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Chemical modification of starch and the application of expanded starch and its esters in hot melt adhesive

Zhanrong Zhang,[a] Duncan J. Macquarrie,[a] James H. Clark [a] and Avtar S. Matharu*[a]

Adhesives are of pivotal importance in modern society as over 6 billion pounds of adhesives are used globally per annum. Among these, hot melt adhesives (HMAs) represent the most dynamically developing area, reaching 15 – 21 % of the global volume of production and usage of adhesives. The application of expanded high amylose corn starch (HACS) and its propionate derivatives with differing degrees of substitution (DS) in a formulation comprising polyvinyl alcohol (PVOH) and glycerol to afford 100% biodegradable HMAs is reported. Esterification of expanded starch was conducted to increase the stability and hydrophobicity of starch. The effects of amounts of esterifying reagent and reaction time on DS of starch propionates were investigated. Native starch was expanded (BET surface area, 176 m^2 g^{-1}; DS = 0) and derived propionate esters were studied by ATR-IR, TGA, ^{13}C CPMAS NMR, ^{1}H NMR and titrimetric methods. The HMAs, irrespective of DS, displayed a T_g at approximately 0 ^{o}C, melting (T_{peak}) at approximately 160 ^{o}C and crystallisation (on cooling) at approximately 115 ^{o}C. The adhesive properties (tensile strength) with respect to DS of expanded high amylose corn starch and its propionate esters show a distinct structure-property relationship. Expanded high amylose corn starch (DS = 0) gives the strongest adhesion, outperforming native (non-expanded) starch. The expansion process is beneficial in promoting adhesion which may be linked to the increased availability of hydroxyl moieties promoting better non-covalent interactions and mixing with PVOH and glycerol. Adhesion decreases with increasing DS and the adhesive strength starch propionate with DS in the range 1.46 – 1.82 is comparable to that of native (non-expanded) starch. This is the first reported occurrence of the use of expanded starch and its propionate esters as HMAs.

1. Introduction

Since firstly introduced to the market in the 1950s, hot melt adhesives (HMAs) have become increasingly important and now occupy a special place in the adhesive family, reaching 15-21% of the global volume of production and consumption of adhesives around the world.[1] More importantly, the total average annual growth rate of the consumption of HMAs is 1.5 – 2 times higher than that for other types of adhesives.[1]

HMAs are solid materials at low temperatures (<80 ^{o}C) and can melt to liquid or viscous-flow state at elevated temperatures, in which form they are applied on the surface of substrates. They regain their solid form and cohesive strength during cooling by solidification and/or crystallization, thus bonding two substrates together.[2] Compared with conventional solvent-based adhesives which generally involve evaporation and/or removal of solvents or polymerization to bond substrates together, hot melt adhesives show significant advantages. For example, the elimination of a carrier fluid or solvent in HMA formulations not only overcomes the hazards associated with solvent usage and emissions of volatile organic compounds (VOCs), but also allows for faster production speeds and lower costs. Also, their properties could be relatively easily modified to meet different application requirements. Last but not least, they are clean and easy to handle.[3]

Currently, almost all the base/major polymers for HMAs on the market are primarily derived from petroleum resources, such as ethylene vinyl acetate (EVA), block copolymers of styrene and butadiene (SBS) or isoprene (SIS), polyesters, polyamides, polyurethanes and polyolefins. To this, a variety of tackifiers, plasticizers, waxes, and antioxidants are incorporated to meet special application requirements.[3,4] However, such compositions derive from depleting petroleum resources, and there are concerns over their degradation ability. Concerns of bio-degradation abilities are not only about the adhesive themselves, but also the substrates bonded with them, especially in the paper and pulp industry.[3]

To reduce the environmental impacts associated with substrate recycling and to overcome the shortcomings associated with

traditional petroleum resource based HMAs and meet the global growing demand for HMAs, especially when over 6 billion pounds of adhesives (most derived from petroleum based feedstock) are consumed annually,[5] considerable research has been done to develop natural product based HMAs, such as starch and its derivatives,[6,7] (poly) lactic acid,[8] soy protein isolate,[9] and blends of some of these polymers[10]. Among these, starch has attracted much attention due to its abundant and guaranteed supply, low cost, renewability and biodegradability. In an U.S. patent, Billmers *et al*. reported several HMA formulations comprising selected modified starch esters with ester component of about 2 to 18 carbons with DS varying from around 0.3 to 3.0.[6] No work was reported on expanded starch or its derivatives.

However, natural starches are water/moisture unstable and mechanical properties of starches are poorer than those of synthetic polymers, something which hampers more widespread use of these materials in modern industry. Native starches are generally chemically and/or physically modified to overcome the limitations associated with starch and to improve its performance as an adhesive. Esterification of starch has been intensively studied and employed due to the large number of hydroxyl groups within starch molecules. However, access to these hydroxyl groups is significantly hindered due to the dense packing of polysaccharide chains within starch granules. Harsh pretreatments and chemical modification conditions are required to obtain desired starch derivatives. Expansion of starch has been proposed as an effective method to increase the accessibility of hydroxyl groups by increasing the surface area of native starch (<5 m^2 g^{-1}) to around 180 m^2 g^{-1}.[11,12] After expansion of starch, chemical modification, including esterification could take place under relatively mild conditions. This is of pivotal importance, especially when mild, environmentally friendly process conditions are desired.

Herein, we report our preliminary research on the application of expanded starch and its propionates with various degrees of substitutions as the base / main polymer in 100% biodegradable HMA formulations. For esterification of expanded starch, the effects of amounts of esterifying reagent (propionic anhydride) and reaction time were investigated. The propionates were characterized by titration, Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), solid state ^{13}C CPMAS and liquid ^{1}H NMR spectroscopy. Properties of formulated HMAs were characterized with differential scanning calorimetry (DSC) and FT-IR. Tensile stresses of the HMA bonded aluminium plates were tested.

