

# Novel starch–polyalkane composite materials

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The polymerisation of dibromoalkanes adsorbed in potato starch leads to a novel class of hydrophobic starch–polyalkane composite materials with very high capacity for surface derivitisation.

Starch is the second largest biomass on earth and depleting fossil hydrocarbon resources will require an increasing range of novel applications for starch-based materials.<sup>1</sup> More than 6 MT y<sup>-1</sup> of starch materials are currently produced in industry with chemically modified starches (through fundamental processes such as hydrolysis, esterification and oxidation) as well as native starches finding diverse uses.<sup>2</sup> Composite materials incorporating starch are less well known although physical mixtures of starch with polyethylene for example, have value as films, coatings and biodegradable plastics.<sup>3</sup> The high degree of functionality of starch along with its low cost, widespread availability and biodegradability makes it a potentially attractive surface-active material but this is hindered by the apparent low site availability and its hydrophobicity and instability in many environments.

The helical structure of native starch leads to hydrophobic channels in which polarisable organic molecules such as haloalkanes can be adsorbed.<sup>2</sup> We have attempted to polymerise intercalated  $\alpha,\omega$ -dihaloalkanes so as to create a thermally and chemically stable hydrocarbon polymeric core which could open up the starch structure creating a more surface-active material and making it more accessible to derivitisation. Our strategy for accomplishing these goals is illustrated by the following example. Native potato starch was stirred together with 1,10-dibromodecane in cyclohexane. The slurry was then reacted with sodium metal at 80 °C for 24 h. The mixture develops a distinct blue colour over this period and filtration under nitrogen gives an intensely colored blue solid. The FTIR spectrum of the solid shows a number of remarkable features notably a highly resolved hydroxyl stretching region and further sharp bands at 1615, 600 and 450 cm<sup>-1</sup> (Fig. 1). These bands can at least in part be attributed to a composite matrix stabilised sodium colloid that is also likely to be the origin of the colour.<sup>4</sup> The blue colour of the solid slowly disappears on exposure to the atmosphere and can rapidly be destroyed by washing with water to give a highly particulate white solid. The well resolved

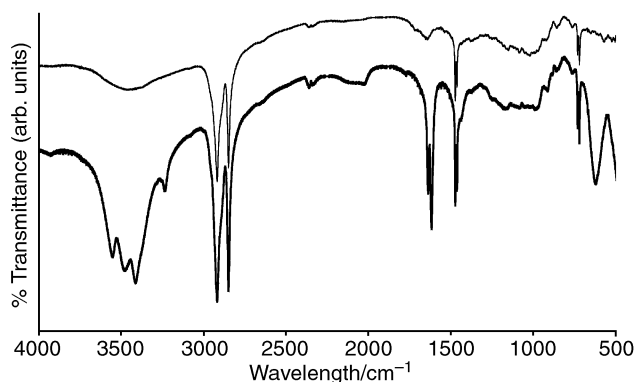


Fig. 1 Diffuse reflectance FTIR spectra of a starch–polyalkane material (STPAM) before (—) and after (---) removal of sodium colloid by water washing.

FTIR bands noted above are absent in the white solid that has a spectrum essentially consistent with a combination of starch and a polyalkane (Fig. 1). The following discussions refer to the water-washed white solid.

We have carried out materials preparations as described above at various starch–dibromodecane ratios and thermal analysis can be used to determine the relative amount of the starch and polyalkane (an example of which is shown in Fig. 2). Thermal analysis shows weight losses typical for starch (*ca.* 200 °C) and a polyalkane (*ca.* 400 °C) although it also shows a small but reproducible weight loss between these temperatures which suggests that the two components are not entirely distinct. The bulk of the starch can be removed from the composite materials by treatment with aqueous acid and GPC analysis of the residual polymer shows that it has a rather low molecular weight comparable to that of a polydecane prepared in the absence of starch (Table 1). Bromine analysis reveals the presence of small amounts of organobromine (residual NaBr can be removed by thorough washing) which can be accounted for as polymer terminating CH<sub>2</sub>Br groups (based on a 'true'  $M_w$  for the polyalkane of 4000).

