Quantitative evaluation of tackiness in polymer-oil solutions using modified probe tack method

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Tackifiers are high molecular weight polymers dissolved in oil that contribute tack to formulated lubricating oils. One problem that has emerged in the industry is the inability to measure the degree of tackiness in polymer-oil solutions. Several methods have been put forth to quantify tack including string length and the rotating disk method. The degree of tackiness is related to the amount of internal energy or cohesive energy of the fluid. A simple, inexpensive method was developed to quantify the tackiness of an oil solution by measuring the force required to pull a known mass from the solution. The force was correlated with other fluid properties including viscosity, contact angle, and capillary height. A linear relationship has been shown between string length and pull-off force and between viscosity and pull-off force.

KEYWORDS:
Tackifier, Friction, Adhesion, Probe Tack

INTRODUCTION

Tackifiers are important in the lubrication of many processes. They may be used to provide adherence in way oils and chain lubricants, stringiness to greases, and anti-mist properties to metalworking fluids (1). Tackifiers are typically polymeric additives that impart tack or stringiness to a lubricant. Tack is considered a composite property; the ability of a material to function as a tackifier is determined by its cohesive and adhesive forces, viscosity and other factors such as the molecular weight and concentration of the polymeric additives used in the formulation of such additives. Tackifiers have high cohesive and adhesive forces. High cohesive forces allow the tackifier to remain together as a single mass while high adhesive forces cause the tackifier to remain on the surfaces to be lubricated (2).

Due to the many factors that influence tack, it has been difficult to quantitatively determine how tacky a particular solution is (3). Several methods have been developed which are able to measure some, but not all, of the relevant driving forces of tackiness.

Current Test Methods

Test methods for measuring tackiness are generally most suited to the adhesives market including pressure sensitive adhesive tapes and adhesive coatings. Several organisations provide test standards to the adhesives market including the American Society of Testing and Materials (ASTM), the Pressure Sensitive Tape Council (PSTC), the European Association of the Self-Adhesive Labelling Industry (FINAT), the British Standards Institution (BSI) and the Tag and Label Manufactures Institute (TLMI). The test methods currently used for the pressure sensitive tapes market include probe tack (ASTM D2979), loop tack (BS EN 1719, TLMI LIB 1/2), rolling ball tack (ASTM D3121, BS EN 1721) as well as tests for double-sided tapes (BS 7116) (4).

These methods use a technique where the adhesive is coated onto a solid support or applied on a tape and then placed in contact with a second surface. The force required to separate the surfaces is then measured as an indication of adhesiveness or tackiness. These tests are useful for comparing adhesives to one another but are not suitable for use in the lubricant tackifier industry. This is due to the fact that these tests measure pressure sensitive tackiness rather than adhesiveness as it relates to cling or adherence of an oil solution to a metal part. Cohesion is also an important property that is generally not assessed using test methods desi`gned for the adhesives industry. Cohesion provides the string-forming ability of a tackifier solution due to the interaction of the individual polymer molecules of the solution.

Further test methods have been developed specifically for use in the lubricant tackifier industry. One such method is the Brookfield spindle method. This method determines the amount of oil left on the surface of a Brookfield spindle. The spindle is submerged in the tackifier in oil solution then spun for 10 minutes at a high rpm and then the weight of the spindle and adhered tackifier solution is recorded. The amount of tackifier left on the spindle is an indicator of its ability to adhere to a metal surface. Depending upon the concentration, base oil properties and the temperature the effectiveness of a tackifier can be assessed relative to each other (5). Another test is the open (or ductless) siphon test method. In this test, a capillary tube attached to a vacuum pump is used to withdraw a dilute tackifier solution from a graduated cylinder. The tackiness is quantified by the maximum length of the polymer string measured before the string breaks (1). Neither of these tests has been standardised by ASTM or any testing body.

In this study, the pressure sensitive tack of adhesives using an inverted probe machine (ASTM D2979) method used in the adhesives industry is modified to make this test more suitable for the lubricant industry. In the standard test the force required to remove the adhesive from a solid surface shortly after it has been in contact after a short period of time is measured using an inverted probe machine. The adhesive is removed from the solid surface at a constant rate and the maximum force required to break the adhesive bond is measured. A further modification of the test procedure is required because of differences in the rheological properties and the expected pull-off force (3). The standard ASTM test is also simplified in order to eliminate the need for expensive test equipment.

