

Silica–Polyacrylate Nanocomposite Pressure Sensitive Adhesives

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ABSTRACT

Pressure sensitive adhesive (PSA) performance is dependent upon bulk dissipation of debonding energy more than it is on adhesion to substrates. Performance is increased with gel content due to crosslinked structures, however physical crosslinks are suitable for increased energy dissipation without detracting from ease of application of the PSA. Nano-silica is suitable for imparting thixotropy on co-polyacrylate based PSA. Silica agglomerates were disrupted by shear during application of the adhesive, then they reformed to enhance cohesion, thereby resisting and enhancing the damping of debonding forces. PSA characterisation by modulated force thermomechanical time–temperature superposition mastercurves replicated changes to the debonding mechanisms found with peel tests, that is cohesive failure, slip–stick failure and adhesive failure.

Keywords: adhesion, cohesion, peel performance, viscoelasticity, debonding, energy dissipation

1 INTRODUCTION

Pressure sensitive adhesives (PSA) are permanently tacky so that they can form an adhesive bond and that the adhesive bond can be disrupted at a later time. PSA usually consist of an inert decorative or sealing film coated with the PSA. Alkyl acrylate copolymers are the most common type of PSA. A combination of monomers is used to provide a balance of tack, cohesion and adhesion [1]. Tack requires a low glass transition temperature ($T_g = -30\text{ }^\circ\text{C}$), which reduces cohesion. Polymerization via an emulsion usually results in a proportion of copolymer gel that increases the cohesion [2]. Gel can be reduced or controlled by polymerization in conjunction with a chain transfer agent [3] that reduces gel and molar mass, and hence cohesion. Adhesion and cohesion can be increased by including a polar monomer and more particularly a hydrogen bond forming monomer, such as acrylic acid [4]. Polyurethanes-chitin whisker nano-composites were found to have enhanced adhesion due to increased strength provided by reinforcement of the matrix [5]. Epoxidised natural rubber adhesives containing calcium carbonate were found to exhibit enhanced adhesion [6].

Bond formation by PSA takes place by an initial attachment, called tack, followed by a stronger attachment with applied pressure and time for flow within the adhesive.

The bond strength is a combination of adhesion and cohesion, the later causing bond strength to be greater than the adhesion. Bond strength is measured as the force to disrupt the bond between two surfaces joined by the PSA. Failure in a peel test depends on the rate of peel. A slow peel rate will allow time for molecular motions and cohesive failure predominates. A fast peel rate causes failure first at the PSA–rigid substrate surface, and then at faster rates failure occurs between the peeled surface and the adhesive. Between the slow and fast peel rate is an unstable region where stick-slip occurs with both adhesive and cohesive failures alternating (Figure 1). Novel polyacrylate PSA with crosslinking combined with thermal treatment resulted in improved adhesive properties [7].

The aim of this research is to increase cohesion of a PSA by including silica nanoparticles. The silica nanoparticles form reversible agglomerates and bind polymer molecules by adsorption.

2 EXPERIMENTAL

2.1 Materials and Nano-composite Preparation

Polyacrylate PSA preparation was by starved feed emulsion polymerisation of butyl acrylate, 2-ethylhexyl acrylate, styrene and acrylic acid (mass ratio: 50:35:9:6 data is presented) according to the detailed description presented elsewhere [2]. All compositions were calculated using the Fox equation to have the same glass transition temperature, $-30\text{ }^\circ\text{C}$. Iso-glass transition temperatures were confirmed by differential scanning calorimetry (DSC) and modulated force thermomechanometry (mf-TM) measurements. Note the designation as mf-TM instead of dynamic mechanical analysis (DMA) conforms to recommendation of the International Confederation of Thermal analysis and Calorimetry (ICTAC) since the force is correctly described as modulated not dynamic, consistent with other thermal analysis techniques.

Direct dispersion of silica (Aerosil A300) into the emulsions was by using an Ultra Turrax (model T45) disperser with shear attachment at 12000 rpm. The co-polyacrylate–silica emulsions were cast as films onto glass sheets that had been rendered hydrophobic by treatment with hexamethyldisilazane to facilitate removal of the adhesive for thermomechanical analysis. The PSA films were dried at $50\text{ }^\circ\text{C}$ under vacuum.

2.2 Nano-Composite Characterisation

The copolyacrylate–silica PSA films were analysed using thermogravimetry (TGA) to measure the copolyacrylate thermal degradation with composition and silica content. TGA data are not presented in this paper due to size restriction.

