedly enhanced dye uptake.

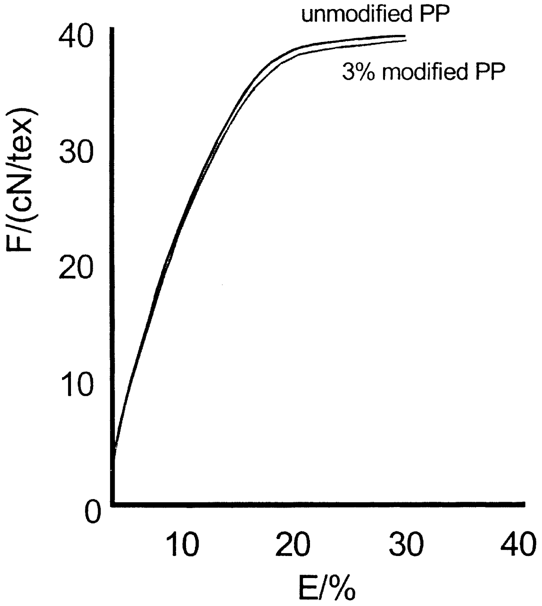

Fig. 5. Force/elongation curves.

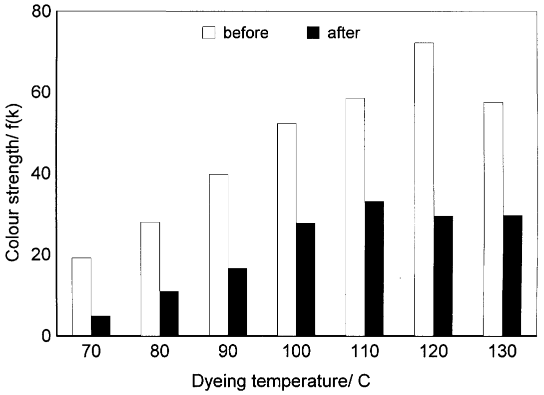

Fig. 7. Colour strength of 1% omf dyeings on 3% modified PP as a function of dyeing temperature before and after reduction clearing.

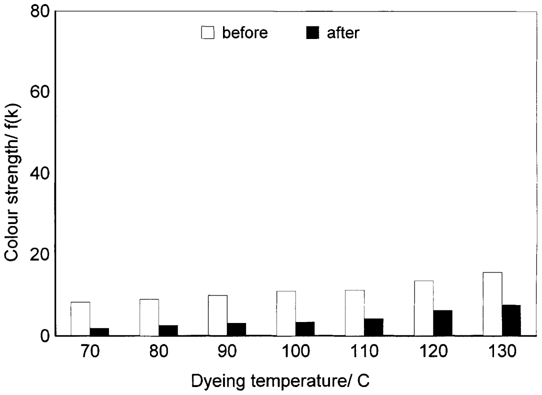

Fig. 6. Colour strength of 1% omf dyeings on unmodified PP as a function of dyeing temperature before and after reduction clearing.

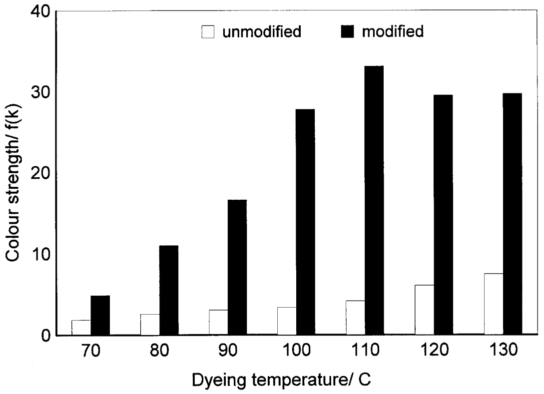

Fig. 8. Colour strength of 1% omf dyeings on modified and unmodified PP as a function of dyeing temperature after reduction clearing.

The observed enhancement of dye uptake can be attributed to the introduction of polar groups provided by the stearate-modified hyperbranched polymer.

A further comparison of Figs. 6 and 7 reveal that the modified and unmodified polypropylene substrates differed in terms of the effect of dyeing temperature on dye uptake. In the case of the unmodified fibre (Fig. 6), the observation that dye uptake increased with increasing dyeing temperature over the range 70 to 130 °C can be attributed to a corresponding increase in the amount of accessible volume available for dye diffusion, in accordance with the free volume model of dye diffusion [8]. However, Fig. 7 shows that for the modified substrate, dye uptake reached a maximum at 120 °C before reduction clearing and at 110 °C after reduction clearing. This latter finding implies that dye uptake on to the modified fibre may have reached a "saturation value" as a result of the adsorbed dye molecules having occupied all of the (limited number) of introduced polar groups. The observation (Fig. 6) that in the case of the unmodified substrate, dye uptake did not reach a plateau at a given temperature, can be attributed to the lack of polar groups within the fibre.