2. Experimental

2.1 Materials

High amylose corn starch (HACS) under the trade name Hylon® VII with amylose content up to 75% was obtained from National Chemical Starch Company. Propionic anhydride, 4-dimethylaminopyridine (DMAP), polyvinyl alcohol (PVOH) and glycerol were purchased from Sigma Aldrich and used as received without further purification. DMSO-d6 (99.5% atom D) for ^{1}H NMR analysis was also purchased from Sigma Aldrich. Aluminium plates were obtained from the mechanical workshop of the Chemistry Department, the University of York. Commercial LOCTITE hot melt glue was purchased from B&Q, York, UK.

2.2 Expansion of high amylose corn starch (HACS)

The expansion method employed was a modified procedure previously reported.[12] HACS (150 g) was added to distilled water (3 dm^3) in an adapted All American pressure cooker 915. The mixture was stirred vigorously (mechanical stirrer) until all the starch had dispersed before further agitating at 140 °C for 90 minutes to gelatinise the starch. The clear homogeneous gelatinised starch was kept in a fridge at 5 °C for 72 h for retrogradation. Then the water trapped in the aquagel was solvent exchanged with low surface tension solvents, ethanol and toluene, to afford white powdered, expanded starch (143 g, 95.3%) with a surface area (BET) of 176 m^2 g^{-1}.

2.3 Esterification of expanded starch

A series of HACS propionates with various degrees of substitution (DS) were prepared by changing the amounts of esterifying reagent (propionic anhydride) and reaction time. Expanded HACS (10 g, 0.062 mol) was added to toluene (140 ml) in a 250 ml round bottom flask, and to this, varying amounts of propionic anhydride was added. The mixture was heated to 90 °C and stirred for 5 minutes with a magnetic stirrer. Then the catalyst 4-dimethylaminopyridine (DMAP, 0.4 g, 3.3 mmol) was added. The reaction was kept at 90 °C for 6 h while stirring to allow esterification. In one case with propionic anhydride (40g, 0.307 mol), the reaction was kept at 90 °C for 12 hours to further increase degree of substitution. Detailed conditions (amounts of propionic anhydride, reaction time *etc.* are summarized in Table 1 in section 3.1. After that, the mixture was cooled to room temperature (around 25 °C) and ethanol (100 ml) added. The formed precipitate was stirred for 5 minutes, filtered, and washed. This was repeated a further 4 times with ethanol (100 ml), yielding a white powdered product. Then the resulting material was dried in a vacuum oven for 24 h at room temperature under reduced pressure.

2.4 Determination of degree of substitution

Determination of DS of starch esters by titration involved complete basic hydrolysis of ester linkages and back titration of excess alkaline. The titration method employed is based on literature.[12-14] Accurately weighed starch esters (0.5 g) were finely ground and added to 75% ethanol in distilled water (25 ml). The slurry was agitated at 50 °C for 30 minutes. It was then cooled down to room temperature followed by addition of an exact amount of aqueous solution of potassium hydroxide (0.5 N, 20 ml). After that, the solution was stirred for 72 h at room temperature. Then 2-3 drops of indicator (phenolphthalein) was added, and the excess of alkali was back-titrated with hydrochloric acid (0.5 N). Reference samples (original unmodified expanded starch) and triplicate starch ester samples were tested similarly. For starch propionates, the propionic content (% propionyl) was calculated according to the following equation:

$$\% \text{ Propionyl} = \frac{[(V_0 - V_n) \times N \times 0.057 \times 100]}{M}$$

Where 57 is the molar mass of the propionyl group. V_0 is the volume of HCl (0.5 N) used to titrate reference blank samples (unmodified expanded starch); V_n is the volume of HCl (0.5 N) used to titrate starch ester samples, N is the molarity of HCl used, and M is the sample weight. Then the DS could be calculated according to following equation:

$$D.S.=\frac{162\times\%\text{Propionyl}}{[5700-(56\times\%\text{Propionyl})]}$$

Where 162 is the molar mass of the repeating unit of starch, 5700 is the molar mass of propionic group multiplied by 100%. The value 56 is the actual molar mass increase if one propionic group is added to one starch unit. The reported DS values were the mean value of three measurements with error bars.

2.5 Characterization of starch esters

BET surface area measurement (nitrogen adsorption / desorption measurements) of expanded HACS were carried out on a Micromeritics ASAP 2010 volumetric adsorption analyser at 77 K. Prior to analysis, expanded HACS (around 100 mg) was degassed at 65 °C for at least 3 h and mass differences were corrected after the experiment. The resulted data were subjected to proprietary software for BET specific surface area determination. The reported value is mean value of three measurements. **FT-IR** spectra of expanded HACS, starch propionates and formulated HMAs were obtained on a PerkinElmer® Spectrum™ 400 FT-IR/NIR spectrometer (PerkinElmer, Inc., Shelton, CT USA). All the spectra were recorded in attenuated total reflectance (ATR) mode, using a resolution of 2 cm^{-1} and 64 scans. **Thermogravimetric (TGA) analysis** was conducted on a Netzsch STA 409 to study the thermal properties of expanded HACS and starch propionates. The furnace was first evacuated and then back filled with nitrogen three times before testing. Then the samples were heated under a nitrogen flow (100 ml min^{-1}) from 30 °C to 625 °C with a heating rate of 10 °C min^{-1}. **Solid-state ^{13}C CPMAS NMR spectra** of expanded HACS and starch propionates with various D.S. were obtained using a Varian VNMRS 400 spectrometer at 100.56 MHz for ^{13}C referenced to neat tetramethylsilane. **^{1}H NMR spectra** of expanded HACS and starch propionates were recorded on a Jeol ECX-400 NMR spectrometer at 100 MHz for 64 scans at 25 °C. Samples (20 mg) were dissolved in DMSO-d6 (1 ml, 99.5% atom D) by agitating at 80 °C for 1 h to obtain homogeneous clear solutions. **Differential Scanning Calorimetry (DSC)** of HMA formulations were characterized using a TA Q2000 differential scanning calorimeter. The HMAs were accurately weighed (10 mg) into Tzero hermetic aluminum pans, sealed and subjected to a heat-cool-heat-cool cycle from -50 °C to 210 °C at 10 °C min^{-1}.