2.3 Viscoelasticity Cohesion Performance

Viscoelasticity was measured using modulated–force thermomechanometry(mf-TM) using a Perkin-Elmer Diamond DMA in 10 mm parallel plate compression mode, over a temperature range -60 to +120 °C using a step-isothermal temperature program with 10 °C increments soak time 300 s, 10 μm deformation, 10 frequencies with a frequency range 0.01 to 100 Hz. Mastercurves were constructed using the time-temperature substitution principle by shifting using a quadratic fit of each isothermal temperature curve and using a least square minimisation to superposition the storage modulus curves.

3 RESULTS AND DISCUSSION

Modulated force thermomechanical (mf-TM) results for a PSA without and with 1%·w/w silica are shown in Figure 1.

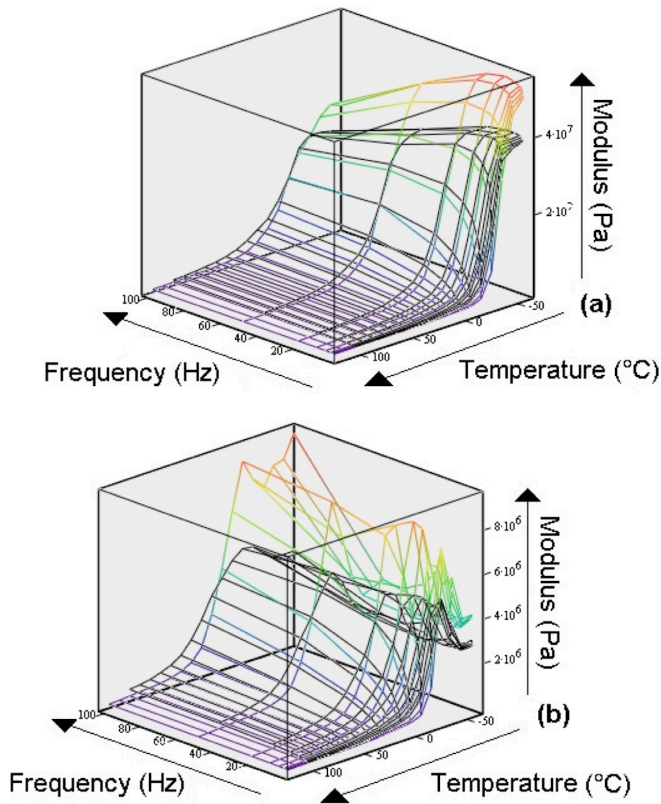


Figure 1. Storage (a) and loss (b) modulus curves for copolyacrylates, the lower curve sets are without silica and the upper lighter shaded curve sets are for the silica filled adhesive.

The curves show decline in storage modulus and a peak in loss modulus followed by a decline with temperature, and a small change with frequency. The silica filled PSA exhibited higher moduli particularly in the damping region associated with the glass transition temperature. The curves displayed in Figure 1 allowed comparison of moduli with changes in temperature and frequency. The temperature response curve were then shifted according to the Williams–Landel–Ferry (WLF) equation to form frequency(time)-temperature-superposition (TTS) master curves. The curves for a series of PSA with difference silica compositions are plotted in Figure 2. Increasing silica content increased the storage and loss modulus at all frequencies. The loss modulus maximum shifted to lower frequencies (increased temperature) with increase in silica content.

The mastercurves shown in Figure 2 extend over a sufficient frequency range to show approach to a low frequency plateau zone, a transition zone (corresponding to the glass transition) and a terminal zone (corresponding to the glassy state). These frequency–modulus zones control performance of PSA. The work of adhesion can be assumed to be constant since no changes in surface tension occur with applied stress frequency. The change in behaviour of the PSA with frequency and silica content originate from modification of cohesive (bulk) properties.

