Engineering Biopolymers: Homopolymers, Blends, and Composites

Homopolymers, Blends, and Composites

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Chapter 5

Starch-Urethane Polymers: Physicochemical Aspects, Properties, Application

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5.1. Starch as a biorenewable polymer feedstock

Over the last two decades, starch has been extensively studied and applied in the manufacturing of easily processable materials of technical importance. Starch is a biorenewable and cheap polymer; the price of starch-based plastics was 1.25–1.40 euro/kg in 2001 and in some applications it is competitive with conventional petrochemical plastics [1]. In the same year, the world production of biodegradable starch-based plastics was evaluated as *ca.* 25 000 tons [1]. Biodegradable polymeric materials are developed with the aim of a gradual replacement of synthetic polymers based on petrochemical feedstock. Such a strategy will allow for a partial solution of environmental problems associated with post-consumer polymer waste.

Starch consists of two polymer components: linear amylose and branched amylopectin, in a proportion depending on the respective botanical origin (Table 5.1) [2]. Native starch is *ca.* 15–45% crystalline [3]; usually, only amylopectin takes part in the formation of the crystalline structure [4].

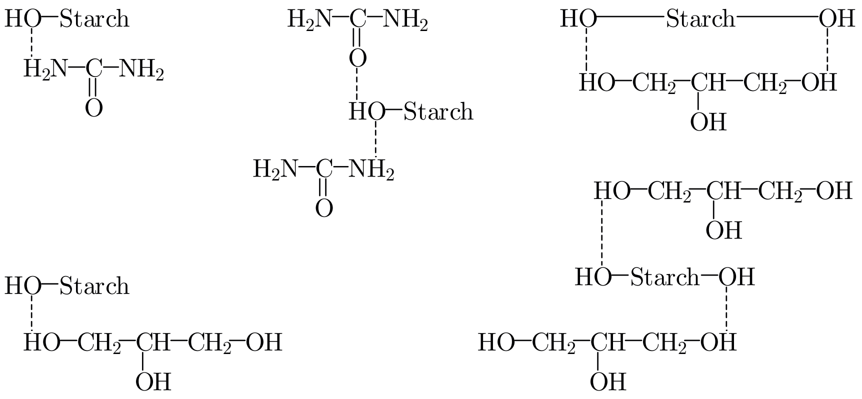
In order to obtain an amorphous thermoplastic mass from starch, the granular structure has to be disordered (*i.e.*, gelatinized or destructured) [5]. When heated in the presence of water, under high-shear conditions, starch granules swell, losing crystallinity and birefringence [1].

The glass transition temperature, T_g, and the melting temperature of dry pure starch are higher than its decomposition temperature [1]. The presence

Table 5.1. Extrapolated values of the glass transition temperature and amylose-to-amylopectin weight ratio in various types of starch [2]

Starch	T_g (°C)	Amylose/amylopectin (by wt)
Pea	75	2:1
Potato	152	1:4
Wheat	143	1:4
Waxy maize	158	1:99

of a plasticizer lowers the T_g value, *i.e.*, at elevated temperatures starch undergoes gelatinization rather than degradation. For instance, at a high moisture content (30 wt% and more), T_g of wheat starch is observed at about 50°C, followed by the crystalline melting transition [6]. The plasticizer molecules could form hydrogen bonds with the polysaccharide chains of starch (Scheme 5.1), disrupting the inter- and intramolecular hydrogen bonds of native starch [7]. The stronger the hydrogen bonds between starch and the plasticizer, the more difficult starch recrystallizes during storage [2].



Scheme 5.1. Formation of hydrogen bonds between starch/glycerol and starch/urea

Generally, low molecular weight substances with rather low viscosity are efficient plasticizers; they should also exhibit a high boiling point [2]. The most common starch plasticizers are water and glycerol. Urea and formamide are known starch plasticizers capable of preventing recrystallization [7]; the resulting hydrogen bonds with starch are even more stable than those formed by glycerol (the most popular starch plasticizer) [8]. However, since urea is a high-melting solid with little internal flexibility, urea-plasticized starch becomes rigid and brittle [8].