2.6 Adhesive preparation, characterization and application

Expanded HACS and its propionates were mixed with glycerol and polyvinyl alcohol (PVOH) at the same weight ratio in glass vials and equilibrated in oven at 50 °C for 48 h. The adhesive (50 mg) was applied to the middle of aluminium plates (surface sizes: 50 mm x 50 mm). For each adhesive formulation, four samples were prepared and pressed in a hot press machine. The samples were bonded at 190 °C for 30 seconds under pressure.

2.7 Mechanical strength tests

Tensile strengths of the Al–HMA–Al bonds were measured using an Instron 3367 Dual Column System universal testing machine fitted with 3000 N capacity load cell with a crosshead speed of 5 mm min^{-1}. Obtained results were normalized to effective tensile stress by calculating the effective bonding area using Adobe Photoshop CS6 (Figure 10). The results reported

are the mean value of four measurements for each HMA formulation with error bars.

3. Results and discussion

3.1 Modification of starch

HACS was gelatinised in hot water and retrograded at 5 °C for 3 days. After that the formed matrix was solvent exchanged with less polar solvents (ethanol and toluene) to yield white powders (expanded HACS), which were characterized by much higher surface area (176 m^2 g^{-1}) compared with that of non-expanded HACS (<5 m^2 g^{-1}).[11, 12] The increased surface area of HACS could facilitate chemical modifications to take place at relatively milder conditions, as the accessibility of hydroxyl groups within starch molecules were dramatically increased.

In this work, we prepared a series of starch propionates with various degree of substitution (DS) by changing the amount of esterifying reagent (propionic anhydride) and reaction time using 4-dimethylaminopyridine (DMAP) as catalyst. The reaction conditions and DS of yielded starch propionates are summarized in Table 1. For 6 h reactions, with increasing amounts of propionic anhydride, the DS of starch propionates significantly increased from around 0.38 (5 g, 0.038 mol, propionic anhydride) to 1.91 (17.5 g, 0.134 mol, propionic anhydride). Thereafter, the reaction equilibrium was reached, DS increased from around 1.91 (17.5 g, 0.134 mol, propionic anhydride) just to 2.05 (40 g, 0.307 mol, propionic anhydride). To further increase the DS, one more experiment was conducted with propionic anhydride (40 g, 0.307 mol) for 12 h. By doubling reaction time, DS increased from 2.05 (6 h) to 2.54 (12 h).

Table 1 Esterification reaction conditions and DS of resulted starch propionates[a]

Propionic anhydride (g)	Propionic anhydride (mol)	Expanded HACS[b] (mol)	Reaction time (h)	DS
5	0.038	0.062	6	0.38
7.5	0.058	0.062	6	0.78
10	0.077	0.062	6	1.00
12.5	0.096	0.062	6	1.46
15	0.115	0.062	6	1.82
17.5	0.134	0.062	6	1.91
20	0.154	0.062	6	1.95
30	0.231	0.062	6	1.99
40	0.307	0.062	6	2.05
40	0.307	0.062	12	2.54

[a] For all the reactions, DMAP (0.4 g, 3.3 mmol) was added as catalyst
[b] Expanded HACS with surface area 176 m^2 g^{-1} (10 g, 0.062 mol) was used as base polymer for esterification

For reference, the esterification of non-expanded HACS was conducted with propionic anhydride (10 g, 0.077mol) and DMAP (0.4 g, 3.3 mmol) for 6 h. The DS of resulted starch propionate is around 0.02, which is dramatically lower than that of the one obtained with expanded starch under the same reaction conditions (1.00).

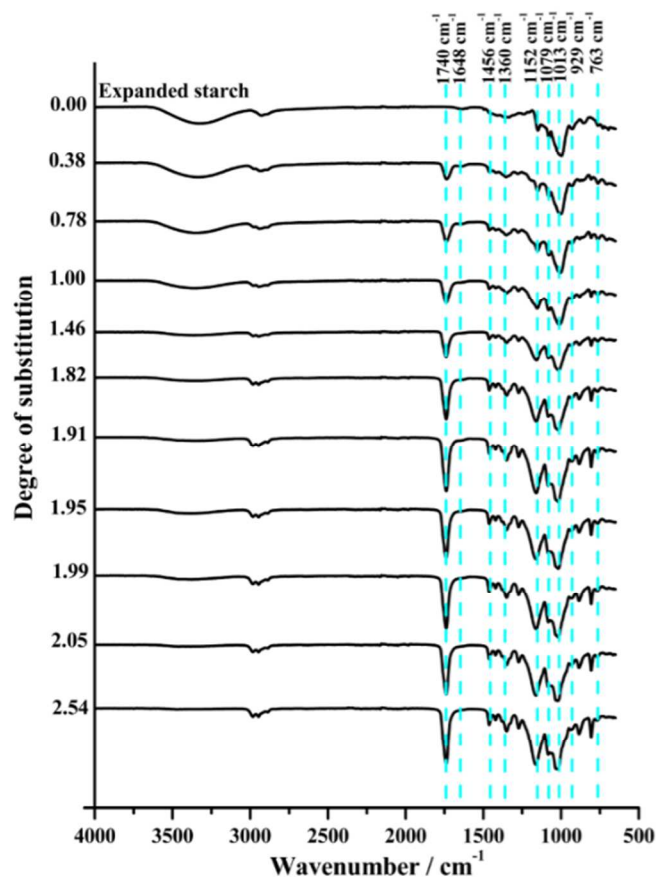### 3.2 FT-IR analysis of expanded HACS and its propionates