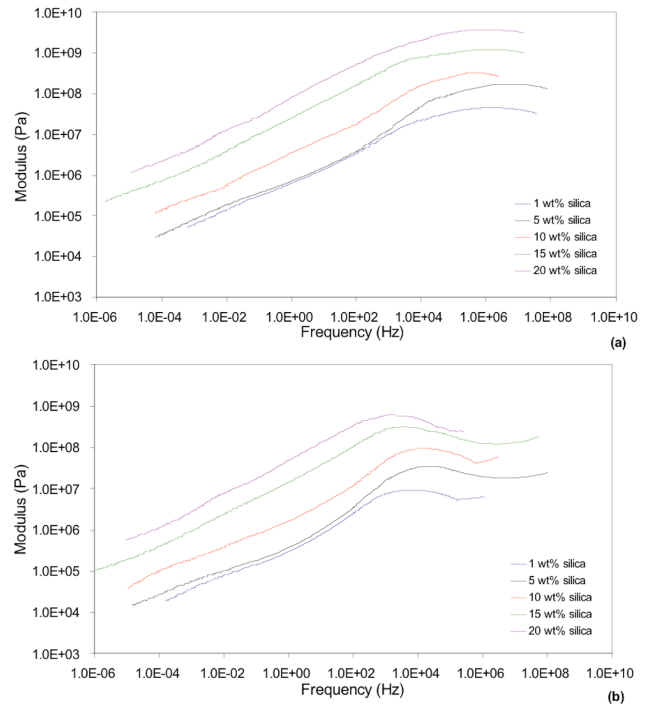


Figure 2. TTS mastercurves for silica-PSA with different silica compositions

The adhesive became a reversible gel with addition of nano-silica. The PSA has become more solid-like with addition of nano-silica. In parallel the PSA become more solid-like when exposed to increasing shear rates as experienced during a debonding or peel stress regime.

Under pressure over a time suitable for bond formation the PSA can still flow due the time scale for the reversible silica physical gel to respond. Under slow peel rates the physical silica gel increases cohesion and resists bond rupture. As the peel rate increases the silica gelation effect is less pronounced because even the unfilled PSA molecules have relaxation times long enough to resist flow.

The effect of cohesion on PSA bond formation can be characterised using modulated force thermomechanical analysis. The time-scale requires construction of a time-temperature-superposition mastercurve (Figure 2) that parallels the peel test mastercurve over the wide frequency range obtained [8]. The change in relaxation of a nano-silica filler on an elastomer, analogous to a PSA, has been measured using stress relaxation [9]. The mastercurve measurements on bond strength (peel test) and viscoelastic cohesion (modulated force thermomechanical analysis) demonstrates the contribution of a bulk property (cohesion) to a surface property (bond strength) and reveals the mechanism of PSA debonding.

The PSA debonding mechanism leads to the concept that an adhesive bond can be enhanced through formation of physical crosslinks by the high surface to volume ratio of a nanofiller. PSA-silica nanocomposites enable better control of adhesive bond formation and subsequent removal than adventitious chemical gelation during polymerization.

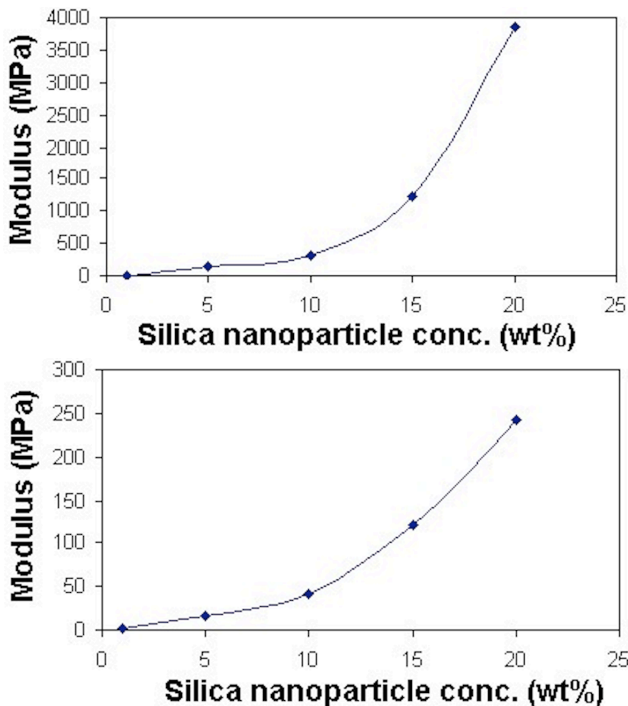


Figure 3. Change in modulus of filled (a) E' mastercurves and (b) E'' mastercurves with respect to increasing silica content.

Figure 3 shows the shift in storage modulus and loss modulus with incremental inclusion of nano-silica. The nano-silica shows an increasing trend since agglomeration (floculation) of silica aggregates is expected to increase with proximity of silica particles. This is the same

mechanism that occurs when silica is used as a thixotropic agent in liquids. Except for presence of some gel, the PSA are liquids because their glass transition temperature is sub-ambient, though they are displaying solid-like properties because the storage modulus is greater than the loss modulus except at the lowest frequencies (see Figure 2). This is why at very low frequencies cohesive failure of PSA is the dominant mechanism.

