Potato starch stabilized synthetic latexes
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CHAPTER 6

The use of polyvinyl acetate latexes stabilized by extruded octenyl succinate (waxy) potato starch as wood adhesives
Abstract
Modified starch can be used as protective colloid in free radical polymerization of polyvinyl acetate. The resultinglatexes are potential alternatives for commercial available wood adhesives stabilized with synthetic additives. The wood bonding strength (DIN EN 204 D2) was determined and showed that latexes based on extruded octenyl succinylated (waxy) potato starch are suitable wood adhesives. The wood bonding strengths of the latexes are 2 to 3 times larger than the target 8 MPa value. The use of extruded (octenyl succinylated) waxy potato starch as protective colloid offers flexibility in latex viscosity (1,000 to beyond 10,000 mPa·s) with only limited impact on the wood bonding strength. Mowilith DHS S1 appears to be a proper benchmark for the starch stabilized latexes but this product has a considerably higher latex viscosity (50,000 mPa·s) and wood bonding strength (33 MPa). However, there are indications that the starch based latexes can be tuned to match the commercial benchmark more closely by modifications in the polymerization process.

Introduction
Current available synthetic wood adhesives emerged at the beginning of the 20th century and became good alternatives for natural ones (animal, casein, starch, cellulose, etc), of which animal glue being first reported as far as the ancient Egyptian pharaohs times [1,2]. This transition from natural raw materials to synthetic varieties started with the development of phenolic and urea-formaldehyde adhesives (1920) and was followed by the discovery of polychloroprene adhesives after a few decades (1940). Vinyl polymer based emulsion (i.e. latexes) adhesives were invented in the fifties together those based on polyurethane. Another important category in adhesives is a hot melt and this type of product finds its origin in the sixties [1-4].

Wood is a heterogeneous material, mainly consisting of fibres aligned in one direction. The material is sensitive for changes in climate conditions, in particular as function of temperature and humidity [1,2]. Climate differences between the manufacturing site and customer countries are therefore usually kept small in order to minimize unnecessary deformation of the final product (e.g. cupboard) during use. The adhesive bonding of wood involves mechanical interlocking (i.e. filling of irregular voids), physical interaction and chemical bonding. Among all possible interaction forces between wood and adhesive, physical ones (e.g. hydrogen bonds and Van der Waals forces) are frequently mentioned as the most relevant ones [1-4]. A durable structural bond requires penetration of the adhesive between several (two to six) layers of fibres and penetration of the fibre cells on a molecular scale [1-4]. Mechanical interlocking is also crucial in the process because the adhesive must also penetrate beyond the damaged wood fibres and fill up voids between the two wood surfaces. Wood adhesives require therefore a good interaction with the substrate (adhesion) and need to have a high internal strength (cohesion) as well [1-4].

A standard test (DIN EN 204) has been designed for the evaluation of wood adhesives for non-structural application and divides the adhesives into durability classes D1 to D4 [5]. The division is based on the dry and wet strengths of bond-lines measured under specified conditions after various conditioning treatments. The adhesives that meet this standard are suitable for the use in furniture and interior structures (e.g. panels, doors, windows, stairs.
etc...) made of wood or derived timber products. Polyvinyl acetate (pVAc) based adhesives are usually classified as D1 (for use in dry and temperate climates including indoor furniture) or D2 (for use in relative damp indoor, e.g. kitchen furniture). However, some special formulations can even meet D3 (application in damp indoor or outdoor environment) and D4 (water resistant) [5-6]. This set of characteristics and wide applicability spectrum renders these adhesives particularly attractive for further developments.

Spray guns, rollers and trowels are frequently used in woodworking and each application technique requires a different level of viscosity. Viscosities in the range of 300 - 1 000 mPa·s are suitable for spray application whilst rollers require values in the range of several thousands mPa·s [1,2]. A target value of at least 20 000 mPa·s is required if a trowel is used for application [1,2]. Shear thinning behaviour with a reversible nature (pseudoplasticity or thixotropy) is desired because this improves the workability significantly [7]. This type of adhesive cannot only be added to a substrate more easily but the chance of dripping is reduced as well [7]. Other important application related parameters are pot life, open time, wet tack, curing time and bond strength [1,2]. Additives (plasticizers, fillers, solvents, thickeners and tackifiers) are abundantly available to optimize these parameters [1-4]. A drawback in the use of post-additions is the additional labor and costs that this fine tuning entails, as well as the environment contamination. [8,9]

