Macromol. Symp. ***127****, 257–263 (1998)*

SURFACE MODIFICATION OF POLYPROPYLENE: HYDROPHILIC FINISHING WITH CARBOHYDRATES

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Abstract: Conversion of hydrophobic polypropylene surfaces to hydrophilic, water wettable surfaces by adsorption of amphiphilic carbohydrates ("surfactant immobilization") as well as by covalent bonding of sucrose residues via azid photolysis ("photochemical immoblization") was investigated. Improvement of surface hydrophilicity was determined by contact angle measurements and application of special test inks for polyolefines.

INTRODUCTION

Many applications of polymers in industrial, medical and "every-day" uses depend upon physical, chemical and biological interactions of molecules or microorganisms at their surfaces. Therefore special properties of polymer surfaces, which are different from the bulk polymer, are required for many applications. In recent years many advances have been made in developing surface treatments to alter the chemical and physical properties of polymer surfaces. Methods such as surface grafting, plasma modification, corona discharge and flame treatment are applied to modify polymer surfaces, e.g. to increase or to reduce hydrophilicity, adsorption of molecules, roughness, ionic charge, biocompatibility etc. without affecting bulk properties (Ref. 1).

CCC 1022-1360/98/$ 10.00

One of the most active research areas of surface modification concerns the conversion of nonpolar, hydrophobic surfaces to polar, hydrophilic and water wettable surfaces (Ref. 2). In this paper we present our recent works to increase hydrophilicity of polypropylene surfaces by adsorption of amphiphilic carbohydrates as well as by covalent bonding of carbohydrate residues.

SURFACTANT IMMOBILIZATION

For hydrophilic modification of polypropylene surfaces the principle of dispersion dyeing of hydrophobic fibres was used. By this treatment the hydrophobic "tails" of the surfactants are adsorbed or incorporated (Fig.1).

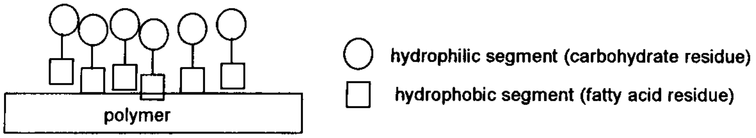
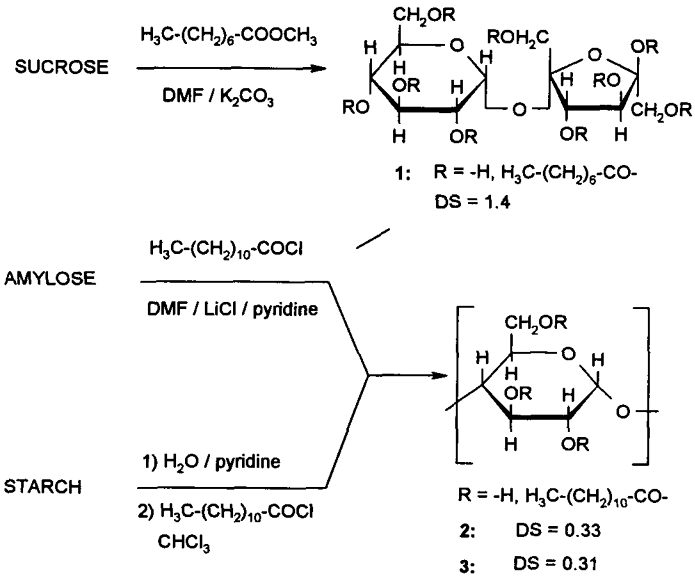


Fig.1: "Surfactant Immobilization"

Amphiphilic carbohydrate esters, which have already been applied successfully for improvement of the water absorbing capacity of PET fibres (Ref. 3), were prepared by esterification of sucrose, amylose and "activated" starch (Ref. 4) with caprylic acid methyl ester and lauric acid chloride, respectively (Scheme 1). Depending of the molar ratios of the reactants, esters **1**, **2** and **3** with degrees of substitution (DS) of 0.3 and 1.4 were obtained.

To immobilize the amphiphilic carbohydrates polypropylene films were treated with aqueous solutions containing the carbohydrate surfactants, ammonium sulfate, commercial carriers (Invalon-HTC®) and dispersants (Irgasol-DAM®) at 60 - 100°C.



1: R = -H, $H_3C-(CH_2)_6-CO-$
DS = 1.4

R = -H, $H_3C-(CH_2)_{10}-CO-$
2: DS = 0.33
3: DS = 0.31

Scheme 1. Synthesis of Carbohydrate Surfactants

PHOTOCHEMICAL IMMOBILIZATION

Aromatic azides are known to decompose by UV radiation yielding highly reactive nitrenes which can undergo a multitude of reactions, for example, insertion into C-H, N-H and O-H bonds, addition to olefins or proton abstraction reactions to give the corresponding amine (Ref. 5-7). The precise mechanism of surface modification with azides is not fully understood; one proposed mechanism which is consistent with known nitrene chemistry is shown in Fig. 2 for the photomodification of polyolefines.

Azidobenzoic acid ester **4** was synthesized by esterification of sucrose with 4-azidobenzoyl chloride in a molar ratio of 1:5 (Scheme 2).

