HIGH SOLID CONTENT TACKIFIER DISPERSIONS: LESS WATER IS MORE SUSTAINABLE

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1. Introduction

Adhesives are abundant in today's society, come in many forms, and can be found in many applications: in glues, tapes, labels, band aids, and so on. They perform a critical task in holding things together either permanent or temporarily, and as such the adhesives need to be tailor-made depending on the application. For example, duct tape needs to resist high amounts of shear stress, whereas band aids should be removed with relative ease.

In formulations, adhesives can be categorized in their appearance. Hotmelt adhesives are solid(-like) materials that can flow at elevated temperatures and can bond materials after cooling down. Solvent based adhesives can be readily coated at room temperature, and after subsequent removal of the solvent, an adhesive layer is formed on the coated surface. Curable adhesives are a mix of a (pre-)polymer and free monomers that can for an adhesive after initiating polymerization with an external energy source, such as heat or UV radiation. Another adhesives category is the waterborne adhesives. Advantages of this type of adhesives is that it is easy to coat due to its wet form and film formation relies on the evaporation of water instead of the environmentally unfriendly organic solvents in solventborne adhesives.

Adhesives often are polymers with a low glass transition temperature T_g. Additives can be used to optimize the performance of adhesive polymers. An example is a tackifier. Tackifiers can promote peel strength and initial tack of adhesives and like the polymer adhesive, tackifiers are available in different forms including aqueous dispersions.

A common type of tackifiers are rosin based tackifiers. Rosin is a natural raw material that, after some modification, can be tailored to specific adhesives applications. As such, dispersions of rosin resins are available on the market. Commonly, these dispersions have a solid content of approximately 55%. This is significantly lower than polymer adhesives, which typically have a solid content of up to 70%. Hence, from a sustainability perspective, despite the high bio-renewable content of rosin resins, there is much to be gained by increasing the solid content of rosin tackifier dispersions: reduced water consumption, reduced water transport, faster coating line-speeds, and reduced energy consumption for water evaporation on coaters.

In this paper, we present an overview of the process of making high solid content rosin tackifier dispersions and a comparison of the physical properties and adhesive properties of these dispersions with their lower solid content counterparts (1).

2. Rosin based tackifiers

2.1 Rosin

Rosin is a natural resin that can be obtained in several ways, but predominantly, two different sources are available. When resin is tapped from a pine tree, gum rosin is obtained from subsequent distillation of the exudent. Tall oil rosin is obtained by distillation of tall oil from wood chips, a side stream from wood pulp in the paper industry, which is then extracted with an alkaline solution. This leaves the rosin as a salt. Adding an acid (commonly sulphuric acid) will convert the soap back into rosin acids. Rosin acid is a mixture of C_{20} monocarboxylic diterpene acids of which abietic acid (Figure 1) is the most common form (2).

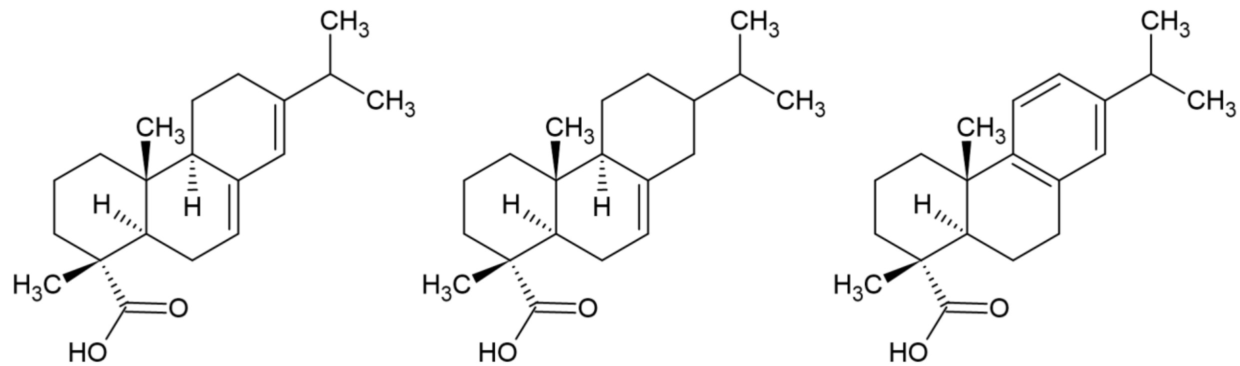


Figure 1. From left to right: abietic acid, dihydro abietic acid, dehydro abietic acid. The latter two isomers can be obtained by disproportionation of abietic acid.