Fig. 1 FT-IR spectra of expanded HACS and its propionates

Table 2 Major bands assignment

Wavenumber (cm^{-1})	Assignment
3600 - 3000	O-H stretching vibration
2960 - 2850	C-H vibrations
1745	C=O stretching vibration
1648	Tightly bound water
1456	CH_3 asymmetric bending vibration
1360	CH deformation vibration
1152	ester C-O-C asymmetric stretching
1079, 1013	C-O vibration (anhydroglucose ring)
929, 763	Anhydroglucose ring stretching vibration

FT-IR spectra of expanded HACS and its propionates are presented in Figure 1. The key band changes with increasing DS were highlighted in Figure 1 with dashed lines, and the assignment of these bands are summarized in Table 2. Esterification is confirmed by the carbonyl stretching vibration band centred at 1745 cm^{-1}. Intensity of this band increases and that of hydroxyl O-H stretching vibration band (3000 cm^{-1} to 3600 cm^{-1}) decreases with increasing DS, suggesting the conversion of hydroxyl groups to ester groups. This is further evidenced by the band at 1152 cm^{-1} due to the ester C-O-C asymmetric stretching vibration, the intensity of which also increases with DS. The O-H stretching vibration band drifts to higher wavenumbers with increasing of DS, indicating a reduction in inter- and intra- molecular hydrogen bonding and increasing of hydrophobicity with DS. Increasing of hydrophobicity with DS is also indicated by the weak but slightly broad band at 1648 cm^{-1} which is associated with

tightly bound water. This band gradually diminishes up until a DS of 2.0 when it is no longer apparent. Furthermore, the esterification of expanded starch also imparts obvious changes in the fingerprint region. For example, new bands appeared at 1456 cm^{-1} and 1360 cm^{-1} and the intensities of these bands also increase with DS. These two bands are assigned to methyl asymmetric bending vibration and C-H deformation vibration, respectively.

In the spectrum of expanded HACS, some characteristic absorption bands for starch could be identified, such as bands centred at 1079 cm^{-1}, 1013 cm^{-1} which are assigned to C-O bond stretching.[15,16] Also, there are several additional characteristic absorption bands due to the entire anhydroglucose ring stretching vibrations, such as bands at 929 cm^{-1} and 763 cm^{-1}.[15] All these bands also exist in the spectra of starch propionates.
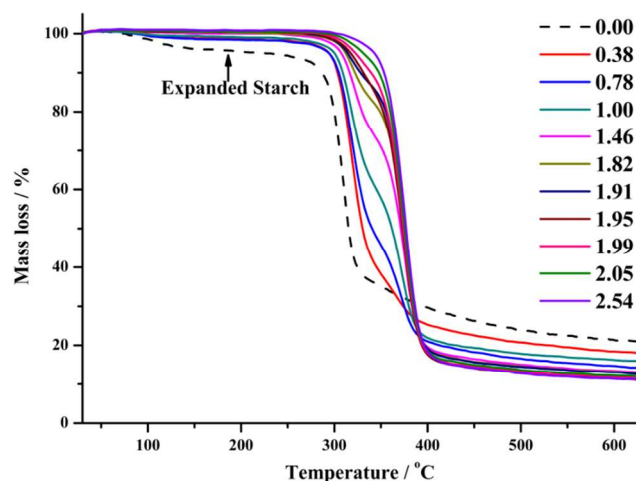
3.3 Thermogravimetric analysis

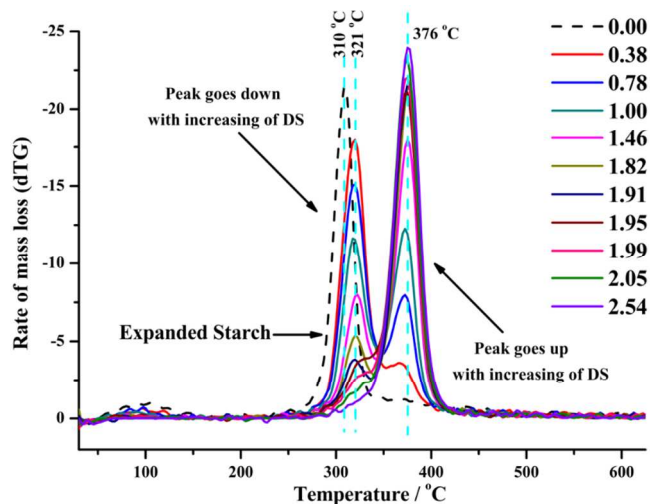**Fig. 2** TGA traces for expanded HACS and its propionates

Fig. 3 dTG traces for expanded HACS and its propionates

Thermal properties of expanded HACS and its propionates were studied with TGA. The TG and dTG traces of these materials are shown in Figure 2 and 3, respectively. It is obvious that esterification considerably affects the thermal decomposition of starch. The first mass loss step for expanded HACS starts immediately as heat begins and finishes around 150 °C with around 5% mass loss, which is mainly attributed to the evaporation of water moisture. For starch propionates, the weight loss in this temperature range is much smaller than that of expanded HACS and decreases with increasing of DS. For example, the starch propionate (DS, 0.38) lost around 2.5% between 30 °C – 150 °C, while the starch propionate (DS, 2.54) shows almost no weight loss in this region. This results from increased hydrophobicity of starch propionates and is consistent with FT-IR analysis.