A test similar to the ASTM probe tack test has been used in greases to determine the pull-off force (6). The expected pull-off force in a grease is much higher than for a lubricant tackifier solution.

Adhesion and Cohesion

In many industrial applications the lubricating oil must not drip or form a mist when bearings or machine surfaces are in motion; the addition of a tackifier will decrease the tendency of a lubricant to do so. Oil mists have been associated with various health issues in plant workers so the impetus is to lower the misting of oils in the workplace (7). To alleviate oil mists, a tackifier can be added to the oil. Cohesion is determined by the attractive forces between the molecules of a substance that tends to hold the substance together. Materials with high cohesive energies are able to resist separation of the oil into separate small droplets thus the mist does not form (7). Adhesion is determined by the attractive forces between dissimilar molecules and causes one material to stay in place on another.

Adding a tackifier to a lubricant package will tend to increase the cohesiveness and adhesiveness of the lubricant without substantially increasing its viscosity. The cohesive forces within a tackifier result in the string forming ability that is a key component of tackiness. Cohesion also drives the elastic nature of these materials. Adhesion is also increased when using a tackifier. Higher adhesiveness is required to make a lubricant stick to bearing surfaces at high speeds than at low speeds. At low speeds, greater cohesiveness is required to keep the lubricant from being squeezed out from between the bearing surfaces (8).

Contact Angle

Cohesion and adhesion are important to the performance characteristics of tackifiers in the lubricant industry. One way to measure the relative strength of these two forces is by determining the contact angle.

Cohesive forces between molecules cause the surface of a liquid to contract to the smallest possible surface area. This general effect is called surface tension. Molecules on the surface are pulled inward by cohesive forces, reducing the surface area. Molecules inside the liquid are surrounded by other liquid molecules on all sides and therefore experience zero net force (9).

Interfacial tension is proportional to the strength of the cohesive force, which varies with the type of liquid and the surface that it is in contact with. Interfacial tension, γ, is defined to be the force, F, per unit length, L, exerted by a stretched liquid membrane, as shown in Equation 1.

$$\gamma = \frac{F}{L} \qquad (1)$$

The contact angle, θ, of a droplet is defined as the angle within the droplet between a tangent line drawn on the droplet surface at the solid-liquid interface and the solid surface, as shown in Figure 1. A θ of less than 90° indicates wetting behaviour while a θ of greater than 90° indicates non-wetting behaviour.
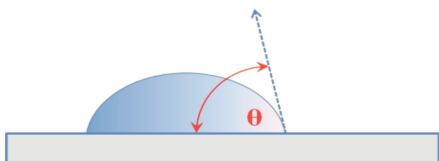

Figure 1: Contact angle of a liquid droplet on a solid surface.

The relative strengths of the cohesive and adhesive forces of the droplet determine the shape of the droplet. A material that is more cohesive than adhesive will show more non-wetting behaviour, i.e. the contact angle will be larger. The forces between the molecules of the drop are stronger than the forces between the molecule and the surface which results in droplet molecules that are more stable when interacting with other droplet molecules rather than the surface molecules (10).

Capillary Action and Surface Tension

The adhesiveness of a tackifier is related to the surface tension which can be determined from the contact angle and capillary height. Liquids in contact with confined spaces such as small pores will fill these spaces without an external force, even against the force of gravity. The cohesive forces between the molecules of the fluid and the adhesive forces between the fluid molecules and surface molecules create the driving pressure that will force the fluid into the capillary space (11).

The Lucas-Washburn equation describes the rate of fluid flow through a cylindrical capillary of radius r as a function of the driving pressure. Making the assumptions that flow is laminar viscous and incompressible and that the capillary is much longer than it is wide, Washburn applies Poiseuille's Law for the pressure drop in a fluid flowing through a cylinder to derive Equation 2.

$$\frac{dl}{dt} = \frac{\sum P}{8\eta l}(r^2 + 4\epsilon r) \qquad (2)$$

where η is viscosity and ΣP is the sum of atmospheric pressure (zero if the ends of the capillary are open), hydrostatic pressure, and capillary pressure. ϵ is the coefficient of slip, taken to be zero for a fully wettable surface (11). Capillary pressure is given by Equation 3.

$$P_c = \frac{2\gamma \cos\theta}{r} \qquad (3)$$

where γ is interfacial energy and θ is the solid-liquid contact angle.