Extrusion in the presence of low molecular plasticizers is the simplest method of starch thermoplasticization; the latter seems to be the most common way of starch modification. Numerous reports describing process conditions, various kinds of plasticizers, as well as the properties of the final starch-based products are available in the literature [3,5,7–12]. However, starch thermoplasticization by itself is not the subject of interest of this chapter.

The most important problems associated with conventional starch-based materials are their sensitivity to water and brittleness, which can even increase during storage due to a phenomenon termed *retrogradation* [2]. Retrogradation (spontaneous recrystallization) is caused by the tendency of polysaccharide macromolecules to form hydrogen bonds [2]. This phenomenon is also responsible for another common drawback during processing, *e.g.*, by injection molding, namely shrinkage.

Physical and chemical (or physicochemical) methods of modification are utilized in order to transform starch into a thermoplastic material processable by conventional techniques including melt extrusion, kneading, injection molding, or compression molding.

In practice, there are three general ways of starch thermoplasticization: (i) chemical derivatization (substitution of the polysaccharide hydroxyl groups by reacting with other functional moieties), (ii) extrusion in the presence of low molecular polar plasticizers or other thermoplastic (usually biodegradable) polymer(s), and (iii) graft copolymerization.

Problems associated with native starch processing by conventional methods typical of thermoplastic polymers and the disadvantages of goods produced by thermoplasticization have led to the conclusion that blending of starch with other biodegradable thermoplastics can be appropriate. Two general ways of blend production (mainly by extrusion) can be considered, *i.e.*, compounding and reactive extrusion.

In this chapter, the following biodegradable starch-polyurethane materials are described: (i) products of starch chemical derivatization by the reaction of hydroxyl groups with isocyanates, (ii) materials obtained by starch melt blending with polyurethane(s) alone or with a third biodegradable polymer component, (iii) urethane graft copolymers of starch, and (iv) starch-polyurethane foams. The last group of materials belongs to crosslinked polymers rather than to thermoplastics. Chemical or physicochemical aspects of starch modification, properties of starch-polyurethane materials (including susceptibility to biodegradation), and relevant areas of their application are considered.

Starch-polyurethane materials are of particular importance for the following reasons: (i) susceptibility to biodegradation (Scheme 5.2), (ii) high reactivity of the hydroxyl groups of polysaccharide chains with isocyanate groups and

$$\underset{\text{Anhydride}}{\mathrm{RCOO\text{-}O\text{-}OOCR}} > \underset{\text{Ester}}{\mathrm{RCOOR_1}} >> \underset{\text{Urethane}}{\mathrm{RNHCOOR_1}} \approx \underset{\text{Amide}}{\mathrm{RNHCOR_1}} > \underset{\text{Ether}}{\mathrm{ROR_1}}$$

Scheme 5.2. Susceptibility to hydrolysis of different functional groups in the heterochain polymers [13] no low molecular weight by-product formation, (iii) the reaction of starch urethanization can possibly be catalyzed (*e.g.*, by the addition of dibutyltin dilaurate or other catalysts), (iv) hydrogen bond formation between the polysaccharide chains (*i.e.*, OH groups) and the urethane (or urea, amide, ether, or ester) groups of the second polymer component, thus improving the compatibilization between starch and the polyurethane components.

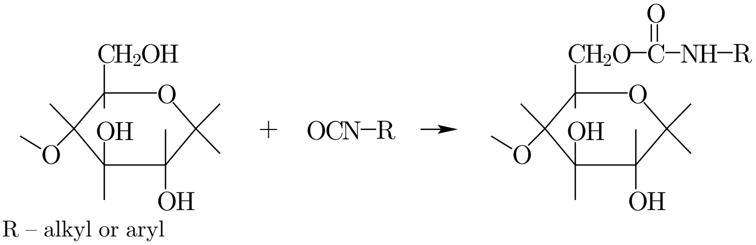
The term "biodegradation" is very common, but is often misused [14]. In biodegradation, enzymes of the biosphere essentially participate at least in one step during the cleavage of the chemical bonds of the material; degradation does not necessarily proceed over a short period of time. Therefore, it is important to combine the term "biodegradable" with the specification of the particular environment where biodegradation is expected to occur and the process time-scale. Composting is among the most valuable methods to assess the polymeric material bioassimilation during biodegradability tests.