A typical wood adhesive contains 1 to 15 wt % synthetic additives (e.g. emulsifiers, protective colloids, anti-foam, etc) with respect to the amount of polymer [10]. These additives can be replaced with granular starch, with or without derivatization, where the latter is dissolved and modified just before, or during, the actual polymerization [11,12]. However, the dissolution of granular starch does not only involve a considerable peak viscosity but there is a risk of partial dissolved starch granules as well. Polymerization procedures can be designed to overcome these problems, but there are also starch treatments that can avoid these risks a priori. Extrusion is an example of an energy efficient starch modification which results in a starch product without the presence of starch granules and a viscosity peak during dissolution. Moreover, the amount of water needed during modification is much less than its enzymatic conversion counterpart, for example. Extrusion based processes are therefore frequently favored from a green chemistry and engineering point of view [13,14]. However, the level of modification introduced by extrusion is usually not enough to prevent the amylose part from retrogradation. Therefore, the use of waxy starch is recommended when starch is used without considerable (bio)chemical treatments. The waxy potato (WP) starch is preferred because this type of starch does not only contain the highest amount of phosphate groups, which provides additional stabilization after dissolution, but the granules disintegrate easier after gelatinization as well [15,16].

Latexes stabilized with enzymatically converted WP starch fall in the viscosity range of 700 to 2300 mPa·s while the use of extruded regular potato (RP) and WP starch, with and without an octenyl succinylation, results in latexes with viscosities ranging from 1 000 (without derivatization) and beyond 10 000 mPa·s (with derivatization) [17,18]. Both types of latexes are potential wood adhesives and not yet evaluated in literature as such. Modification by extrusion is more energy efficient than enzymatic conversion and the corresponding products are therefore selected for this investigation. The latex stabilized with extruded WP starch
(WO0) is selected together with the latex stabilized with the octenyl succinic anhydride (OSA) modified counterpart with a maximum degree of substitution (DS_{max}) of 0.02 (WO2). This choice was based on earlier studies showing a latex recovery exceeding 98 wt % and generating a final latex viscosity range of 1 000 to 10 000 mPa·s. The RP starch counterpart (RO2) of WO2 is added in order to garner insight into the effect of using this type of starch as raw material as well. Latexes stabilized with WO0, WO2 and RO2 were prepared in triplicate (a-c) and this allows detecting differences between batches and the effect of mixing them. Method DIN EN 204 D2 was selected for investigating the wood bonding characteristics of the three selected latexes. Commercial available pVAc adhesives Mowilith DHS S1 (DHS) and Mowilith LDL 2555 W (LDL) were used as a benchmark.

**Experimental Materials**

PVAc latexes stabilized with WO0 (Extruded WP) WO2 (Extruded WP, DS_{max} OSA 0.02) and RO2 (Extruded RP, DS_{max} OSA 0.02) [18]. Commercial available wood adhesives Mowilith DHS S1 (DHS) and Mowilith LDL 2555 W (LDL) were selected as benchmarks for DIN EN 204 D2 and D3 respectively.

**Characterization**

Viscosity, pH and dry matter were determined with the help of a Brookfield DV-II+ (20 RPM), WTW pH320 and Mettler Toledo PM100/LP16 (80°C) respectively. Ethanal and residual vinyl acetate in the latexes were determined with a Perkin Elmer gas chromatograph equipped with a headspace sampling device, a Poraplot Q fused silica column (25 m x 0.32 mm) gas and a flame ionization detector detector. The gas chromatography measurement was performed on water diluted dispersion (10 wt %).

About 2 ml of the diluted dispersion was centrifuged at 13 000 relative centrifugal force for 10 minutes and the supernatant was mixed 1:1 with 5 mM NaOH. This mixture was used to quantify the anion composition with a Dionex DX50 equipped with an ATC-1 ion trap, two Ionpac columns (AS11-2 mm and AG11-2 mm) and an electrochemical detector. The separation of the different anions was achieved with a gradient of sodium hydroxide. The obtained results were corrected for differences in dry matter content of the latexes evaluated. The dry matter content was used to calculate the amount of water in 100 g of latex and the obtained value was multiplied with the determined concentration of acetate, sulfate and thiosulfate ions.

Particle size distributions (PSD) were obtained with a Sympatec laser diffractor equipped with a Quixel wet dispenser and a Helos laser diffraction sensor (range: 0.13-32.5 μm). Fraunhofer theory based calculations are used and the obtained particle size distributions are ISO 13320 compliant.