If a capillary tube is placed vertically into a liquid capillary action will raise or suppress the liquid inside the tube depending on the materials at the interface. The effect depends on the relative strength of the cohesive and adhesive forces and, thus, the contact angle. If θ is less than 90°, then the fluid will be raised; if θ is greater than 90°, it will be suppressed.

In the cases of horizontal and vertical capillaries, where hydrostatic and atmospheric pressure are negligible, the surface tension σ for non-steady state conditions is given by Equation 4.

$$\sigma = \frac{2h^2\mu t}{r \cos\theta} \qquad (4)$$

where h is the height in the capillary, μ is the dynamic viscosity, r is the radius of the capillary tube, θ is the contact angle, and t is the time it takes the solution to rise in the capillary (12).

However, when evaluating polymer solutions some assumptions need to be made in regard to time. For long liquid rise times in a capillary tube the Lucas-Washburn equation is not the best method to determine the surface tension of a fluid as the equation predicts a continuous rise in height. In reality, the liquid height will eventually stop rising as an equilibrium is reached between the capillary force and the force of gravity (12).

Zhmud (13) derives an equation and solutions for different time intervals specifically over long time intervals. This equation was modified by the Lambert function to describe the behavior using an inverse exponential function. The modified equation results in an equilibrium height that a liquid will reach in a capillary tube under the force of gravity when solutions are considered at infinite time. The surface tension of the liquid can be calculated from steady state capillary height using Equation 5.

$$\sigma = \frac{hr\rho g \sin\varphi}{2 \cos\theta} \qquad (5)$$

where ρ is the polymer solution density and φ is the inclination of the capillary tube from the horizontal plane.

EXPERIMENTAL METHODS

Tackifier solutions were prepared with a total polymer concentration of 3% (w/w). Solutions of an olefin copolymer (OCP), polybutadiene (PBR), natural rubber (NR) and polyisobutylenes (PIB) were used as shown in Table 1. Solutions with more than one component are listed with the major component first. The PIBs used have viscosity average molecular weights ranging from 1000 to 4000 kDa.

Solutions were prepared by dissolving polymer in the diluent at 95°C with low shear mixing to avoid shear degradation of the polymer.

|	Polymer	Molecular Weight	Diluent Oil
A	OCP	Low	Group I Paraffinic
B	PBR	Med	Vegetable
C	PBR/NR	Med/High	Vegetable
D	PIB	Low	Group I Paraffinic
E	PIB/PIB	Med/Low	Group I Paraffinic
F	PIB	Med	Group I Paraffinic
G	PIB	Med	Group III Paraffinic
H	PIB	Med	Group I Paraffinic
I	PIB	High	Group I Paraffinic

Table 1: Properties of the 3% (w/w) polymer solutions prepared for use in this study.

Modified Probe Tack Test

A small dish having a radius of 7.3cm was used to perform this test. The centre of the dish had three raised ridges of about 1mm height. A 50 gram hooked weight was placed on three small ledges at the bottom of the dish in order to minimise the capillary force generated when liquids are placed in confined spaces. The polymer test solution was added to the dish so that the weight was submerged to a depth of 3mm. A hand-held spring scale was attached to the hook. A steady upward force was applied to the weight, normal to the surface of the liquid, over a 3 second period. The weight registering on the scale was recorded by a camera. The mass of the weight was subtracted from the weight registering on the scale. This yields the pull-off force required to remove the mass from the polymer solution. This operation was repeated 10 times for each polymer solution. The highest mass recorded on the scale is recorded just before the weight is lifted from the solution. From the maximum mass the pull-off force, F, can be calculated using Equation 8.