5.2. Starch-urethane polymers *via* derivatization of hydroxyl groups

The chemical modification of starch is a method for broadening the range of its applications. From the chemical point of view, the addition reactions are preferred for starch derivatization, since no by-products are formed [15]. Starch-urethane polymers can be obtained in a reaction between starch and isocyanates, urea or its derivatives, such as alkylureas. However, starch-urea and starch-alkylurea derivatives tend to swell or even dissolve in water [16,17]. Moreover, the substitution efficiency is rather low [17] and the reaction with urea is difficult to control, because of the possibility of crosslinking and by-product formation [16].

The reaction of starch with isocyanates follows the general pattern of addition reactions (Scheme 5.3). Since moisture present in the reaction system causes transformation of the isocyanates into the corresponding substituted ureas, the process is preferably carried out under anhydrous conditions. Elevated temperatures are preferred, although the reaction proceeds even at room temperature [18]. Some examples of this interaction are described in [15,18,19].

Early reports refer to the preparation in suspension of starch-urethane derivatives, using organic solvents, such as benzene, toluene, pyridine,



Scheme 5.3. Scheme of reaction between starch and monoisocyanate (for a degree of substitution, DS = 1)

dimethylsulfoxide (DMSO), N,N-dimethyl formamide, N-methyl pyrrolidone or morpholine [18,19].

The efficient chemical modification of starch requires a large amount of solvent (Figure 5.1) [15]; thus, the reaction efficiency is reduced at higher starch concentrations, since less solvated starch hydroxyl groups are available for an effective addition to isocyanate groups [15].

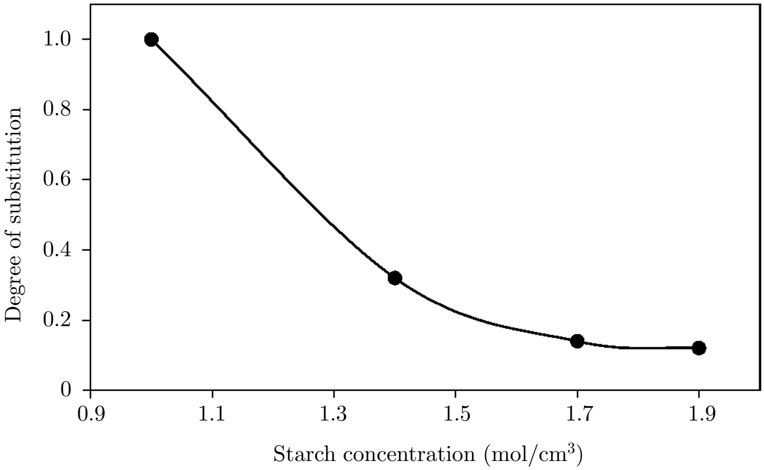


Figure 5.1. Relationship between starch concentration and degree of substitution; solvent DMSO, residence time 4 min, theoretical DS = 2 [15]

The reaction between starch hydroxyl groups and the isocyanate groups is often catalyzed by dibutyltin dilaurate [20–22], but other catalysts are also used [15,23]. However, the reaction proceeds even in the absence of a catalyst [17,24].

Reported isocyanate modifiers used for starch carbamoylation are both aliphatic, such as hexamethylene diisocyanate (HMDI) [18] and monoisocyanates containing 7 to 18 carbon atoms in the aliphatic chain [15,17], and aromatic, such as tolylene 2,4-diisocyanate (TDI) [19], methylene–4,4′-bisphenyl diisocyanate (MDI) [21], phenyl diisocyanate (PI) [18,20], toluene poly(propylene oxide) diisocyanate [24], *etc.* In the past, aromatic isocyanates were mainly used for the preparation of starch-urethane derivatives [25,26]. The reaction rate of starch urethanization depends on the nature of the reaction medium, the temperature (Figure 5.2), the kind of isocyanate used (Figure 5.3), the degree of starch pregelatinization, and the presence of catalysts [25].

The properties of starch-urethane derivatives are strongly influenced by the degree of substitution as well as by the type and the chain length of the attached aliphatic or aromatic substituent. However, the use of diisocyanates, *e.g.*, HMDI and TDI, leads to starch crosslinking. In this case, the addition of even a small amount of modifier changes the product properties.