Decomposition of expanded HACS starts at approximately 260 °C and is a one step process with peak decomposition temperature (dTG peak) at 310 °C. It is noteworthy that there is a clear shift towards higher decomposition temperatures with increasing of DS. For instance, the major peak decomposition temperature of starch propionate with DS 2.54 (376 °C) is much higher than that of expanded HACS, indicating the thermal stability increased with DS. With the increasing of DS, more hydroxyl groups on anhydroglucose units were converted to ester groups. As the thermal decomposition of starch is primarily due to inter- and/or intra-molecular dehydration reactions with water as a main product, the dehydration reactions became increasingly difficult and slow with increasing of DS.[17, 18] This effect finally results in higher thermal stabilities of the derived starch propionates.

Unlike expanded HACS, thermal decomposition of starch propionates mainly consists of two steps. From the dTG traces (Figure 3), it is obvious that the 1st and 2nd decomposition step of starch propionates show almost the same peak decomposition temperatures: around 321 °C for the 1st step and 376 °C for the 2nd decomposition step. Also, from the TG traces (Figure 2), with increasing of DS, mass loss in the 1st decomposition step decreased from approximately 60% (DS, 0.38) to 3.6% (DS, 2.54). On the contrary, mass loss in the 2nd decomposition step increased from around 20% (DS, 0.38) to 82% (DS, 2.54). This phenomenon probably indicates that inter- or intra-molecular dehydration reactions primarily occur during the 1st decomposition step. As the amounts of available hydroxyl groups reduce with increasing DS, mass loss of the 1st decomposition step decreases, while that of the 2nd decomposition step increases. For both expanded HACS and its propionates, approximately 15 ± 5 % wt. remains after heating to 600 °C.

3.4 NMR characterization

Both expanded HACS and its propionates were characterized by solid-state ^{13}C CPMAS NMR spectroscopy and liquid ^{1}H NMR spectroscopy in DMSO-d6. Figure 4 illustrates the ^{13}C NMR spectra of expanded HACS (Figure 4A) and starch propionate with DS of 1.00 (Figure 4B). From the ^{13}C NMR spectrum of expanded HACS (Figure 4A), the corresponding signals for carbon atoms in the starch molecule are assigned in accordance with literature.[19-21] The signals between 106-92 ppm is attributed to the C-1 of the anhydroglucose units. Signals for C-4 and C-6 are observed at 82 and 62 ppm, respectively. The large signal ranging from 70 – 76 ppm is attributed to C-2, C-3 and C-5 of the anhydroglucose units.

From the ^{13}C NMR spectrum of starch propionate with DS of 1.00 (Figure 4B), the characteristic peak for the carbonyl carbon is observed at 174 ppm. Also, the characteristic signals for the methylene and methyl group are observed at approximately 28 and 9.8 ppm, respectively. These results are in good consistency with the FT-IR analysis and further provide evidence for the esterification of starch.
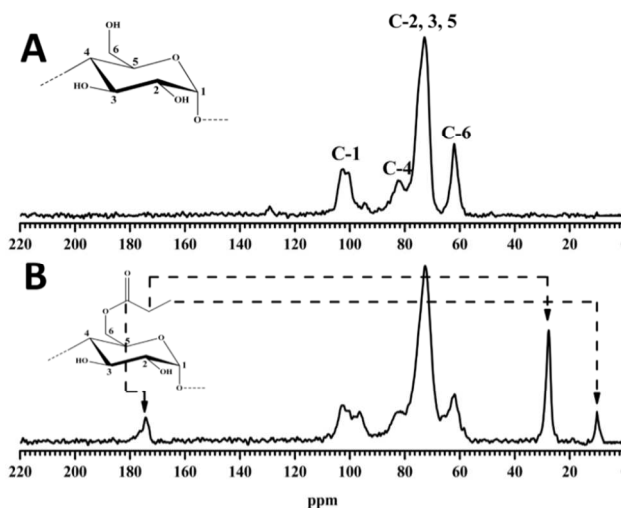
Fig. 4 Solid-state ^{13}C MAS NMR spectra of (A) expanded HACS and (B) starch propionate (DS, 1.00). The repeating unit shown in B is with the ester group connected to the most probable C position (C-6).[18]
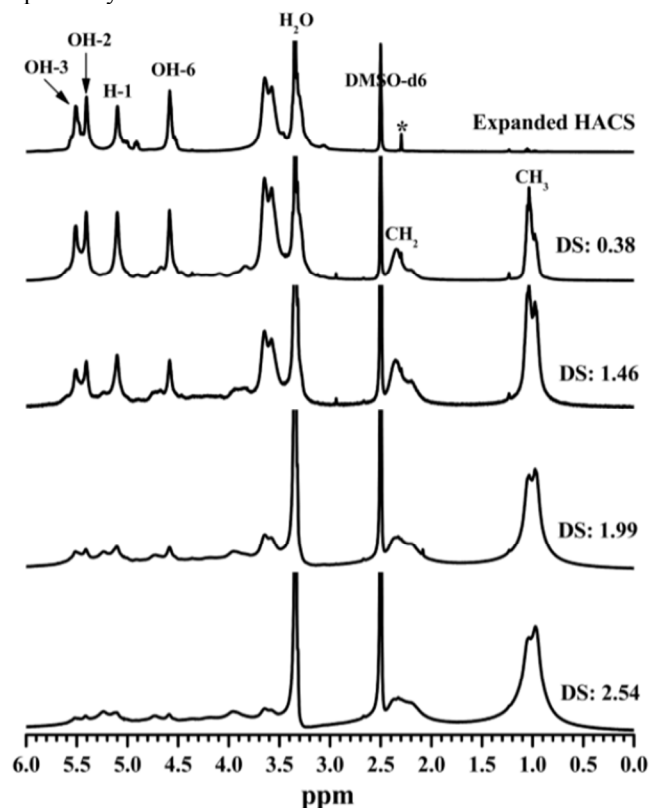
The ^{1}H NMR spectra of expanded HACS and starch propionates with DS (0.38, 1.46, 1.99 and 2.54) in DMSO-d6 are illustrated in Figure 5. The broad, strong signals ranging from 3.2 to 4.0 ppm are assigned to starch chain protons (H-2, 3, 4, 5, 6), but is mainly attributed to residual water (centred at 3.30 ppm), because of the hygroscopic nature of starch and DMSO-d6.[22]