$$F = \frac{m}{a} \qquad (8)$$

where m is the maximum mass recorded on the spring scale and a is acceleration. In this case acceleration is taken to be only the acceleration due to gravity as the weight is stationary until enough force is applied to remove it from the tackifier solution.
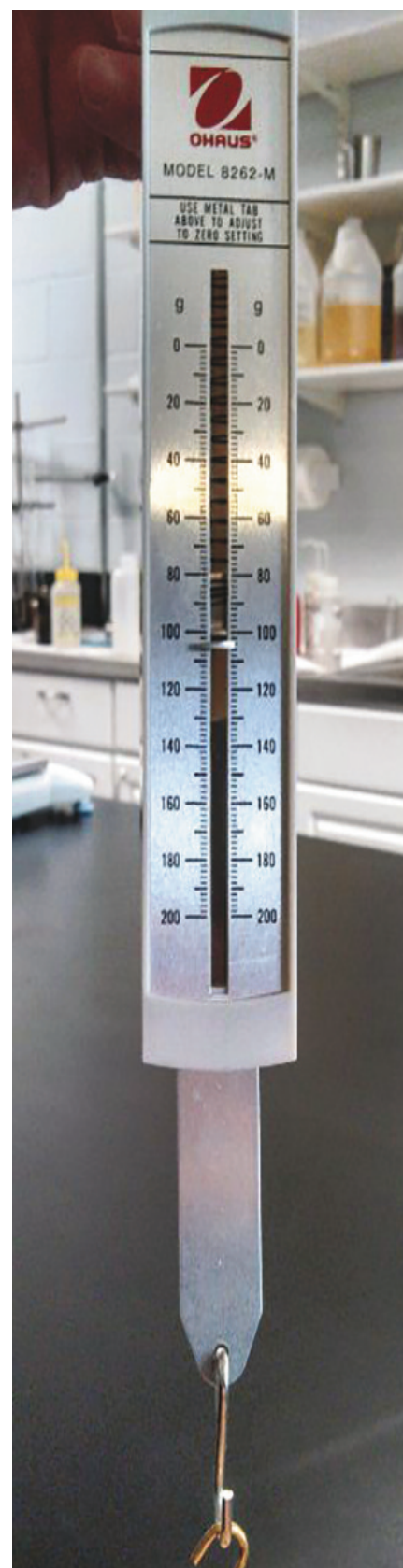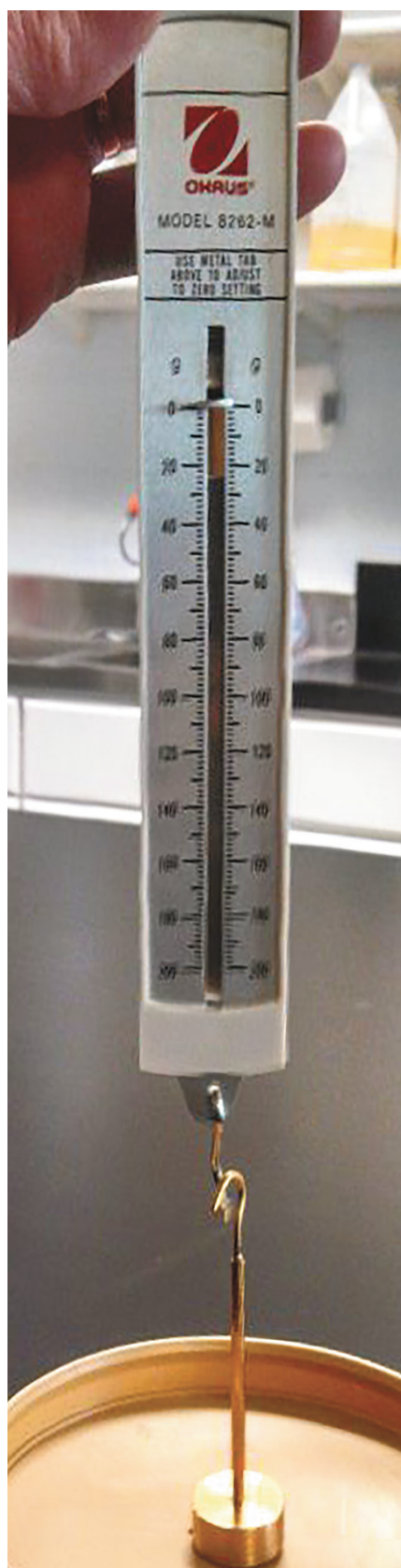
Capillary Test

A borosilicate glass capillary tube having a radius of 0.35 mm was used for the measurement of capillary height of the polymer solutions. The tubes were lowered vertically into a polymer solution to a depth of one mm and the distance that the solution travelled up the tube was measured from the surface of the test solution. A time of 600 seconds was allowed to reach steady state.