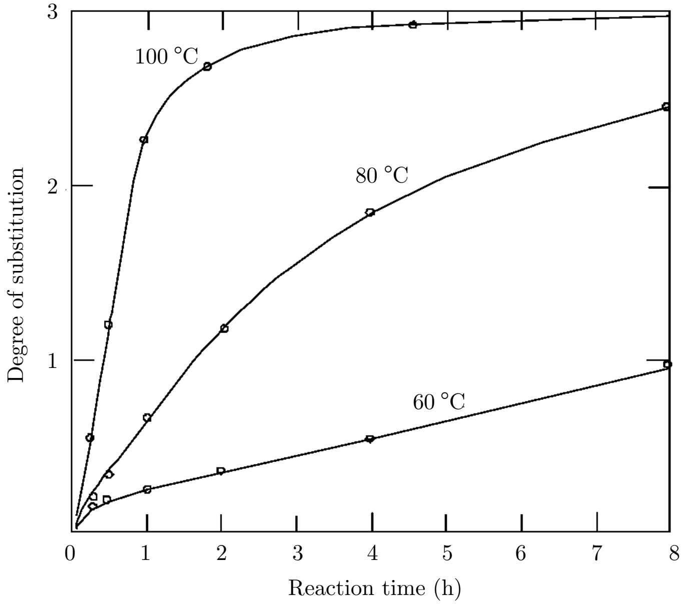


Figure 5.2. Effect of temperature and time on the rate of the uncatalyzed reaction of phenyl isocyanate with corn starch granules in pyridine (a two-fold excess of isocyanate is required to get the maximum degree of substitution, *i.e.*, DS = 3) [25]

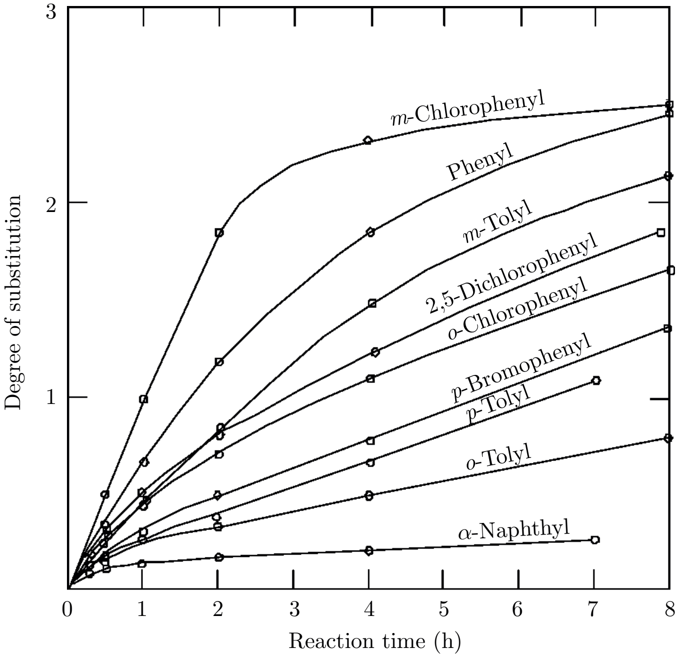


Figure 5.3. Uncatalyzed reaction rate of various isocyanates with corn starch granules in pyridine at 80°C [25]

Starch-urethane derivatives of HMDI that contain at least one urethane group for each polysaccharide unit exhibit limited swelling [17,18]. One of the potential applications of such products is dusting powder for surgical gloves; the powder will not become sticky even after sterilization at 120°C for 1 h [18].

It was found that the product of the starch and phenyl isocyanate reaction with DS = 0.2 exhibited no toxicity to cultures of *Aspergillus oryzae*, *Penicillium expansum* and *A. Niger*, that were grown well on a medium containing this starch derivative as a carbon source [26].

Crosslinking of starch chains could be avoided despite the use of a diisocyanate by blocking one of the −NCO groups through a reaction with substances containing a free hydroxyl, amine, or carboxyl group [19]. Non-symmetrical diisocyanates are preferred, as in this case one of the isocyanate groups is far more reactive. For instance, in the case of tolylene 2,4-diisocyanate, the group in position 4 is about ten times more reactive than that in position 2 [19].