Glass transition temperatures (T_g) were derived from total heat flow and reversing heat flow curves determined with a modulated differential scanning calorimeter (mDSC) from TA Instruments (Q1000; 1°C/min; amplitude: 0.5°C; period: 60 s; large volume stainless steel pans; 20-50 mg dispersion). DIN EN 204 D2 procedures were performed with wood samples made of maple, which were cold pressed with 0.7-0.8 MPa for one hour after application.
of 180 g adhesive per m² (contact area 625 mm²). A climate room was used to maintain the required 23°C and 50% relative humidity during the storage of the samples for 7 days. The samples were dried for 7 days (23°C and 50% relative humidity), soaked in water (3 hours; 23°C) and dried again at 23°C and 50% relative humidity for 7 days before the bonding strength was measured. An Instron 4301 (IX) was used to determine the bonding strength at 50 mm/min. 7 wood pieces were used for each latex.

Results
The wood bonding strength of the nine selected starch stabilized latexes were determined in 7 fold. Only averages and two times the standard deviation (σ) are displayed in Table 1 for brevity. The latex viscosity, thermal transitions and the volume mean diameter (VMD) of the particle size distribution (PSD) are displayed in this table as well.

<table>
<thead>
<tr>
<th>Code</th>
<th>Latex characteristics</th>
<th>Wood test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Viscosity (mPa·s)</td>
<td>Tg_{onset} (°C)</td>
</tr>
<tr>
<td>WO2a</td>
<td>9950</td>
<td>8.5</td>
</tr>
<tr>
<td>WO2b</td>
<td>10253</td>
<td>9.7</td>
</tr>
<tr>
<td>WO2c</td>
<td>10796</td>
<td>9.2</td>
</tr>
<tr>
<td>RO2a</td>
<td>2950</td>
<td>9.3</td>
</tr>
<tr>
<td>RO2b</td>
<td>3000</td>
<td>8.5</td>
</tr>
<tr>
<td>RO2c</td>
<td>2700</td>
<td>8.8</td>
</tr>
<tr>
<td>WO0a</td>
<td>1240</td>
<td>10.4</td>
</tr>
<tr>
<td>WO0b</td>
<td>1300</td>
<td>10.7</td>
</tr>
<tr>
<td>WO0c</td>
<td>1500</td>
<td>10.3</td>
</tr>
</tbody>
</table>

All average bonding strengths exceed the DIN EN 204 D2 criterion of 8 MPa and the average values of WO2_{a-c}, RO2_{a-c} and WO0_{a-c} are 20.8, 22.0 and 18.3 MPa respectively. The difference between WO2_{a-c} and RO2_{a-c} was small and probably even negligible from an application point of view. The use OSA starch leads to a pronounced better wood bonding strength which might be correlated to the VMD, Tg, latex viscosity or combinations thereof. In this respect, WO0 shows a pronounced difference with respect to RO2 and WO2. Additional research is required to explain the origin of this difference in wood bonding strength. Latex viscosity and hydrophobicity of the starch derivative used are probably the two most interesting responses to investigate because they influence the level of penetration into the wood sample and the susceptibility of the adhesive layer to water.

The bonding strength as function of the measuring sequence between the batches of WO2_{a-c}, RO2_{a-c} and WO0_{a-c} (samples: a = 1-7, b = 8-14 & c =15-21) and the observed variation occurs in an essentially random way (Figure 1).
Figure 1: Wood bonding strength according DIN EN 204 D2 for WO2 a-c, RO2 a-c, WO0 a-c and D2 criterion. Sample sets 1-7, 8-14 and 9-21 represent batch a, b and c respectively.

However, the Anderson-Darling goodness of fit calculations (Minitab 16) reveal p-values of <0.005, 0.027 and 0.011 for WO2 a-c, RO2 a-c and WO0 a-c respectively. This is considerably lower than the commonly used a = 0.05 criterion and the sample sets are therefore not normally distributed [19]. The origin of this non-normal distribution behaviour is probably related to the inevitable heterogeneity of the wood samples used. The fact that the DIN EN 204 determination requires an average of 20 wood samples is also in agreement with this line of thinking. Figure 1 also shows some exceptional deviations from the general trend which might be considered as outliers. Box plot calculations (Minitab 16) show that the lowest value of sample set WO2 a-c and RO2 a-c meet the criterion for outliers and can be removed, if needed, from the sample set (Figure 2).