2.2 Rosin resin

Although rosin itself can promote tackification in an adhesive, the material needs to be modified to make it chemically stable, i.e. resistant to oxidation, and to optimize its physical properties. By modifying rosin, a rosin resin is formed. One way to do this is, for example, by disproportionation, forming isomeric mixtures of rosin acid by removing or adding conjugated double bonds. This results in a high acid value resin due to the presence of the free carboxylic acid group. In Figure 1 this is exemplified with the disproportionation products of abietic acid (3).

Another way to modify rosin is by esterification with a polyol such as glycerol, shown in Figure 2, or pentaerythritol. Because glycerol is a triol, the end product can vary as mono-, di-, and tri-ester will be formed in a ratio that depends on reactant ratio and reaction time. This composition affects the Softening Point (SP) and polarity of the resulting resin. Because the rosin carboxylic acid reacts with the polyol, these resin types have a low acid value (3).

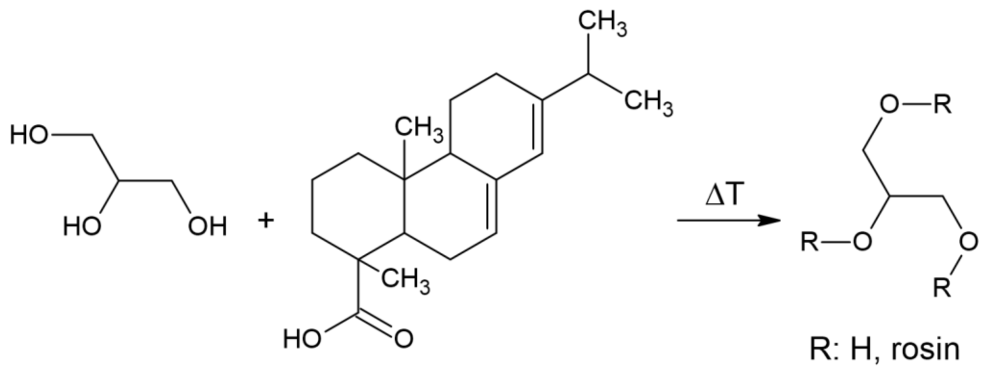


Figure 2. Rosin-glycerol ester reaction

2.3 Rosin resin dispersions

Once a rosin resin is made, it can be used as a tackifier in hotmelt adhesives. For waterborne adhesives, the resin needs to be dispersed in water. This is schematically shown in Figure 3. The resin has to be heated to well above its softening point. Surfactants, are added to the resin and, under stirring, water is added to initially form a water-in-resin emulsion. After reaching the inversion point, this will turn into a resin in water emulsion, where the uniform resin particles are stabilized by the surfactants.

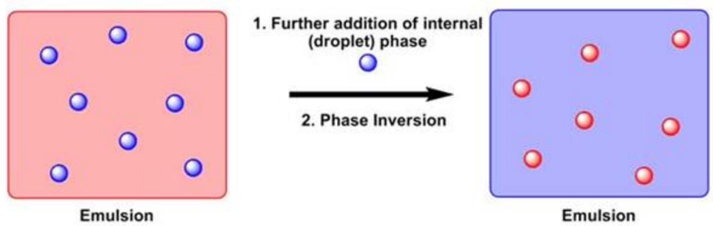


Figure 3. Formation of resin dispersion through phase inversion.

3. High solid content tackifier dispersions

The high solid content tackifier dispersions differ from their traditional counterparts in two ways. One, the surfactant package is optimized to provide a lower viscosity, thereby providing room to increase the solid content. Two, instead of a monomodal particle size distribution, the high solids dispersions have bimodal distributions, allowing a more optimal packing of the particles similar to polymer dispersions.

3.1 Method

Rosin tackifier dispersions are made with a proprietary continuous dispersion installation. Particle size distributions of these dispersions can be changed by adjusting the process parameters, which allows production of both monomodal and bimodal particle size distributions. In Figure 4, an example of a bimodal distribution of a high solid content tackifier dispersion is shown.