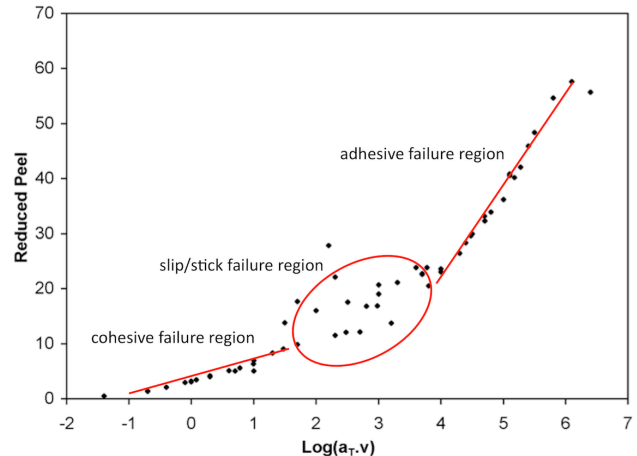


Figure 4. Peel TTS mastercurve for an acrylate PSA showing regions where three mechanisms of debonding dominate.

Figure 4 shows a peel TTS mastercurve for the PSA without silica. The frequency regions three where different debonding mechanisms occur are highlighted on Figure 4. In fact there are two adhesive failure regions, one where the adhesive is removed with the peeled substrate layer and a second where the adhesive remains on the immovable substrate layer. These are usually referred to as adhesive failure I and II regions. At very low frequencies the molecules have time to move to relieve stress and there movement, or flow, results in cohesive failure. Over the range of the glass transition stick-slip behaviour occurs. With stick-slip stress that is unable to cause debonding is stored temporarily, the stick process, until the combined applied and stored stress is sufficient for debonding when the slip process occurs.

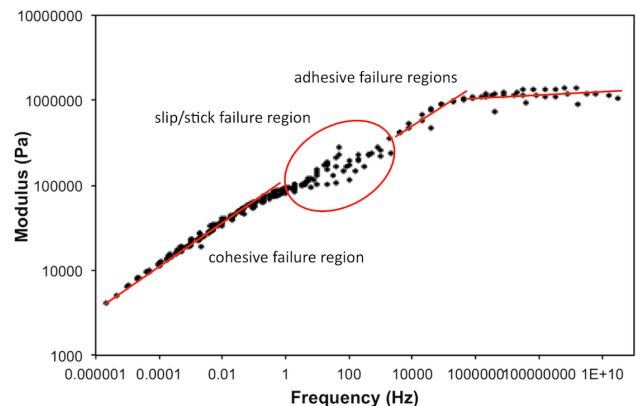


Figure 5. Storage modulus TTS mastercurve for an acrylate PSA showing regions where three mechanisms of debonding dominate.

The storage modulus TTS mastercurve shown in Figure 5 is analogous to the peel mastercurve of Figure 4. This is because the peel test is dominated by the bulk properties of the adhesive layer. When frequency is low stress is stored within the PSA resulting in cohesive failure since the relaxation time of the molecules relative to the stress frequency is sufficient for disruption within the adhesive layer. Adhesive will remain on both substrate surfaces. With higher stress frequencies the molecular relaxation times are too slow for molecules to pull apart and stress is stored resulting in a stick segment. The stored stress will be released, adding to the instantaneous applied stress when that the total stress is sufficient for adhesive rupture. When the stress frequency is very high compared with molecular relaxation times, the adhesive will behave as a glass and debonding will only occur at the interfaces. This glassy or solid-like behaviour region is extended to lower frequencies when nano-silica is included in the PSA.

Viscoelasticity is a bulk property of a pressure-sensitive adhesive, a property of cohesion. Therefore the changes to viscoelasticity observed, caused by the greater increase in storage than loss modulus with silica nanoparticle addition indicated an increase in cohesion (greater attraction between adhesive molecules), producing more solid-like behaviour in the filled PSAs. A PSA with increased cohesion has a greater resistance to deformation and decreased flow and wetting. Both of these are consistent with the observed increase in glass transition temperature.

Since adhesive bonds relieve stresses by dissipation through their viscoelastic processes, a more solid like PSA (i.e. an increase in elasticity) is less able to reversibly flow. Hence, they cannot dissipate applied stresses to the adhesive bond as effectively, resulting in an increase in the available energy that can potentially be returned to the adhesive bond. An increase in cohesion and potential returned energy to the adhesive bond indicates a possible increase in the likelihood of adhesive failure.

CONCLUSION

Nano-silica filled co-polyacrylate pressure sensitive adhesives were prepared. The PSA performance was characterised by modulated force thermomechanical (mf-TM) measurements in shear and the data used to construct time-temperature superposition mastercurves. The mf-TM mastercurves exhibited the same shape as peel mastercurves since the bond strength of PSA was dominated by energy dissipation within the adhesive layer, rather than by the adhesion. Nanosilica provided physical crosslinks within the PSA and enhanced their performance. Physical crosslinks are more convenient and reproducible compared with PSA gel content or chemical crosslinking after application of the adhesive. The results demonstrate the importance of cohesive dissipation of debonding forces compared with the contribution to bond strength of the work of adhesion.

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