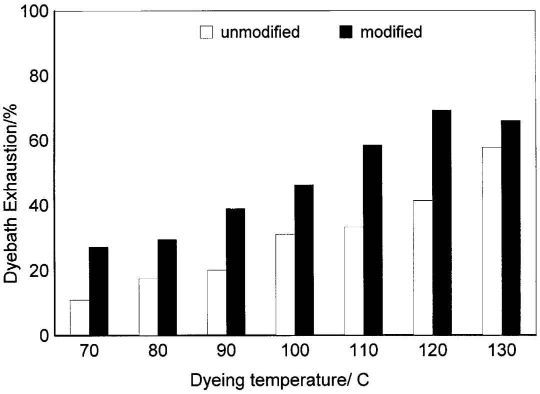

Fig. 9. Dyebath exhaustion achieved for 1% omf dyeings on modified and unmodified PP as a function of dyeing temperature.

Fig. 9 shows that the extent of dye exhaustion increased with increasing dyeing temperature for both the modified and unmodified fabrics. A difference was, however, observed between the two substrates insofar as a maximum in dye exhaustion was achieved at 120 °C in the case of the modified fibre compared to 130 °C for the unmodified fibre. An explanation for this difference in the behaviour of the two types of fibre can be offered in the context of the extents of dye uptake achieved on the two types of substrate discussed above (Figs. 6 and 7). The finding that dye uptake increased with increasing dyeing temperature over the range 70 to 130 °C in the case of the unmodified fibre can be attributed to a corresponding increase in free volume within the fibre while the observed maximum in dye exhaustion achieved at 120 °C for the modified substrate suggests that the available, introduced polar dye sites had become "saturated".

Dyeings (which had been reduction cleared) of fabrics made from unmodified and modified PP fibre were subjected to five repeated wash fastness tests at 60 °C. It was found (Table 1) that the extent of shade change that occurred at the end of

Table 1
Wash fastness results (five repeated ISO CO6/C2 wash tests) for 1% omf dyeings

Washes	Change in shade		Sec. cell. acet. (Dicel)		Staining			
					Nylon 6.6		Polyester (Courtelle)	
	Unmodified PP	Modified PP	Unmodified PP	Modified PP	Unmodified PP	Modified PP	Unmodified PP	Modified PP
1	–	–	4/5	4	4/5	2	5	4/5
2	–	–	5	4	4/5	2	5	5
3	–	–	5	4/5	4/5	2/3	5	5
4	–	–	5	5	4/5	2/3	5	5
5	4	4	5	5	4/5	3	5	5

repeated wash fastness testing was relatively small for both unmodified and modified substrates. In terms of staining of adjacent fibres, the dyeings of the modified PP displayed higher fastness than those of their unmodified counterpart.

In terms of the light fastness of the dyeings, a rating of 2–2/3 was achieved for the modified substrate, a value that is lower than that expected for typical commercial disperse dyes on, for example, PET [8]. The low light fastness rating achieved prompted an examination of the fading behaviour of the hyperbranched polymer. Samples of undyed, unmodified fabric and also undyed, modified fabric were subjected to light fastness testing; the absence of discolouration for both types of fabric suggested that the presence of the hyperbranched polyesteramide in the polypropylene had not impaired the light fastness of the "parent" polypropylene and, also that the hyperbranched polymer had not itself degraded. The cause of the low light fastness of the dyed is under investigation.

4. Conclusions

The incorporation of 3% stearate-modified hyperbranched polymer had little effect on the physical properties of the fibre. The incorporation of 3% stearate-modified hyperbranched polymer markedly enhanced of the dyeability of polypropylene with C.I. Disperse Blue 56. Although reduction clearing removed a large proportion of the dye which had been adsorbed, the dye displayed much greater substantivity towards the modified fibre than its unmodified counterpart. The enhanced dye uptake can be attributed to the introduction of polar groups provided by the stearate-modified hyperbranched polymer. Dye uptake on to the modified fibre reached a maximum at 110 °C after reduction clearing, suggesting that dye uptake had attained "saturation value', possibly as a result of the adsorbed dye molecules having occupied all of the (limited number) of introduction polar groups. The fastness, of reduction cleared dyeings of fabrics made from polypropylene fibre which had been modified with 3% hyperbranched polymer, to five repeated wash fastness tests at 60 °C was good; the fastness of the dyeings to light was, however, poor.

Acknowledgements

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