Monoisocyanates with alkyl chains of different length are useful reagents, imparting hydrophobicity and thermoplasticity to starch materials (Tables 5.2 and 5.3) [15,27].

Table 5.2. Experimental and theoretical values of DS, yield, T_g, and melt flow data of starch carbamates with different alkyl chain lengths [15]

Wrinkled pea starch modified with	Degree of substitution		Yield	T_g	Melt flow test
	Theoretical	Experimental	(%)	(°C)	
C_7NCO	2.0	0.2	31	~150	melting, gas formation
C_9NCO	2.0	1.9	78	~150	melting, gas formation
$C_{11}NCO$	2.0	1.8	71	~160	melting, gas formation
$C_{15}NCO$	2.0	1.9	97	~150	melting, gas formation
$C_{18}NCO$	2.0	1.9	96	~90	melting, gas formation
$C_{11}NCO$	0.5	0.28	37	–	no melting
$C_{11}NCO$	1.0	0.9	75	–	no melting
$C_{11}NCO$	1.5	1.4	87	~155	melting, gas formation
$C_{11}NCO$	2.5	2.1	95	~150	melting, gas formation
$C_{11}NCO$	3.0	2.6	96	~145	melting, gas formation

The hydrophobicity of the modified starch-urethanes could be determined by contact angle measurements [20,28,29]. For the values of 90° and up (in water), the surface is assumed to be hydrophobic [23]. The contact angle value of starch-urethanes containing 2–18 carbon atoms in the alkyl chain (DS = 1.6) was found to be slightly above 100° (Table 5.4) [23].

Table 5.3. Experimental and theoretical values of DS and melt flow properties of urethane-urethane, urethane-urea and urethane-amide starch derivatives [27]

Starch derivative based on HMDI/monofunctional modifier (alcohol, amine or carboxylic acid)	Degree of substitution		Swelling index, 25°C	Hot pressed disc diameter
	Theoretical	Experimental	(cm^3/g)	(cm)
CH_3OH	2	1.57	3.5	7.4
C_2H_5OH	2	1.40	2.3	3.5
C_4H_9OH	2	1.84	2.1	6.0
$C_4H_9NH_2$	2	1.78	2.2	5.7
CH_3COOH	2	1.1	5.6	3.0
C_3H_7COOH	2	1.9	2.0	4.0
$C_{17}H_{35}COOH$	0.25	*	3.9	9.0
	0.50	*	3.2	7.0

*Not determined

Table 5.4. Contact angle values of starch-urethanes with different alkyl chain length [23]

Chain length	Contact angle (°)
C_2	107
C_{11}	109
C_{18}	113

The surface of waxy maize starch nanocrystals obtained by hydrolysis of native waxy maize starch granules with sulfuric acid has been modified by phenyl isocyanate [22]. It has been demonstrated by contact angle measurements that the modification of this form of starch also led to more hydrophobic particles (*ca.* 60°, as compared to 35° for unmodified starch nanocrystals) [22].

The data available lead to the conclusion that the longer the introduced alkyl chain, the better the hydrophobic properties of the starch derivatives. Generally, starch-urethane derivatives exhibit a very low solubility in organic solvents [15,18]. Moreover, melting was observed for aliphatic derivatives with higher DS values (1.0 and above) (Tables 5.2 and 5.3) [15,27,30]. The efficiencies of modifications by alkyl isocyanates performed in DMSO suspension were found to be high, up to 97% [15].

Similar starch derivatives were prepared in an apparatus allowing a more intensive mixing than that in a glass flask [15]. Pea starch and undecyl isocyanate were reacted in DMSO with dibutyltin dilaurate in a kneader. Despite scaling up the process, the determined DS = 1.8 (theoretical DS = 2.0) was comparable to that of a product obtained in the glass flask. The investigations of aliphatic starch-urethane derivative formation in a DMSO slurry (in the presence of dibutyltin dilaurate as a catalyst) demonstrated that the reaction time ranges are favorable for reactive extrusion (Figure 5.4), which enables continuous processing [15]. The extruder plays the role of a stable pump, ensuring constant throughput and efficient mixing even for highly viscous media [31]. Twin-screw extruders were found to be especially effective continuous reactors. The extruder efficiency depends mainly on the design of the screw(s). The extruder having seven separately heated zones with a temperature profile from the feed to the die, *e.g.*, 60/100/120/120/130/140/140°C [15], can be quite efficient. No higher temperatures were recommended because of the product discoloration.