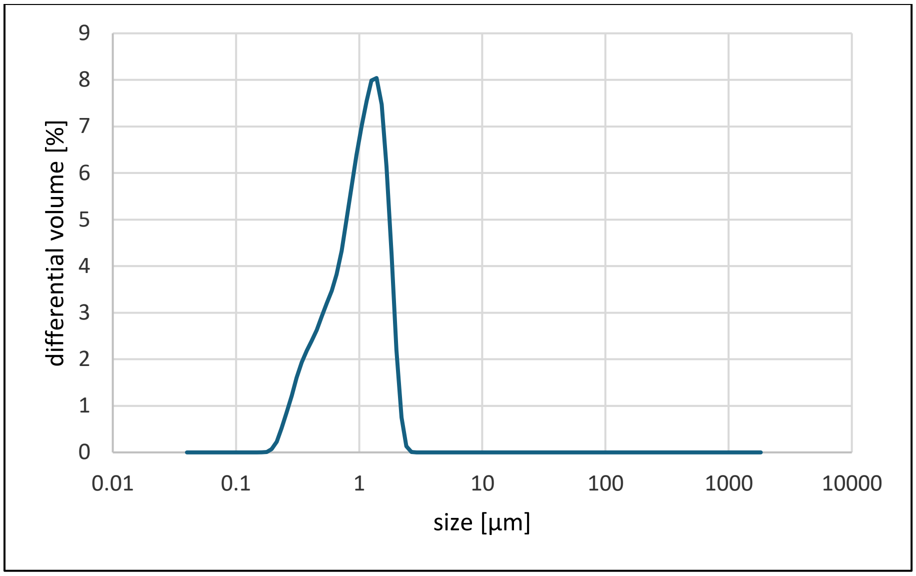
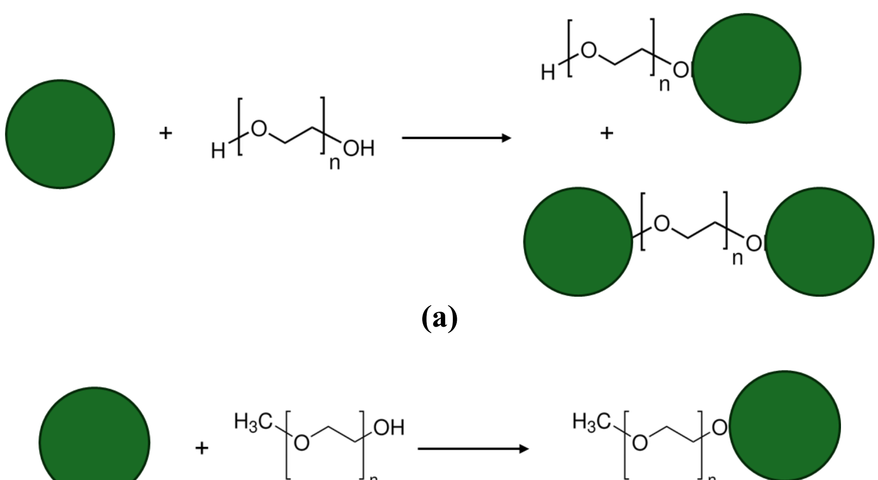


Figure 4. Example of a typical particle size distribution of a high solid content tackifier dispersion. The bimodal distribution shows two overlapping peaks. The smaller particles are therefore visible as a 'shoulder'.

The bimodal distribution provides good colloidal and steric stability of the dispersions due to the higher particle packing density.

The surfactant used for stabilizing particles is non-ionic. The resin soluble part of the surfactant is a rosin ester and has therefore good compatibility with the discontinuous resin phase. The water soluble part is a polyethene glycol (PEG) type polymer that is grafted onto the rosin ester. The composition of this surfactant is typically a mixture of predominantly diblock surfactant and some triblock surfactant, schematically shown in Figure 5. The latter structure causes bridging between particles so that dispersion viscosity increases. For high solid content dispersions, formation this triblock structure during surfactant synthesis should be avoided. Hence, an alkyl-ether capped PEG such as methoxy polyethylene glycol methyl ether (mPEG) is used with only one reactive hydroxyl group.