Contact angle

Contact angles of three of the polymer solutions on borosilicate glass were measured using a contact-angle goniometer.

RESULTS
Modified Probe Tack Test

Based on the results of this study, it can be shown that the pull-off force follows the same trend as the string lengths as measured by the ductless siphon method. Both tests provide a measure of the cohesive energy of the tackifier solution. Materials with high cohesive energies are able to resist separation of the material into separate droplets which would result in their removal from the surfaces to be lubricated.

In the modified probe tack test, the cohesive energy of the tackifier resists the separation of the layers of fluid between the bottom of the weight and the dish. The higher the cohesive force between the layers of fluid within the tackifier solution, the more force must be applied to separate them, resulting in a higher pull-off force. Another point of separation that could occur during pull-off would be the breaking of the adhesive forces between the tackifier solution and the weight or the dish. This is not observed to be the case; there is a film of tackifier that covers the bottom of the weight after it has been removed. Further, strings of tackifier solution form as the weight is lifted from the dish.

As shown in previous studies, an increase in molecular weight of the polymer improves its performance as a tackifier. This has been confirmed in this study where an increase in molecular weight corresponds to a higher pull-off force. This also correlates to an increase in tackifier

Figure 2: *Pull-off force from the modified probe tack test and string length from the ductless siphon test correlate. An increase in polymer molecular weight for PIB samples (E-I) also correlates to improved tackifier performance. Values for pull-off force were averaged and the standard deviation is shown.*

performance as measured by the ductless siphon test, as shown in Figure 2.

The string formed during the ductless siphon test is held together via the cohesive forces within the string. As a result of increased cohesive force a longer string can be formed as the material is able to hold itself together to an increased height.

It has also been determined that the pull-off force follows the same trend as the viscosity, as shown in Figure 3. Viscosity is another parameter that determines how well a tackifier will perform.

Viscosity is determined by several factors. In polymer solutions, the large polymer materials must untangle and move past on anther in order for the fluid to flow.

Another important factor is the cohesive force between the molecules themselves. For one molecular layer to flow past another, the cohesive force between those molecules must be overcome. As a result, the layer in motion will experience a drag force from the next layer which will resist flow. Increasing the cohesive forces will result in higher drag forces, i.e. more resistance to flow and higher viscosity.
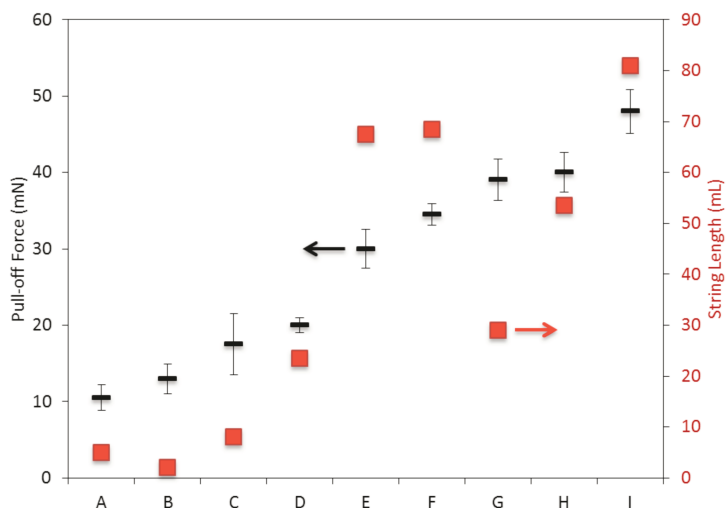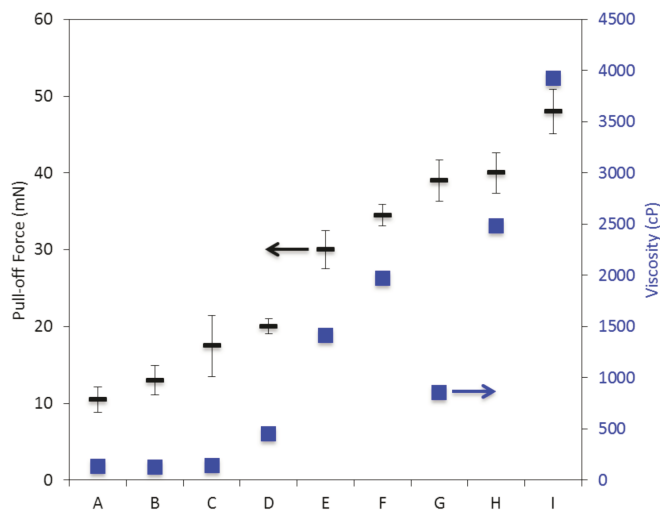