According to Chi *et al.*, we assigned the resonance signals of the three hydroxyl groups on C-2, 3, 6 (OH-2, 3, 6) at 5.40, 5.50 and 4.59 ppm, respectively.[15] Also, resonance signal of the anomeric hydrogen atom (H-1), which corresponding to the internal α-1, 4 linkages, is observed at 5.10 ppm.[15, 22]

During the esterification process, the propionate moieties are gradually introduced into starch molecules. From the spectra of starch propionates, the characteristic resonance bands of anhydroglucose units are still visible, even though the resolution of spectra decreased with increasing of the DS, which is probably due to the subsequent increased viscosity of the NMR solution. However, subtle changes of the resonance of protons on anhydroglucose units can be observed compared with that of expanded HACS, which is resulted from slightly changed chemical environments.

With increasing DS, it is obvious that the resonance bands of OH-2, 3, 6 (centred at 5.40, 5.50, 4.59 ppm) gradually diminish, referenced to the intensity of the anomeric hydrogen (H-1) band at 5.10 ppm. In all the spectra of starch propionates, the resonance signals for CH_2 and CH_3 groups of propionate

moieties are found between 2.0 to 2.45 ppm and 0.6 to 1.3 ppm, respectively.

Fig. 5 ^{1}H NMR spectra of expanded HACS and starch propionates (DS: 0.38, 1.46, 1.99 and 2.54) in DMSO-d6

* Possible artefact

3.5 Characterization of HMA formulations

HACS, expanded HACS and its propionates with various D.S. were incorporated into 100% biodegradable HMA formulations by mixing with glycerol and polyvinyl alcohol (PVOH) at the same weight ratio (this formulation was previously reported in an U.S. patent[6]). Thus obtained materials were characterized with DSC using a heat-cool-heat-cool method to mimic the real industrial application of HMAs. Before being subjected to DSC, the HMA formulations were equilibrated in oven at 50 °C for 24 h. As the materials were mixed with spatula in glass vials, the 2nd cycle of the heat-cool-heat-cool DSC traces is of more interest.
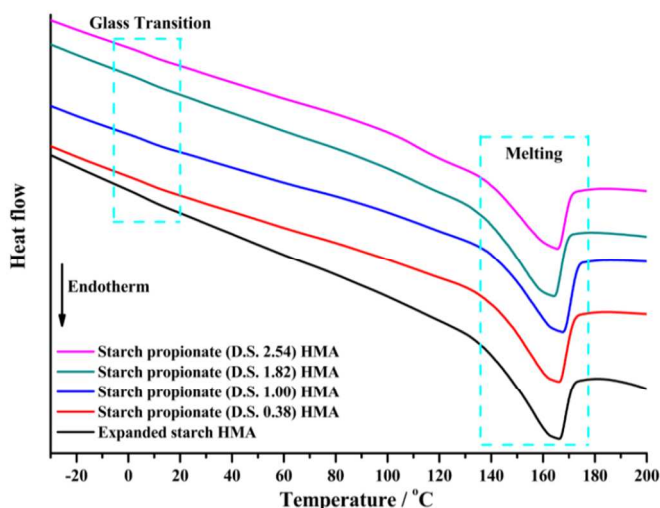

Fig. 6 DSC traces of the 2nd heating run of expanded HACS and starch propionates (DS: 0.38; 1.00; 1.82; 2.54) based HMAs

Figure 6 and 7 shows the 2nd heating and cooling traces of expanded HACS and its propionates with DS of 0.38, 1.00, 1.82 and 2.54 based HMA formulations, respectively. The glass transition of the HMAs (approximately between -5 °C to 5 °C) is observed in both heating and cooling traces. From the heating traces shown in Figure 6, slightly endothermic transitions of the HMAs could be observed around 115 °C; however, a significant large endothermic peak is shown between 135 °C to 175 °C for all the traces, corresponding to the major melting of HMA formulations. From the cooling traces (Figure 7), all the samples show an exothermic crystallization peak between 130 °C to 90 °C. All these transitions are characteristics for HMA formulations. As the major endothermic melting transition for all the HMA formulations ends around 175 °C, a higher temperature (190 °C) is chosen for the application of such HMAs during the adhesion experiments.
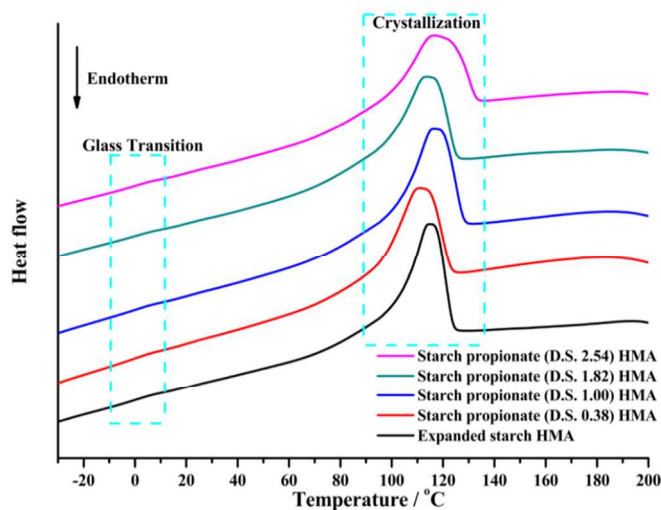
Fig. 7 DSC traces of the 2nd cooling run of expanded HACS and starch propionates (DS: 0.38; 1.00; 1.82; 2.54) based HMAs
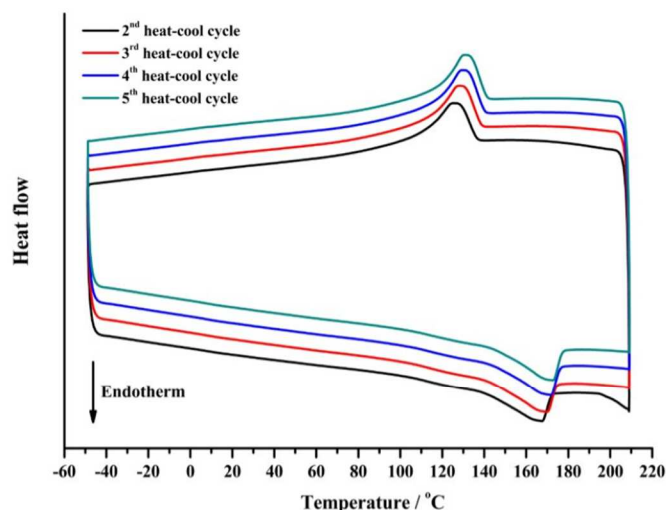
Fig. 8 DSC traces of the 2nd to 5th heat-cool cycle of starch propionate (DS, 1.00) based HMA formulation