(a)

(b)

Figure 5. (a) Grafting of rosin ester (green sphere) with PEG forming a mixture of diblock and triblock surfactants. **(b)** Grafting of rosin ester with mPEG forming only diblock surfactant.

3.2 Physical and mechanical properties

Physical and mechanical properties of tackifier dispersions are important for handling and processing. Poor mechanical properties, for example, can lead to filter clogging during loading and unloading. The mechanical stability of dispersions can be semi-qualitatively tested using a Hamilton-Beach blender (Figure 6a), or by loop-filtration to simulate tank loading or unloading (Figure 6b).

Figure 6. Left: Hamilton-Beach blender. Right: Loop-filtration test set-up.

Another important parameter is foaming. Foaming can cause air-pockets in coatings and should therefore be kept to a minimum. Foam levels can be assessed by vigorous stirring of a set volume of dispersion and comparing foam volume with the total volume after stirring.

In Tables 1 and 2 the physical and mechanical properties of the rosin ester and rosin acid tackifiers are listed, respectively.

Table 1. Physical and mechanical properties of rosin ester dispersions at normal (55%) and high (66%) solid content.

Dispersion solid content [%]	Viscosity [mPa.s / cP]	Particle Size D50 / D90 [µm]	Mechanical Stability Hamilton-Beach [min.]	Mechanical Stability Loop Filtration [min.]	Foam [%]
55	300	0.4 / 1.0	> 20	8	40
66	600	0.9 / 1.5	> 20	13	20

Table 2. Physical and mechanical properties of rosin acid dispersions at normal (55%) and high (66%) solid content.

Dispersion solid content [%]	Viscosity [mPa.s / cP]	Particle Size D50 / D90 [µm]	Mechanical Stability Hamilton-Beach [min.]	Mechanical Stability Loop Filtration [min.]	Foam [%]
55	300	0.4 / 1.0	6 - 7	4	65
66	600	0.9 / 1.5	> 20	3	25

Mechanical stability of the rosin ester dispersion is not affected by increasing the solid content of the dispersion. The rosin acid dispersion, however, appears to give contradictive numbers. Whereas the Hamilton-Beach test shows that the mechanical stability of the high solid content dispersion is significantly better, the loop filtration test is similar to the traditional dispersion. Of course, the two tests are very different in the way destabilization is measured. Early formation of sieve residue in the loop filtration test may be observed due to clogging of the filter, but this effect could be overlooked in the Hamilton-Beach test.

Foaming behavior of both the high solid content rosin ester and rosin acid dispersions appear to improve, most significantly for the rosin acid dispersion. This can be attributed due to the slight change in the composition of the non-ionic surfactant for the rosin ester dispersions, and a change from an anionic to a non-ionic surfactant for the rosin acid dispersions.

4. Adhesive properties

Adhesive mixes were prepared with 25% tackifier in adhesive polymer (dry/dry). Wetting agent (0.5%; DDOSS) was added and the mixture is left to mix overnight on a roller mixer. Silicone release liner was coated with this mix (18 gsm) and the adhesive coating was transferred to plain paper (80 gsm). After applying fresh release liner to the coated paper, the resulting laminate was kept at 23 ± 2 ℃ (73.4 ± 1.6 °F) and 50 ± 5 %RH for 24 hours. The laminate was subsequently cut into strips 7 * 1 inch.

Analyses of adhesive properties were done following the methods described by FINAT. ‘Loop’ tack analysis, 90° peel adhesion, and resistance to shear were done according to methods FTM9, FTM2, and FTM8, respectively (4).

4.1 Adhesives with rosin ester tackifier resin

To compare adhesive properties of a high solid content rosin ester tackifier dispersion with a ‘normal’ grade adhesive properties ‘loop’ tack, peel strength, and cohesion were analyzed. Results are shown in Figures 7 to 9.

