



A molecular simulation analysis of influence of lignosulphonate addition on properties of modified 2-ethyl hexyl acrylate/methyl methacrylate/acrylic acid based pressure sensitive adhesive



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ABSTRACT

A novel PSA formulation that incorporates a bio-sourced lignosulphonate has been proposed. A molecular dynamics simulation study is attempted to explore the effect of lignosulphonate addition on the adhesion, thermal and mechanical properties of a conventionally used acrylic PSA composed of 2-EHA, MMA and AA. A good agreement of conventional PSA density and glass transition temperature, T_g , with literature estimates confirmed the accuracy of the molecular simulations. It is observed that there is an increase in PSA-substrate interaction energy with an increase in lignosulphonate content despite an increase in T_g due to its addition. This is proposed to be primarily due to an increase in polar groups contributed by lignosulphonate. The availability of more polar groups in bulk and increased density of these groups due to significant migration to interface results in an increase in interfacial energy, and hence, improved PSA adhesion. The shear modulus is observed to increase with increase in lignosulphonate content indicating its effectiveness to resist PSA shear deformation. Simulations suggest that in order to form an industrially useful adhesive, that may work well under RT conditions possessing an optimum cohesive strength and surface adhesion, a PSA formulation with ~15 wt.% lignosulphonate may be used.

1. Introduction

The market for industrially important Pressure Sensitive Adhesives (PSA's) has grown very rapidly in the last few decades. A recently conducted study by Grand View Research, Inc. has shown that the usage of PSA's which has been 2800 kilo tons in 2015 may rise to 4000 kilo tons by 2024 [1]. PSA's have a wide range of applications in our day-to-day life including but not limited to vehicle wraps, architectural films, instruction labels and security tracking [2]. Other applications in which a PSA is advantageous include coatings as protective coverings for electronic screens such as mobile phone screens or LCD monitor screens, and recent studies have shown that they have been used in drug delivery systems successfully over the years [3].

As the name suggests, a PSA is an adhesive that shows instantaneous adhesion after an application of small pressure. PSA's may be divided into various categories depending on the base polymer used. Several polymers such as acrylics, silicones, polyurethanes and polyesters have shown promise in PSA applications [4]. Unlike epoxies, which are structural adhesives, PSA's are non-structural adhesives. One of the most important properties of a PSA is that during its application there is no physical transformation and chemical bond formation, thereby,

easing adhesion at room temperature [5]. In recent studies, an increase in interest for synthesizing water-borne PSA's has led to use of non-migratory surfactants which affect the performance of work of adhesion and Shear Adhesion Failure Temperature (SAFT) [6]. Wiebke et al. derived monomers of PSA from fatty acid based bio-sources such as that of vegetable oils and studied their shear, tack and peel properties. The synthesized PSA showed good adhesion on low energy surface substrates and improved hydrophobicity, thereby, showing promise for industrial applications [7].

Lignin is one of the most abundant available green polymer on earth. It contains many cross-linked phenolic rings attached to one another forming a complex polymer structure [8]. Lignin is a waste product of pulping processes, namely sulphite, soda or Kraft pulping employed in paper industries. A large amount of it is utilized inefficiently and is mostly burnt off in recovery boilers for energy recovery. Feldmen et al. have blended plasticized organosolv lignin and a copolymer of vinyl chloride-vinyl acetate and estimated the mechanical and thermal properties of the blend [9]. Depending upon the sources of plants and algae from which lignin may be obtained, it may possess different chemical structures [10]. Previous studies indicate that bagasse lignin in combination with phenol-formaldehyde resin may serve

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as a useful wood adhesive [11]. Lignin has also been previously used as a binder in granules, fibreboard, seed coatings and particleboard products [12–14].

Molecular simulation is one of the fastest growing areas that applies molecular level science to estimate material properties and parameters, enabling design of novel systems. For example, this tool has been used earlier by Xie et al. to estimate the impact of a shock wave on a polymer [15], Castillo-Tejas et al. used molecular dynamic (MD) simulation to study the shear flow properties of highly elastic and viscous systems [16], Yuan et al. used this approach to characterize the interfacial shear strength at the CNT/polyethylene interface [17], Li et al. used MD to study the crosslink density and network structure of epoxy polymers [18]. Researchers engaged in the field of adhesion have demonstrated that MD may be a very useful tool in determining the adhesive properties at the polymer-metal or polymer-metal oxide interface [19]. Further, molecular simulations have been successfully attempted earlier to predict thin film or coating properties for industrial applications [20–23].

In this work, acrylate based solvent-borne PSA's have been molecularly constructed and simulated. Acrylic PSA chains mainly consist of 3 components: a hard monomer, soft monomer and a cross-linkable monomer [24]. The glass transition temperature (T_g) of hard monomer is high and is used to provide cohesion or internal strength to the PSA comparatively. The T_g of soft monomer is low and provides the peel adhesion and tack. For a successful PSA application, it is very important to balance the T_g of monomers such that T_g of formulated PSA is in the feasible range of application. For preparing cross-linked PSA structure, a soft monomer segment represented by 2-ethyl hexyl acrylate (2-EHA, T_g 203 K), a hard monomer segment namely methyl methacrylate (MMA, T_g 378 K) and acrylic acid (AA, T_g 379 K) to provide the active sites for crosslinking need to be individually created. As per the mechanism given by Jin X et al. using the above monomers, a similar system was created for simulation study [25]. In this study, a cross-linking reagent containing nitrogen is used to cure the polymer chain and achieve high holding power and good heat resistant properties [25].