Other analytical techniques show more obvious evidence of the materials being more than an intimate mixture of starch and polyalkane. Molecular probes can be used to give information about the polarity of surfaces. Reichardt's dye for example, a well known indicator of polarity in the liquid phase can also be used on solids.<sup>5</sup> Remarkably, the spectroscopic shift of the dye adsorbed on the starch–polyalkane composites is considerably greater than that observed for ordinary starch or a polyalkane.

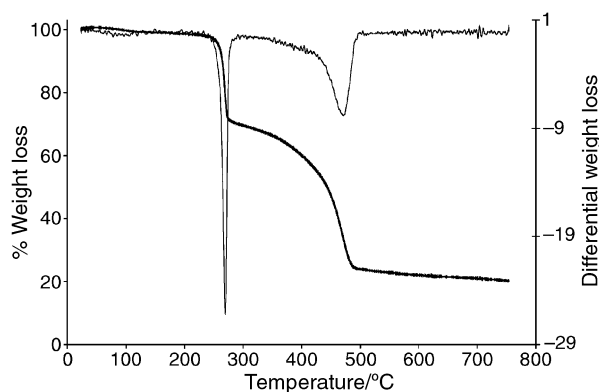


Fig. 2 Thermogravimetric (TG) trace for a typical starch–polyalkane (STPAM) material (10 °C min<sup>-1</sup>; 20 mg in a ceramic pan; flowing N<sub>2</sub> atmosphere).

Table 1 Representative GPC data for polydecane synthesised with (starch–polydecane material, STPDM) and without (polydecane, PD) the presence of potato starch

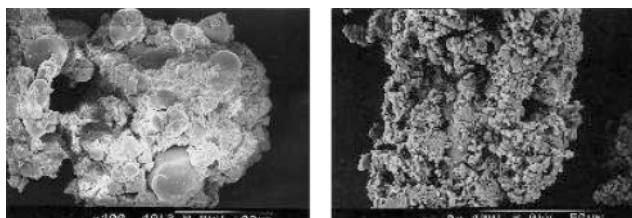
Sample	PD:starch ratio	$\bar{M}_w$	$\bar{M}_n$	Polydispersity
PD 1 <sup>a</sup>	N/A	1980	890	2.2
PD 2 <sup>b</sup>	N/A	3440	1010	3.4
STPDM 4 <sup>a</sup>	2.84:1	1530	620	2.5
STPDM 5 <sup>b</sup>	0.81:1	3120	870	3.6

<sup>a</sup> Sodium metal to 1,10-dibromodecane ratio 2:1. <sup>b</sup> Sodium metal to 1,10-dibromodecane ratio 1:1.

**Table 2** Comparative surface polarities of starch, a typical polyalkane and a typical starch–polyalkane material

Sample	Polyalkane:starch ratio	$\lambda_{\text{max/nm}}$	Sample polarity
Potato starch	N/A	592	0.543
Polyalkane	N/A	630	0.453
Starch–polyalkane material	1.33:1	538	0.693

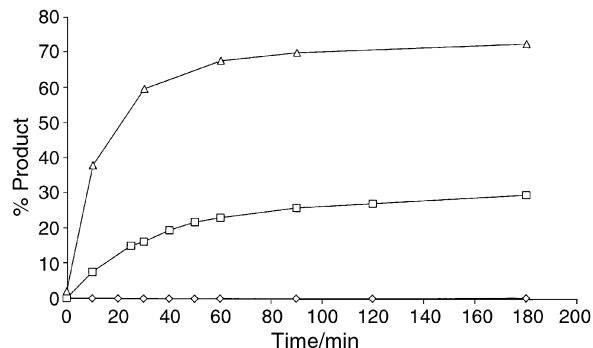
This indicates a surface polarity for the composites that is greater than either of its component parts (Table 2). Scanning electron microscopy may help to explain the origin of this effect (Fig. 3). Potato starch exists as pebble-like granules which vary between 10 and 100  $\mu\text{m}$  in size. The composite materials however, are apparently made up of smaller particles ( $< 5 \mu\text{m}$ ) bound to larger (polyalkane) particles (up to 200  $\mu\text{m}$ ). The higher effective surface area of the starch may also result in a higher available concentration of surface hydroxyl groups leading to greater surface polarity. Despite the relatively high surface polarity as measured by Reichardt's dye, the materials are hydrophobic and float on water unchanged for periods of several weeks before water eventually permeates the structure sufficiently for them to sink.