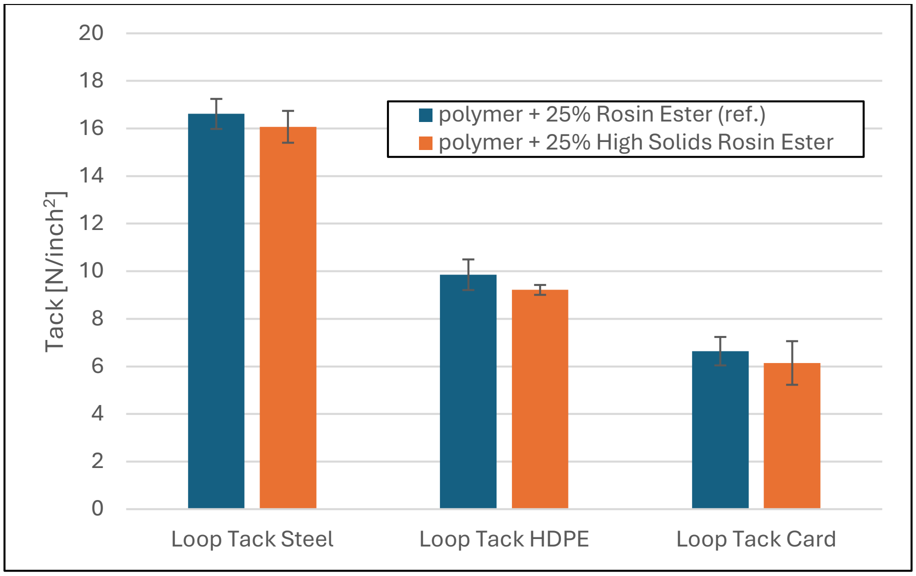


Figure 7. Tack values of adhesive labels using a high solid content and a regular solid content rosin ester tackifier dispersion.

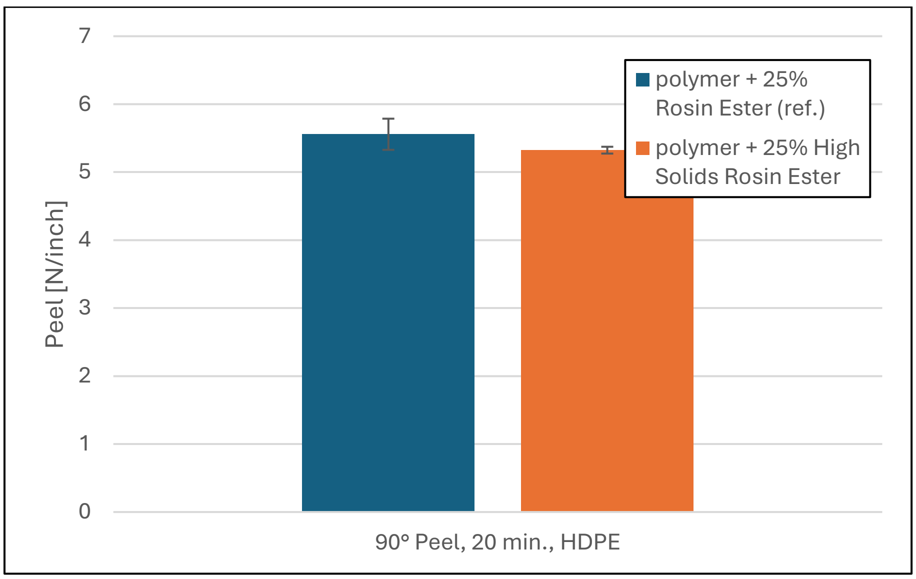


Figure 8. Peel strength at 90° pull off angle and 20 minute dwell time on HDPE using a high solid content and a regular solid content rosin ester tackifier dispersion.