This work attempts to explore the influence of lignin, in the form of lignosulphonate (LS) on the adhesion, thermal and mechanical properties of LS-*m*-PSA (lignosulphonate-modified-PSA) with the help of MD simulations. Although, MMA is conventionally used to contribute hard segment properties in acrylic based adhesives, it can cause various health problems during synthesis such as irritation of eyes, nose, throat, nausea and vomiting [26]. Such health issues associated with MMA, however, are limited only during synthesis while it exists as monomer, and may not persist during and post the polymerization and curing reactions when the monomer gets consumed. This study aims to employ a green and cost effective material namely, LS to substitute the conventionally used MMA. LS has been reported to possess excellent cohesion and good binder properties [27–29]. Apart from this, LS also has a ($T_g = 383$ – 433 K) close to MMA ($T_g = 378$ K) [25,30]. Further, PSA properties such as glass transition temperature, density, solubility parameter, moduli (shear and bulk) and substrate interaction energy have been estimated and the impact of lignosulphonate addition on these explored. However, it is important to highlight some of the limitations of the work. While estimates of some of the adhesive characteristic properties such as glass transition temperature, substrate interaction energy and solubility parameter might be unaffected by the choice of the low molecular weight system and the limited simulation times chosen for simulation, properties such as viscoelasticity and large-strain properties may not be so accurately predicted. These properties depend on determination of entanglement properties that require use of very large systems and huge equilibration and production times for simulations. Also, it is difficult here to prepare (simulate) a rough surface, and ensure simulations that incorporate the formation of mechanical contact of adhesive with such a substrate. T_g has been estimated which provides some useful idea of flowability of the adhesive

at room temperature. The estimates of T_g (lower than RT) through simulation has been considered adequate for understanding adequate flowability and wetting of the surfaces.

2. Simulation methodology

Molecular simulations have been performed using Material Studio 7.0, a commercially available software from Accelrys Inc. [31]. COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) forcefield has been used to calculate the interaction between atoms [32]. Various modules such as Amorphous Cell, Forcite and Discover of Material Studio™ have been used for simulation cell construction, running MD and molecular mechanics (MM). Smart Minimizer function of Discover module in Material Studio™ that employs MM concepts has been used for minimizing the energy of the initially generated random structures. Since, initially generated structure may possess high energy, the function uses a combination of three techniques namely: Steepest Descent, Conjugate Gradient and Newton method, to explore a structure with lowest possible energy. The temperature and pressure within the system are controlled by Andersen thermostat and Berendsen algorithm respectively. The particle motion is controlled by velocity Verlet algorithm. The cut-off distance for calculating non-bonded interactions is fixed at 12.5 Å and an atom based summation method is used for van der Waals force calculations. The simulation procedure described in this section enabled estimation of adhesion, thermal and mechanical properties of pure PSA and LS-*m*-PSA.

2.1. Amorphous cell construction

The PSA polymer chains are first constructed using three acrylic monomers namely 2-EHA, MMA and AA. A snapshot of such an energy minimized PSA chain is shown in Fig. 1(a). For this purpose, two types of chains of chain lengths 13 and 11 are constructed, and then energy minimized using MM for 10,000 iterations. Chains of different length are taken to keep slight polydispersity and imitate a relatively realistic polymer system. 4 chains of chain length 13 and 2 chains of chain length 11 are then used to construct an amorphous cell. This corresponds to a pure PSA based amorphous cell containing 58% 2-EHA, 35% MMA and 7% AA. Subsequently amorphous cells with 5, 10, 15, 20 wt.% LS are constructed. LS is added such that it replaces MMA in wt.% for making the LS-*m*-PSA systems presented in Table 1. An energy minimized structure of LS that is added to a simulation cell is shown in Fig. 1(b). The maximum limit of LS incorporation (20 wt.%) has been kept in line with the literature studies which defines that, it is desirable to use lignin from 7 to 20 wt.% for the formation of adhesives [27,28]. Since, below 7% the cohesive strength of the composite is less than expected and above 20% there is no further increase in cohesive strength, with even a decrease observed in some cases.

Jin et al. described that the crosslinking mechanism in PSA is possible due to the presence of carboxyl groups in the AA segments [25]. The nitrogen atoms of the cross-linker are attacked by the protons supplied by the carboxyl groups of AA. The positive charge on the nitrogen is shifted to the adjacent carbon by ring opening which then reacts with the anion of AA. This gives two reactive sites for cross-linking of each PSA chain with three reactive sites available in each cross-linker shown in Fig. 1(c). The final energy minimized structure of the PSA anion and cross-linker cation obtained just before crosslinking are used for the construction of amorphous cells. In Fig. 1(a) and (c), the terms PSA anion and cross linker cation are used for the convenience of locating the oxygen (from PSA) and carbon (from cross-linker) during simulation of crosslinking. These ions are artificially created for the system to locate cross-linking sites during simulation, and to form a bond appropriately. After the system with desired cross-linking is obtained all the COO- bonds are finally saturated with hydrogen leaving the final structure in a neutral condition.

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