**Fig. 3** Scanning electron microscopy (SEM) images of a typical starch–polyalkane material (STPAM) before (left) and after (right) removal of sodium colloid by water washing.

Perhaps the most dramatic effect of the enhanced surface activity of the new materials is their capacity for chemical modification with silanes. Stirring the materials with 3-(trimethoxy)aminopropylsilane in refluxing toluene for 24 h before filtration followed by through washing with toluene and then refluxing aqueous ethanol gives solid materials which were dried at 110  $^{\circ}\text{C}$  for 24 h. The measured loadings of aminoalkyl groups of up to 0.6  $\text{mmol g}^{-1}$  (1.4  $\text{mmol g}^{-1}$  based on the starch present) are over 10 $\times$  greater than the maximum loading that can be obtained with potato starch (0.05  $\text{mmol g}^{-1}$ ). It is interesting to calculate that the level of derivatisation of potato starch corresponds to  $< 1\%$  of the total number of hydroxyl groups that are present—an indication of the poor availability of these groups. By increasing the availability of the groups in the new materials the degree of functionalisation has increased to ca. 10%.

The derivatisation values that can be achieved with the new materials are comparable to those that can be obtained on a high surface area porous silica gel.<sup>6</sup> This comparison is further reinforced by measuring the activity of the aminoalkyl-derivatised starch–polyalkane materials in a typically base-catalysed reaction. The reaction chosen was the Knoevenagel reaction, a useful carbon–carbon bond forming reaction that relies on the base-activation of a carbon acid. The rates of the Knoevenagel reaction between ethyl cyanoacetate and cyclohexanone in cyclohexane catalysed by a typical aminopropyl-starch–polyalkane composite material, an aminopropyl-functionalised mechanical mixture of starch and a polyalkane, and aminopropyl-potato starch are compared in Fig. 4. The



**Fig. 4** Reaction profiles for the Knoevenagel condensation reaction of ethyl cyanoacetate and cyclohexanone catalysed by aminopropylsilane on starch ( $\diamond$ ), aminopropylsilane on a typical starch–polyalkane material ( $\Delta$ ) and aminopropylsilane on a mechanical mixture of starch and a typical polyalkane ( $\square$ ).

differences are dramatic. While the ordinary starch based material has almost no activity in the reaction and that based on the starch–polyalkane mechanical mixture is low, the derivatised new material is very active and comparable to their porous silica analogues.<sup>6</sup> Starch that has been treated with sodium metal or sodium hydroxide solution but in the absence of the halocarbon gives a material that has an unchanged FTIR spectrum, thermal analysis and interaction with Reichardt's dye compared to ordinary starch. It does however show a higher capacity for reaction with the aminopropylsilane although the resulting material is only as active in the model reaction as the starch–polyalkane mechanical mixture.

We have extended the synthetic methodology to other  $\alpha,\omega$ -dibromoalkanes. 1,6-Dibromohexane and 1,2-dibromoethane can be used in place of 1,10-dibromodecane with apparently very similar reactions occurring. All of the materials are resistant to water over periods of several weeks, all can be derivatised to high levels with aminoalkylsilanes (0.3–0.6  $\text{mmol g}^{-1}$ ) and all of the resulting derivatised solids are active solid base catalysts in the test reaction. The ability to increase substantially the availability of the starch hydroxyl groups enabling high degrees of derivatisation while rendering the materials water-resistant would seem to be an attractive combination of properties. The method of polymerising starch-intercalated monomers to achieve this may well open the door to a family of new and useful materials based on an inexpensive renewable resource.

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