In order to study the stability/reusability of the expanded HACS and its propionates based HMA formulations, the starch propionate (DS, 1.00) based HMA was characterized in DSC for more heat-cool cycles using the same method stated in the experimental section. The traces are shown in Figure 8. Even though the peak temperatures of melting and crystallization shift slightly due to changes of the environment within sealed Tzero aluminium pans, characteristics of glass transitions, melting and crystallization transitions basically remain even after 5 heat-cool cycles, indicating high stability of the formulated HMAs.

Stability of formulated HMAs was further proved by comparing the FT-IR spectra of the base material, formulated HMA before and after DSC measurement. Figure 9 shows the FT-IR spectra of expanded HACS, and expanded HACS based HMA before and after DSC measurement (Figure 9A) and that of starch propionate (DS, 1.82), starch propionate (DS, 1.82) based HMA before and after DSC measurement (Figure 9B). It is obvious that all the characteristic absorption bands of both expanded HACS and its propionate based HMA formulations are still remaining almost the same before and after heating and cooling in DSC, suggesting no thermal degradation and any non-reversible reactions occurred during heating and cooling.
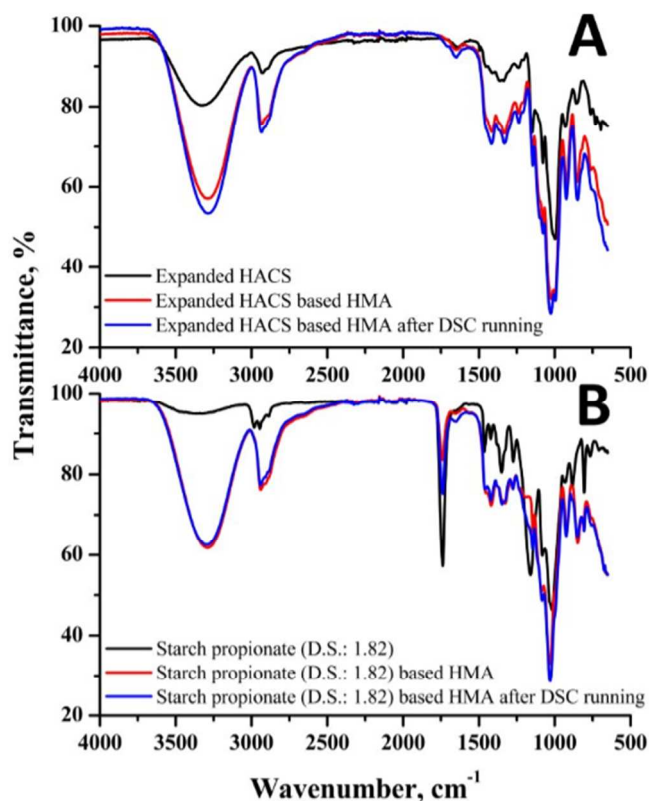
Fig. 9 FT-IR spectra of (A) expanded HACS, expanded HACS based HMA before and after DSC measurement (B) starch propionate (DS, 1.82), starch propionate (DS, 1.82) based HMA before and after DSC measurement

3.6 Tensile stress tests

Non-expanded HACS, expanded HACS and derived starch propionates with various D.S. based HMA formulations (50 mg) were applied to bond Al plates and the tensile strengths of the Al-HMA-Al bond were measured following the procedure described in experimental section. Figure 10 shows a typical failure pattern of the Al plates adhered with formulated HMAs. All the other adhered specimens show a similar failure pattern and broken adhesively, suggesting the cohesive strengths of the HMA formulations are higher than adhesive strengths between HMAs and Al plates.
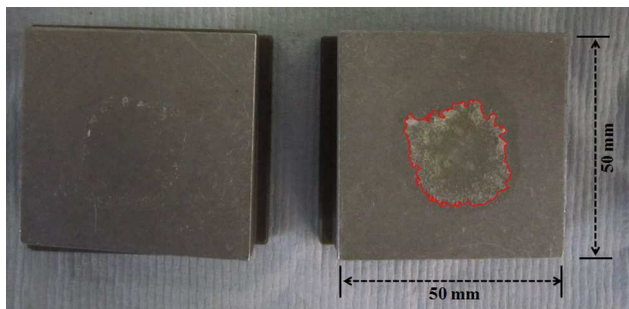
Fig. 10 A typical failure pattern of formulated HMA bonded Al plates (sample shown is expanded HACS based HMA cured Al plates)