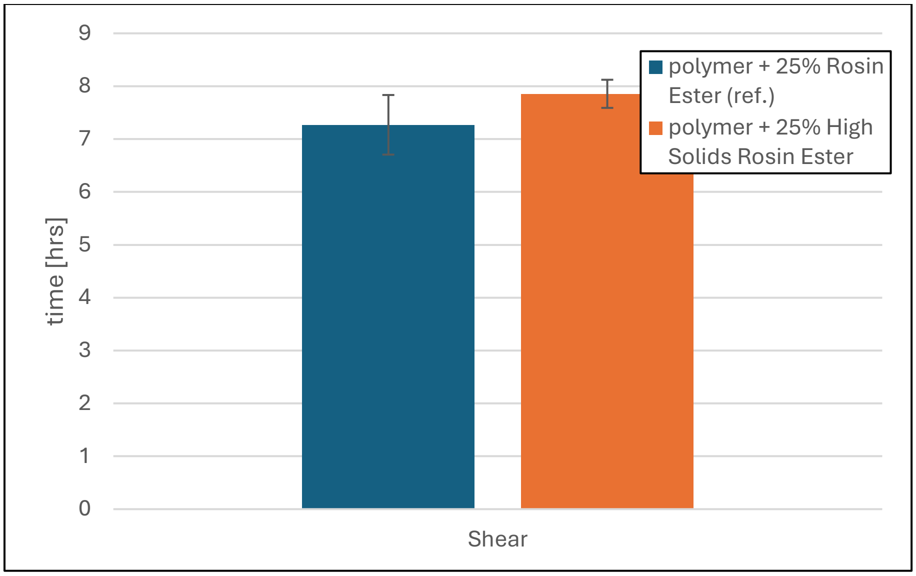


Figure 9. Cohesion values using a high solid content and a regular solid content rosin ester tackifier dispersion.

Based on the analysis results, adhesive properties using the high solid content rosin ester tackifier dispersion have not been affected by the surfactant change or particle size distribution.

4.2 Adhesives with high acid value rosin tackifier resin

To compare adhesive properties of a high solid content rosin ester tackifier dispersion with a 'normal' grade adhesive properties 'loop' tack, peel strength, and cohesion were analyzed. Results are shown in Figures 10 to 12.

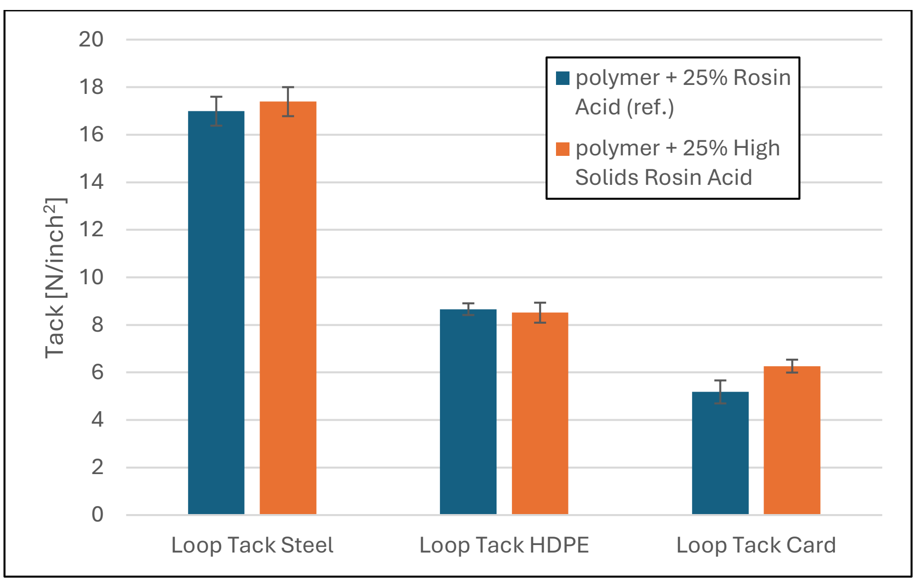


Figure 10. Tack values of adhesive labels using a high solid content and a regular solid content rosin acid tackifier dispersion.