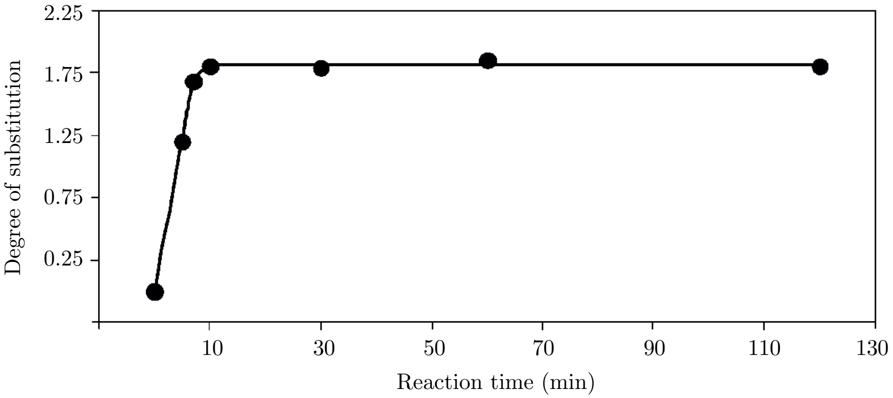


Figure 5.4. Time dependence of the starch-urethane formation; reaction of 1-undecyl isocyanate with wrinkled pea starch in DMSO in the presence of dibutyltin dilaurate catalyst; theoretical DS = 2 [15]

The application of a reactive extrusion manufacturing process to starch-urethanes is associated with some technical problems. The reaction efficiencies were found to be low (*e.g.*, a DS of 0.02 was obtained, whereas the theoretical value was 0.5) as a result of the low viscosity of the monoisocyanates used and the incompatibility of the components, *i.e.*, of ineffective mixing [15].

5.3. Starch/polyurethane blends

The blending of starch granules with synthetic polymers generally results in a filler effect on the polymer properties [32–34]. As the starch content increased in such polymer blends, there was a decrease in the final material elongation at break and tensile strength [35,36], whereas the modulus was increased [37]. The main reason for the observed decrease in the mechanical properties of starch/synthetic polymer blends may be explained by the different properties of starch (a hydrophilic polymer) and synthetic (usually hydrophobic) polymers.

Polyurethane (PU), a unique polymeric material with interesting physical and chemical properties, has been extensively tailored to meet the highly diversified demands of modern technologies, such as coatings, adhesives, fibers, foams, and thermoplastic elastomers [29,38]. The development of waterborne polyurethane or poly(urethane-urea) formulations has increased dramatically in the last fifteen years in view of cost reduction and environmental reasons [39].

Tighzert *et al.* [28,29] developed biodegradable polymeric materials based on thermoplastic starch and a polyurethane aqueous dispersion. PU aqueous dispersions were synthesized from castor or rape seed oil-based polyols. Isophorone diisocyanate and dimethylol propionic acid were used as the residual substrates for the synthesis of aqueous PU dispersions. The effect of the PU content on the morphology, miscibility, and physical properties of the resulting materials (films [29] or extruded strands [28]) was investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), mechanical property measurements, and water sensitivity. The results demonstrated that glycerol-plasticized starch can be mixed with rape seed oil-based waterborne PU on the molecular level when the PU content is lower than 20 wt% [29] (for castor oil-based waterborne PU, lower than 15 wt% [28]), whereas phase separation occurs at higher PU contents. The addition of PU (4–20 wt%) to glycerol-thermoplasticized starch resulted in blends with improved Young's modulus (40–75 MPa), tensile strength (3.4–5.1 MPa), and elongation at break (116–176%) [28]. The mechanical properties of the respective blends are listed in Table 5.5.