The observed behavior can be conveniently compared with that of commercial formulations based on similar components, with the exception of the protective colloid. DHS is a plasticizer-free aqueous latex suitable for adhesion of wood, paper, packaging, floor, wall, ceiling, leather and textiles based on pVAc and protected by polyvinyl alcohol. LDL is also based on pVAc and can be used in the same area of application except for leather and textiles. LDL has an enhanced resistance to moisture and heat due to the presence of N-methylolacrylamide units which introduce a degree of cross-linking in the final adhesive layer [20]. This difference in composition makes this product very interesting to investigate even if it is classified as a DIN EN204 D3 type of adhesive (contrary to the D2 target here). WO2, RO2 and WO0 were physical mixtures of the three corresponding batches and the mixtures were tested as well as DHS and LDL according DIN EN204 D2 with 7 wood samples each. The results are given in Table 2 together with the latex viscosity, thermal transitions and the VMD of the PSD.
The use of polyvinyl acetate latexes stabilized by extruded octenyl succinate (waxy) potato starch as wood adhesives

Figure 2: Box plot calculations for sample sets WO2 a-c, RO2 a-c and WO0 a-c. Outliers are represented by an asterix.

Table 2: Product characteristics: Viscosity, thermal transitions, VMD and wood bonding strength.

<table>
<thead>
<tr>
<th>Code</th>
<th>Type</th>
<th>Viscosity (mPa·s)</th>
<th>T_g,onset (°C)</th>
<th>T_g,inflection (°C)</th>
<th>T_g,endset (°C)</th>
<th>ΔT_g (°C)</th>
<th>VMD (mm)</th>
<th>Average (MPa)</th>
<th>2*σ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHS</td>
<td>DIN EN204 D2</td>
<td>49600</td>
<td>12.9</td>
<td>15.4</td>
<td>17.5</td>
<td>4.7</td>
<td>3.1</td>
<td>33.3</td>
<td>2.3</td>
</tr>
<tr>
<td>LDL</td>
<td>DIN EN204 D3</td>
<td>12500</td>
<td>4.1</td>
<td>7.4</td>
<td>10.0</td>
<td>5.9</td>
<td>3.1</td>
<td>39.0</td>
<td>6.2</td>
</tr>
<tr>
<td>WO2</td>
<td>DIN EN204 D2</td>
<td>10380</td>
<td>8.8</td>
<td>11.6</td>
<td>14.6</td>
<td>5.8</td>
<td>4.4</td>
<td>20.4</td>
<td>6.1</td>
</tr>
<tr>
<td>RO2</td>
<td>DIN EN204 D2</td>
<td>3020</td>
<td>8.8</td>
<td>11.0</td>
<td>13.3</td>
<td>4.5</td>
<td>5.3</td>
<td>24.4</td>
<td>3.9</td>
</tr>
<tr>
<td>WO0</td>
<td>DIN EN204 D2</td>
<td>1280</td>
<td>10.7</td>
<td>13.3</td>
<td>15.3</td>
<td>4.6</td>
<td>1.5</td>
<td>17.2</td>
<td>6.8</td>
</tr>
</tbody>
</table>

It is important to bear in mind that the T_g is determined on latex without being dried and that it is based on the reversing heat flow curve. The obtained values differ therefore considerably from the usually reported T_g and this is confirmed by the results of the two commercial available products. The determined values of DHS and LDL with our method (T_g,inflection) are 15.4 and 7.4 °C whilst their reported T_g are 38 and 26 °C, respectively. The results of the applied method appear to coincide more with the minimum film formation temperature of these products, i.e. 14 and 4 °C, respectively. A correlation is plausible because the minimum film formation temperature and the selected T_g,inflection determination both capture phase transitions of hydrated latex particles. However, this assumption could not be verified in literature.

DHS exceeds the starch based products in wood bond strength and differs considerably in viscosity and T_g,inflection. LDL only differs considerably in T_g,inflection but its average bonding strength exceeded the one of DHS. The strength of LDL was close to the integrity strength of the wood samples used because two samples exhibited wood failure and the remaining samples displayed considerable interface adhesive-substrate failure (wood fibres tear). The DHS samples also showed some distinct wood fibres tear but less pronounced and accompanied with domains at which adhesive (cohesive) failure occurred. The starch based varieties showed some wood fibres tear also but adhesive failure was dominating. A Box plot
shows that only the set of WO2 contains an outlier and that all test results exceed the DIN EN204 D2 criterion of 8 MPa (Figure 3).