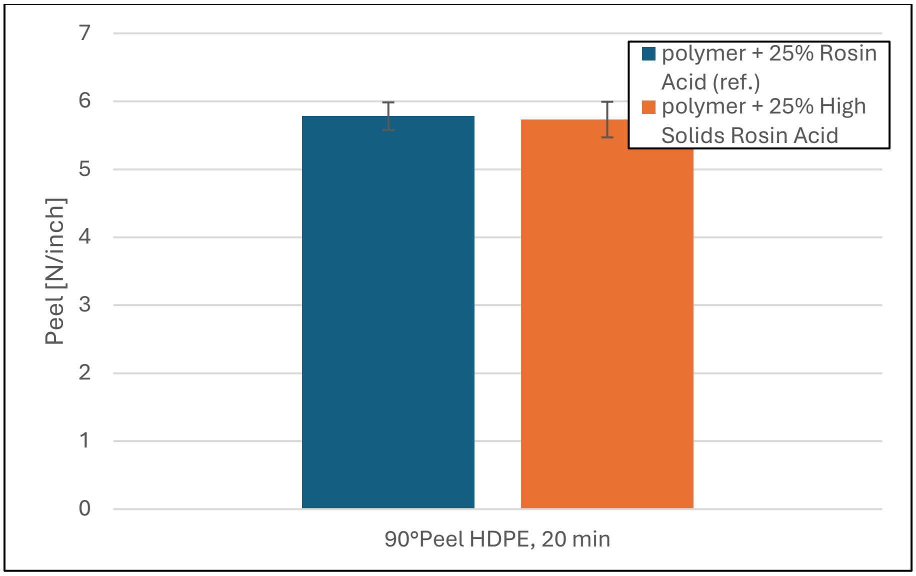


Figure 11. Peel strength at 90° pull off angle and 20 minute dwell time on HDPE using a high solid content and a regular solid content rosin acid tackifier dispersion.

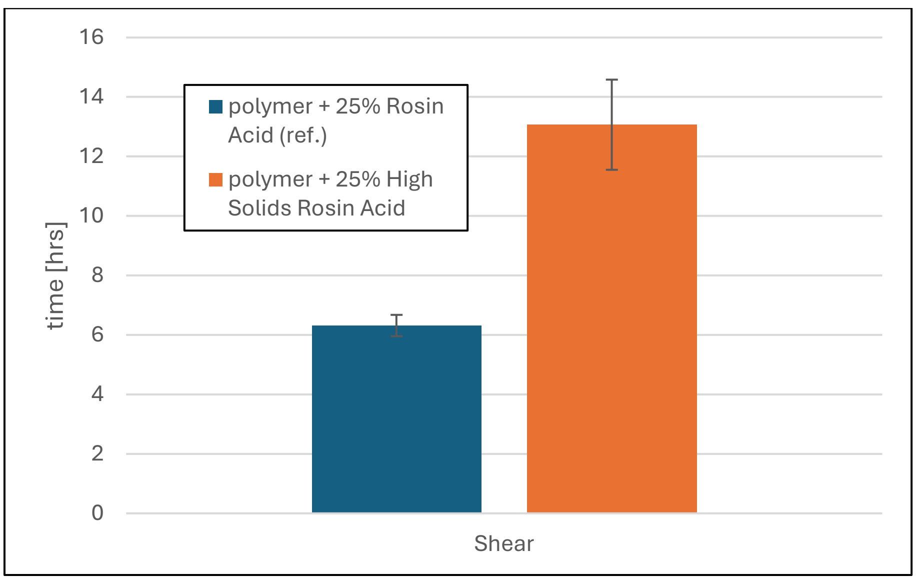


Figure 12. Cohesion values using a high solid content and a regular solid content rosin acid tackifier dispersion.

The analysis results show that tack and peel values of the adhesives containing the high solid content rosin acid dispersions are similar to those using 'normal' solids dispersion. Interestingly, the cohesion appears to increase significantly when using the high solid content tackifier dispersion. A reasonable explanation for this is the difference in surfactant between the two dispersions. The high solid grade makes use of a non-ionic surfactant instead of an anionic surfactant, which may improve compatibility with the polymer matrix.

5. Conclusion

High solid content tackifier dispersions provide several sustainability benefits over the traditional dispersions, which have a typical solid content 55%. At 66% solid content, water demand to produce these dispersions is significantly reduced and less water has to be transported to adhesives users.

Although there is a change in particle size distribution and a marginal change in the non-ionic surfactant used for dispersions of rosin-glycerol ester, the properties appear to be unchanged. Both mechanical properties, necessary for good pumping and filtration stability, as well as the adhesive properties are similar to the traditional counterpart.

The rosin acid tackifier dispersion, or rosin acid dispersion shows similar behavior. Improvements have been seen, however, in significantly reduced foaming behavior and improved shear resistance of the adhesive containing the tackifier. Both phenomena can be explained by the presence of the non-ionic surfactant in the new high solid grade versus the anionic surfactant used in the 'normal' grade.

Overall, replacing tackifier dispersions with a high solid content version has so far not shown any disadvantages and paves the way for more sustainable adhesive formulations.

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