Starch/PU films based on PU with rape seed oil polyol exhibited much higher values of elongation at break (85–480%), toughness (1.8–7.1 MPa), and tensile strength (2.8–4.1 MPa) [29] than neat thermoplastic glycerol-plasticized

Table 5.5. Mechanical properties* of thermoplastic starch (TPS)**, polyurethane (PU) and starch/polyurethane (TPS/PU) blends [28]

Film	Young's modulus (MPa)	Tensile strength (MPa)	Toughness (MPa)	Elongation at break (%)
TPS	40.3±5.1	3.4±0.3	2.6±0.3	116±9.2
TPS/PU 4	58.6±3.2	3.9±0.2	3.7±0.3	120±6.5
TPS/PU 7	74.5±6.9	4.6±0.4	4.5±0.2	138±7.3
TPS/PU 10	67.7±7.2	4.9±0.3	5.2±0.3	176±8.4
TPS/PU 15	43.3±6.4	5.1±0.4	5.1±0.3	158±6.8
TPS/PU 20	35.2±5.6	3.4±0.2	3.5±0.2	145±7.7
TPS/PU 30	27.4±2.7	2.6±0.3	2.5±0.2	143±5.1
PU	44.5±3.8	11.8±2.0	14.9±2.1	279±11.2

*Mechanical data measured after 2 weeks of aging

**Glycerol-plasticized starch

starch. The surface properties (contact angle) and water absorption of the starch/PU blends as a function of PU content in the polymeric material are shown in Figures 5.5 and 5.6, respectively. It can be seen that the introduction of PU into the plasticized starch matrix leads to an improvement of the polymer surface and bulk hydrophobicity and a better water resistance of the resulting materials [28,29].

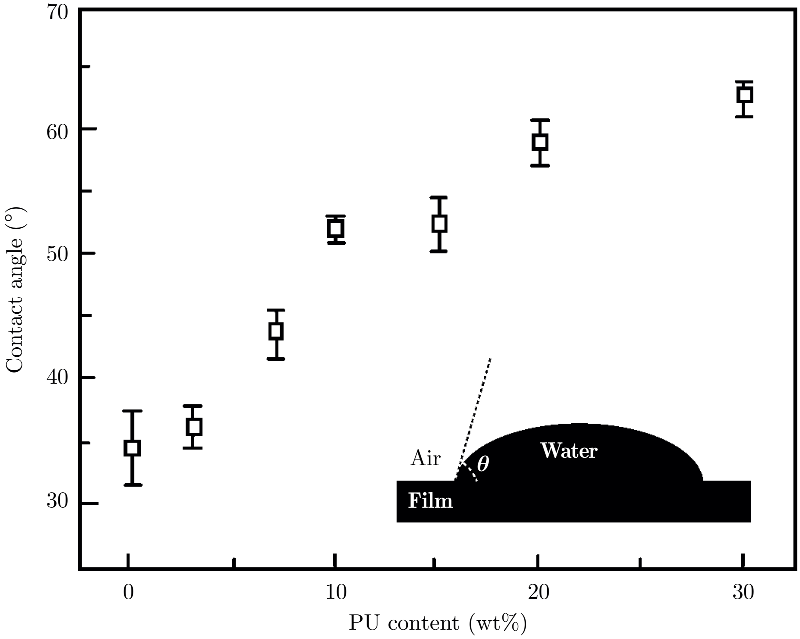


Figure 5.5. Contact angle of TPS/PU blends *vs.* PU content [28]

Transparent sheets made of polymer blends of thermoplastic starch and waterborne polyurethanes were prepared by compression molding and studied by Wu and Zhang [40]. These materials were obtained from a polyester-type waterborne polyurethane based on poly(butylene glycol adipate) ($M_w = 2150$ g/mol), dimethylol propionic acid, tolylene-2,4-diisocyanate, and thermoplastic starch (no data concerning a plasticizer were provided). The results showed that the tensile strength (*ca.* 30–35 MPa), elongation at break (*ca.* 5–40%), and water resistance (317→34 wt% of water) of the TPS/PU sheets were all improved, as compared to TPS, when the PU content was varied in the range of 5–30 wt%. Infrared (IR), X-ray diffraction (XRD), DSC and SEM analyses of the samples indicated that an interaction took place between TPS and PU in the obtained sheets, resulting in a certain level of miscibility. The sheets also revealed a higher crystallinity than PU and amorphous TPS and a slightly lower light transmittance than TPS (decrease from *ca.* 95% for TPS to 85–88% for TPS/PU blends), suggesting a partial recrystallization of starch. The authors