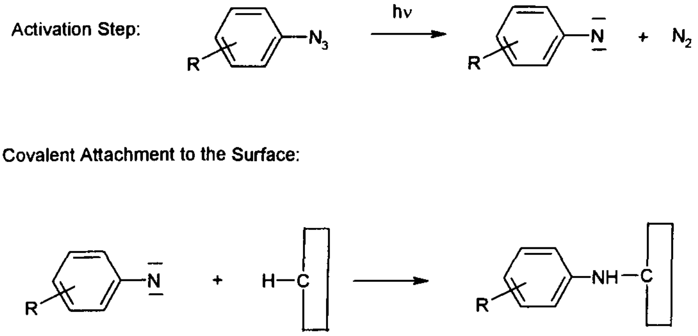
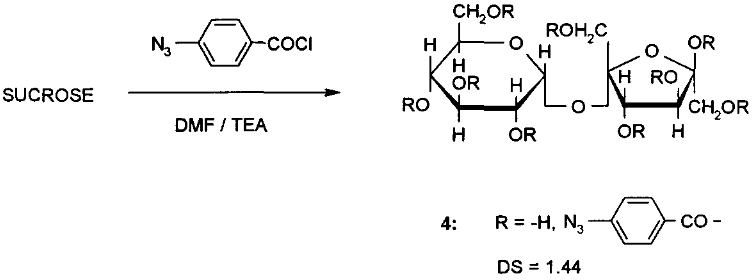


Fig. 2. Modification of polyolefines via photolysis of aromatic azides



Scheme 2. Synthesis of Sucrose Azides

To enhance the diffusion of **4** into the polymer surface polypropylene sheets and films were pretreated with swelling agents (n-hexane, toluene, xylene; 60-120 min, 25-40°C). Then the polymer was immersed in acetone solutions containing azide **4** (20 mMol/l) and after drying the materials were irradiated with a high pressure mercury lamp (Heraeus, TQ-150, λ = 200-600 nm, distance from the substrate 15 cm, irradiation time 5-20 min). Unreacted azide and byproducts were removed by rinsing with acetone. FT-IR spectra of polypropylene films modified via the photolysis of **4** are shown in Fig. 3.

WETTABILITY TESTS

The properties of the modified PP surfaces were investigated by contact angle measurements and by application of special test inks (Arcotec®), suitable for simple and quick evaluation of surface tension of polyolefines. The results are summarized in Table 1 and Table 2, respectively.

Table 1. Surface tension and contact angles of polypropylene modified by "surfactant immobilization"

Surfactant	surface tension (mN/m)	contact angle (°)
-	32	90
1	36	89
2	36	89
3	36	89

Table 2: Surface tension and contact angles of polypropylene modified by "photochemical immobilization"

swelling agent	irradiation time (min)	surface tension (mN/m)	contact angle (°)
-	-	32	90
n-hexane [a)]	5	> 44 [c)]	58 [d)]
n-hexane [b)]	5	> 44 [c)]	64
toluene [b)]	5	40	62
toluene [b)]	30	> 44	55
o-xylene [b)]	5	42	65

[a)] polypropylene sheet [b)] polypropylene film

[c)] test inks available only for surface tensions between 30 and 44 mN/m

[d)] blank trial without azide: surface tension 38 mN/m, contact angle 85°

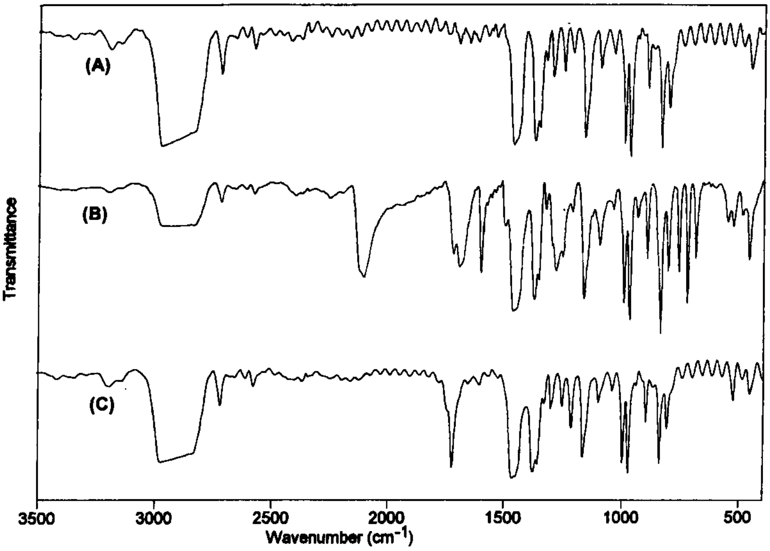


Fig. 3. IR spectra of unmodified polypropylene (A), polypropylene + azide **4** before irradiation (B) and modified polypropylene after photolysis and rinsing with acetone (C)

CONCLUSIONS

In contrast to the negligible improvement of wettability by adsorption of amphiphilic carbohydrates, surface hydrophilicity of polypropylene is strongly increased by covalent attachment of sucrose residues. Due to their polyfunctionality, thus enabling further derivatizations, photolysis of sucrose azides provides a useful route for surface modification of „difficult" surfaces exhibiting no reactive centers such as polyolefines.

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