Figure 3: *Pull-off force from the modified probe tack test and viscosity show a correlation as both properties are dependent on the cohesive forces within the tackifier solution.*

	Height (mm)	Density (22°C, kg/m³)	Contact Angle (°)	Dynamic Viscosity (100°C, cP)	Surface Tension* (N/m)
A	15	857	24.4	137.3	0.024
B	15	898		130.2	
C	16	922		145.4	
D	12	860		455.5	
E	10	846		1411	
F	8	857	33.7	1971	0.014
G	8	830		857.8	
H	7	864		2483	
I	6	845	41.0	3925	0.012

*Values calculated using Equation 5.

Table 2: Experimental data obtained from the capillary test including steady state capillary height and the calculated surface tension values.

Capillary Test

Based on the data obtained from the capillary test.

Table 2, it can be shown that the calculated surface tension values show an inverse correlation to both the string length and the pull-off force of the polymer solutions. The capillary height is dependent on the adhesive strength of the material. As a material is better able to adhere to the surface of the capillary, the higher it will be able to rise in the tube against the force of gravity.

Tackifiers require some adhesive strength, as well as high cohesive strength, in order to stay in place during lubrication. The capillary test is a measure of adhesive strength rather than cohesive strength as the modified probe tack test and ductless siphon tests are. As the adhesive strength of the material increases, the surface tension increases, but the cohesive force decreases. There is a trade-off between increasing cohesive forces and decreasing adhesive forces as shown by the inverse correlation between the pull-off force and the surface tension calculated from the data obtained using the capillary test.

The capillary test shows that as the surface tension increases, i.e. the adhesive forces also increase, the solutions are becoming less effective tackifiers. In order for a tackifier to be effective it must stay in place on the part surface and it must also have high cohesive energy in order for the tackifier to not be removed easily. A balance of adhesiveness and cohesiveness is required for the best performance of a tackifier.

CONCLUSIONS

A correlation exists between the pull-off force and string length as measured by the ductless siphon test of a tackifier solution. There is also a correlation between the pull-off force and the solution viscosity. Both the string length and viscosity of a tackifier solution are dependent on the cohesiveness of the material. Cohesiveness is partly responsible for the property of a lubricant known as tack. Another property that determines how well a tackifier performs is the adhesiveness of the solution. The capillary height of a tackifier solution is related to its adhesiveness. An inverse relationship between the adhesiveness as determined by the capillary test and the cohesiveness as determined by the probe tack test of a tackifier solution has been demonstrated.

Tack is a composite property and therefore must be measured indirectly. Multiple tests are necessary to understand how well a tackifier will perform as a lubricant additive. The pull-off test and the ductless siphon test quantify only a portion of tackifier behaviour, the cohesiveness. The addition of the capillary test allows an understanding of another important property of a tackifier, the adhesiveness.

The pull-off and capillary test used in this study are relatively quick and simple to perform and require minimal equipment. Potential tackifiers can be quantitatively evaluated and judgments can be made about their performance. Based on the results of this study, a potential tackifier should have a high pull-off force and a low capillary height. Combined with previous tests such as the ductless siphon

method and knowledge of the polymer molecular weight, a tackifier solution can be developed and evaluated more readily.

A similar method to determine pull off force in grease using expensive equipment was previously developed. Further work using the simplified probe tack method developed in this paper will be performed to determine its suitability for the characterisation of tackiness in grease.

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