The measured tensile strengths were normalized to effective tensile stress by calculating the surface area of effective bonding area (circled by red lines, Figure 10). Normalized tensile stress of the HMA formulations with error bars are shown in Figure 11. The reported values are average values of four specimens adhered with each kind of HMA formulation (50 mg).
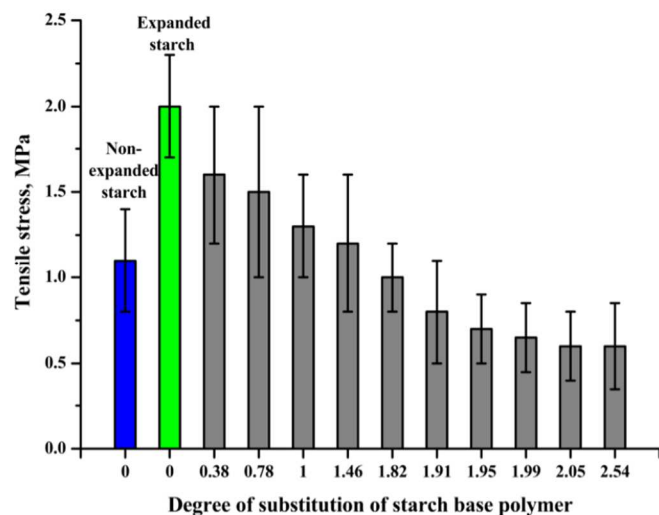
Figure 11 Normalized tensile stress of non-expanded HACS, expanded HACS and its starch propionates based HMA formulations (50 mg) bonded Al plates

It is significant that the tensile stress of expanded HACS based HMA (2.0 MPa) is dramatically higher than that of HMA based on non-expanded HACS (1.1 MPa). This effect might result from the significant increased surface area of expanded HACS and subsequent improved accessibility of hydroxyl groups within starch molecule. This effect probably leads to higher extent of interaction (non-covalent or cross-linking) between starch, glycerol and PVOH, resulting in significant increase of tensile stress. For the starch propionates based HMA formulations, tensile stress decreased with increasing of DS. When DS increased from 0.38 to 2.54, the tensile stress of the starch propionate based HMAs dropped from 1.6 MPa to 0.6 MPa. As more and more hydroxyl groups were converted to ester groups during esterification, the amounts of available "free" hydroxyl groups decreased. As a result, the crosslinking effect between the three HMA components deteriorated, leading to decreased tensile stress. Also, as hydrophobicity of starch propionates increases with DS, starch propionates with higher DS might sacrifice their abilities to be compatible with glycerol and PVOH, which will also leads to decreased tensile stress. However, tensile stress of starch propionates (DS <1.5) based HMA formulations are still higher than that of non-expanded HACS based HMA formulation, despite lower than that of the one based on expanded HACS.

For reference, the tensile stress of commercial ethylene vinyl acetate (EVA) based LOCTITE hot melt glue (around 6 MPa,

purchased from B&Q, York, UK) was tested under the same conditions. Due to the nature of our HMA formulations and the fact that they were not engineered, the maximum tensile stress of our HMAs is around 2.3 MPa obtained with expanded HACS based HMA. However, within this work we demonstrated the great potential of application of expanded starch in HMA formulations, which to our knowledge, has never been reported previously.

Conclusions

Following the expansion (gelatinisation, retrogradation, solvent exchange) procedure, surface area of HACS was dramatically increased to around 176 m^2 g^{-1} compared with that of non-expanded HACS (<5 m^2 g^{-1}). Thus the accessibility of the hydroxyl groups in starch molecules was significantly improved, allowing chemical modification, including esterification, to take place at relatively milder conditions. To take advantage of this effect, esterification of expanded HACS was conducted with propionic anhydride (esterifying reagent) and DMAP (catalyst) in toluene at various reaction conditions. The results revealed that DS of derived starch propionates increases with increasing of the amounts of propionic anhydride used. For instance, DS increased almost linearly from around 0.38 (with 5 g, 0.038 mol, propionic anhydride) to 1.95 (with 20 g, 0.154 mol, propionic anhydride) for 6 h reaction. After that, the esterification reaction reaches equilibrium; D.S. remains around 2 even if the amounts of propionic anhydride increased to 40 g (0.307 mol). D.S. also increases with reaction time, for example, D.S. increased from 2.05 (6 h) to 2.54 (12 h) with 40 g (0.307 mol) propionic anhydride. The derived starch propionates with various DS were characterized with FT-IR, TGA, solid-state ^{13}C CPMAS and liquid ^{1}H NMR spectroscopy.

Thus obtained expanded HACS and starch propionates were incorporated into 100% biodegradable HMA formulations by mixing them with glycerol and PVOH at the same weight ratio. The developed HMA formulations were characterized with Differential Scanning Calorimetry (DSC) using a heat-cool-heat-cool method. The glass transition generally occurs between -5 °C to 5 °C and the major melting step occurs between 135 °C to 175 °C. During cooling, the HMAs recrystallized between 130 °C to 90 °C.

The adhesion properties of HMAs were studied by applying each HMA formulation (50 mg) in the middle of two Al plates (surface area: 50 mm x 50 mm), and specimens were adhered in a hot press machine for 30 seconds at 190 °C. Tensile stress of the Al-HMA-Al bond was normalized. The tensile stress of expanded HACS based HMA (2.0 MPa) is dramatically higher than that of the one based on non-expanded HACS (1.1 MPa). For those based on starch propionates, tensile stress decreases with increasing of DS of the base polymer. However, tensile stresses of starch propionates (DS <1.5) based HMAs are still higher than that of the one based on non-expanded HACS, even though lower than that of expanded HACS based HMA.

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[a] Green Chemistry Centre of Excellence, Department of Chemistry, University of York. York, England. YO10 5DD.

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Development of expanded starch and its propionate esters as hot melt adhesives for metal-metal bonding is reported.