Figure 3: Box plot calculations for sample sets DHS, LDL, WO2, RO2 and WO0. Outliers are represented by an asterix.

There was a distinct difference between the two benchmark latexes and the starch stabilized counterparts. The superior bonding characteristic of LDL finds its origin in the fact that it is able to crosslink whereas the other four products lack this feature. The differences found between DHS and the starch based counterparts were probably related to viscosity level, PSD, nature of protective colloid used, pVAc structure and combinations thereof. The deviating behaviour of WO0 with respect to WO2 and RO2 can probably be attributed to its lower viscosity and smaller VMD. These two features make a higher degree of penetration in the wood structure possible and this process leaves less adhesive available for the actual bond formation between the two substrates. The observed differences in particle size between DHS, WO2 and RO2 were not only modest in VMD but in their PSD also (Figure 4).

Figure 4: PSD’s of WO2, RO2 and DHS. Error bars represents 2 times the σ of a measurement in five fold (DHS only)
As a consequence it is difficult to speculate that the degree of polydispersity alone explains the observed differences in bonding strength. Similarly, the difference in viscosity (and thus in level of penetration of the adhesive into the wood) cannot solely explain the observed differences between DHS, WO2 and RO2 either. A proportional relation between latex viscosity and bonding strength could be an explanation for DHS (~50 000 mPa·s; 33 MPa) with respect to either WO2 (~10 000 mPa·s; 20 MPa) or RO2 (~3 000 mPa·s; 24 MPa). However, the results of WO2 and RO2 display an inverse proportional relationship between both responses. On the other hand, the measured $T_g^{infection}$ indicated a structural difference in pVAc between DHS (15 °C; 33 MPa) and both starch based varieties (12-11 °C; 20-24 MPa). This seems to correlate with the bonding strength. A lower $T_g$ is associated with a difference in composition or branching of the polymer and indications of the occurrence of the latter were already found at the polymerization stage. The reaction temperature of WO0 was considerably lower than its WO2 and RO2 counterparts and resulted in a pronounced difference in $T_g^{infection}$ [18]. The level of branching was inversely proportional to the $T_g$ and DHS should have a lower degree of branching from this line of reasoning. A lower degree of branching should increase the cohesive strength of the adhesive and this was actually the case. The wood bond strengths of WO2 and RO2 were limited due to adhesive (cohesive) failure whilst the failure of DHS was dominated by wood fibre tear (a sign of a higher cohesive strength).

Specific details about the polymerization procedure of DHS and LDL are not known and several product responses (i.e. dry matter, hydrogen ion, ethanol, VAM, acetate, sulfate and thiosulfate content) are therefore determined. The results are displayed in Table 3 together with the results of the three selected starch stabilized counterparts.

Table 3: Product composition: dry matter, pH, ethanol, VAM, acetate, sulfate and thiosulfate.

<table>
<thead>
<tr>
<th>Code</th>
<th>Type</th>
<th>Dry matter (mg/g)</th>
<th>Acetate (mmol)</th>
<th>Sulfate (mmol)</th>
<th>Thiosulfate (mmol)</th>
<th>pH</th>
<th>Ethanal (mg/g)</th>
<th>VAM (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DHS</td>
<td>DIN EN204 D2</td>
<td>492</td>
<td>139</td>
<td>52.4</td>
<td>n.d.</td>
<td>4.6</td>
<td>n.d.</td>
<td>0.2</td>
</tr>
<tr>
<td>LDL</td>
<td>DIN EN204 D3</td>
<td>494</td>
<td>199</td>
<td>5.9</td>
<td>n.d.</td>
<td>3.1</td>
<td>n.d.</td>
<td>0.1</td>
</tr>
<tr>
<td>WO2</td>
<td>DIN EN204 D2</td>
<td>521</td>
<td>324</td>
<td>30.0</td>
<td>2.42</td>
<td>5.3</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>RO2</td>
<td>DIN EN204 D2</td>
<td>514</td>
<td>330</td>
<td>30.3</td>
<td>2.46</td>
<td>5.3</td>
<td>3.1</td>
<td>1.6</td>
</tr>
<tr>
<td>WO0</td>
<td>DIN EN204 D2</td>
<td>514</td>
<td>279</td>
<td>31.2</td>
<td>2.74</td>
<td>5.3</td>
<td>3.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

n.d. = not detected

WO2, RO2 and WO0 contained similar amounts of free acetate and the level found was significantly higher than in DHS and LDL. Acetate is partly generated during the anion determination because the sample treatment involves a pH at which saponification of pVAc can occur rapidly. The water phase will still contain some water soluble pVAc after the centrifugation step and this will be totally converted to acetate after the NaOH addition in the sample treatment. The actual amount of water soluble pVAc in the latexes is not known and additional research is therefore required if the actual origin of the acetate ions needs to be known. WO2, RO2 and WO0 were prepared in the same way according the responses sulfate, thiosulfate and pH whilst DHS and LDL show pronounced differences between each
other and the three starch stabilized latexes. A persulfate initiation system is still plausible according the sulfate content of DHS (entry 1) but the absence of thiosulfate is indicative for the use of an initiation system in combination with a different reducing agent (or none at all). The use of persulfate in the preparation process of LDL is highly unlikely based on the sulfate content of this latex (entry 2).

The preparation process of DHS and LDL appeared to be much more efficient with respect to residual ethanal and VAM than their starch based counterparts. However, these two commercial products might have had a post-treatment to achieve this level of VAM conversion but there is no evidence found that such a post-treatment is actually applied. The amount of volatile organic components in the latex is bound to stringent regulations and there are different techniques (e.g. vacuum or steam stripping) available to meet these regulations properly [21]. The presence of volatile organic components in the latex might have a side effect due to the fact it can be stored in the particles and act as a plasticizer [22]. However, the amounts of volatile organic components found in the starch based latexes are very low and a considerable impact on the Tg, for example, is therefore not expected.

From the considerations above, it is clear that a full and comprehensive comparison of the adhesive performance between the prepared formulations and the two commercial ones is still possible at a qualitative level. A more detailed (i.e. molecular) comparison would be needed in order to fully relate the observed differences with the structure of the corresponding latexes.

Conclusions

The evaluated potato starch stabilized latexes can be marked as DIN EN204 D2 wood adhesives because they have wood bonding strengths in the range of 17 – 24 MPa whilst only 8 MPa is required for this classification. An octenyl succinylation of the starch used did not only increase the latex viscosity but improved the wood bonding strength as well. The latex viscosity of octenyl succinylated waxy potato based products was 3 to 4 times higher than its regular potato counterpart.

Mowilith DHS S1 appears to be a proper benchmark for the starch derivative protected latexes because a product composition evaluation points to a main difference in the use of protective colloid only. The wood bonding strength of this product was 33 MPa and its viscosity of 50 000 mPa·s was also considerably higher than the 17-24 MPa and the 1 280 – 12 500 mPa·s for the evaluated starch based counterparts. However, there were indications of structural differences in the polyvinyl acetate present in Mowilith DHS S1 and the starch stabilized varieties which might be reduced significantly by a change in polymerization conditions. A change in level of octenyl succinate derivatization or degree of extrusion induced degradation might also offer opportunities to reduce, or even close, the gap between the starch protected latexes and formulations based on Mowilith DHS S1.

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Abbreviations

DIN EN 204: Wood adhesive test for non-structural application.
- D2: For use in relative damp indoor (e.g. kitchen furniture).
- D3: Application in damp indoor or outdoor environment.

pVAc: Polyvinyl acetate.
WP: Waxy potato starch.
RP: Regular potato starch.
OSA: Octenyl succinic anhydride.

DS\textsubscript{max}: Maximum degree of substitution based on the amount of reagent added.

WO0: Extruded WP starch.
WO2: Extruded WP starch with OSA a derivatization of 0.02 (DS\textsubscript{max}).
RO2: Extruded RP starch with OSA a derivatization of 0.02 (DS\textsubscript{max}).

XXX\textsubscript{a-c}: Triplicate.
DHS: Mowilith DHS S1
LDL: Mowilith LDL 2555 W
PSD: Particle size distribution.

T\textsubscript{g}: Glass transition temperature.

mDSC: Modulated Differential Calorimeter.

σ: Standard deviation.

VMD: Volume Mean Diameter.

T\textsubscript{g, onset}: Onset point based glass transition temperature.
T\textsubscript{g, inflection}: Inflection point based glass transition temperature.
T\textsubscript{g, endset}: Endset point based glass transition temperature.

\Delta T\textsubscript{g}: T\textsubscript{g, endset} - T\textsubscript{g, onset}.
References


