

Investigating Pressure Relief on SBC-based Adhesives for Intimate Healthcare Products

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Abstract

To know the ability of the adhesive to relieve pressure is important for better development of bandages. It depends highly on the balance of the adhesive melt components. In this thesis I investigate how these components influence pressure relieve and try to define a good adhesive for pressure relieve. I do so by performing two kind of experiments; pressure experiment, where I subject adhesive samples of different thickness to constant pressure and measure the dissipation of it thorough the material. And rheological experiments, since they can give insight into the adhesive properties such as adhesion and cohesion, which is also needed to be adequate. I show that good adhesion is often a trade off for pressure relieve, however there is a possibility for both. I define pressure relief and its parameters and make very simple linear models for seven different polymer blends. I conclude that mixture 2 is the best adhesive for the defined specifications, but that further experimental work is needed.

Preface

This project is an experimental master thesis in physics and chemistry completed at Department of Science, Roskilde University in collaboration with Coloplast and corresponds to 60 ECTS points. It was supervised by Dorthe Posselt from department of Physics, Søren Hvidt from department of Chemistry and Tune Bjarke Bonne from Colopast. Experimental work was done at Chloroplast headquarters in Humlebæk.

The main intended audience of the thesis is students and scholars of material science, pertaining to polymers, although it would not be lost on laymen interested in the subject. Overall it was a learning experience not only in my academic life but also for the social aspects. Having to work at the company, which was unfamiliar setting and with people of different backgrounds was a delightful challenge. I learned a lot and in the end I enjoyed it immensely. I would like extend many thanks to my supervisors Dorthe Posselt, Søren Hvidt, Tune Bjarke Bonne for all their help and patience. Also many thanks to Roskilde University and Coloplast, which made it all possible.

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Glossary

- alternating copolymer contains two monomer units M_1 and M_2 in equimolar amount in regular alternating distribution: $\sim M_1 M_2 M_1 M_2 M_1 M_2 M_1 M_2 \sim$. VIII, 13, 51
- amorphous non-crystaline, lacking lon-range order, shapless, having no definite form. VIII, 9, 13, 51
- **block copolymer** is comprised of different blocks of homopolymers in the linear chain. If A and B are homopolymers: $A = \sim M_1 M_1 M_1 M_1 M_1 M_1 M_1 M_1 \sim$, $B = \sim M_2 M_2 M_2 M_2 M_2 M_2 M_2 M_2 \sim$, then di-block copolymer has $A_m B_p$ structure, tri-block: $A_m B_p A_m$, tetra-block: $A_m B_p A_m B_p$ and multi-block: $(A_m B_p)_n$. VIII, 13, 19, 23, 51
- **copolymer** is a polymer comprised of 2 or more different kind of monomers. Copolymers can have different arrangements such as alternating, statistical, graft or block. VIII, 12, 51
- **cross-linking** can refer to both chemical and physical cross-linking, chemical cross-linking is synonymous with vulcanization. VI, VIII, 9–15, 19, 21, 47, 48, 51
- crystallinity describes a degree of structural order in a solid. VIII, 9, 51
- **elasticity** capacity of the material to store deformational energy and regain its original shape after being deformed. VIII, 51
- **elastomer** is a viscoelastic amorphous polymer with very weak inter-molecular forces, having high elongation and flexibility or elasticity. Their primary uses are for seals, adhesives and moulded flexible parts. VIII, 9, 10, 13, 18, 23, 51
- **graft copolymer** as in block copolymer is comprised of blocks of homopolymers, however in the branching structure instead. VIII, 13, 51
- intermolecular forces are the forces of attraction or repulsion which mediate interaction between individual molecules or other types of neighbouring particles (e.g. atoms). VIII, 9, 14, 51
- **number average molecular weight** is the statistical average molecular weight of all the polymer chains in the sample, and is defined by

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. VIII, 13, 15, 51

polydispersity or polydispersity index is used as a measure of the broadness of a molecular weight distribution of a polymer, and is defined by

$$M_{WD} = \frac{M_w}{M_n}$$

the larger the polydispersity, the broader molecular weight distribution symbol. VIII, 15, 51

- **polymerization** is a chemical reaction or a process in which individual monomer molecules are combined into long chains of polymers. VIII, 9, 51
- **statistical copolymer** has a monomer distribution which follows some statistical law, for example Bernoulli distribution, which makes the distribution random and hence such copolymers are also called random copolymers. However, statistical copolymers often are referred to as random, independent of statistical law used. VIII, 13, 51
- thermoplastic elastomers sometimes referred to as thermoplastic rubbers, are a class of copolymers or a physical mix of polymers (usually a plastic and a rubber) which consist of materials with both thermoplastic and elastomeric properties. Do not require chemical cross-linking, in order to have elastic properties, hence can be moulded and reused by means of increasing and lowering temperatures. VIII, 11, 51
- **viscoelasticity** is the property of materials exhibiting both viscous and elastic characteristics when deformed. VIII, 9, 14, 18, 33, 51
- vulcanization is a chemical process for converting natural rubber or related polymers into more durable materials by the addition of sulfur or other equivalent curatives or accelerators. VIII, 51
- vulcanizite A vulcanized product. VIII, 9, 46, 51
- weight average molecular weight takes into account the molecular weight of a chain in determining contributions to the molecular weight average and is defined by

$$M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

where M_i is the molecular weight of a chain and N_i is the number of chains of that molecular weight. VIII, 15, 46, 51

1 Introduction

Coloplast Denmark A/S is the Danish subsidiary which markets and sells nursing articles in the areas of ostomy, continents and urology, as well as skin care and wound care. This thesis is put together in collaboration with Coloplast Denmark. The company was started in 1954 by the nurse Elise Sørensen who designed a revolutionary ostonomy bag for her sister who suffered from colon cancer, and today they are leading the market within intimate healthcare. One of the area they specialize in is wounds and skin care for people with difficult to heal wounds such as pressure ulcers also known as pressure sores, bedsores, decubitus ulcers. Such localized skin injuries occur over a bony prominence as a result of constant localized pressure or pressure in combination with shier or friction. Prevention of such injuries is a major focus of intimate healthcare industry. Bandages are used to dress up these type of wounds. Favourable redistribution of pressure is of major importance in manufacturing and usage of such products, since curing or preventing ulcers would increase the quality of life for inordinate amount of patients. In addition, the cost for society for these type of disorders is relatively high, thus improving the care and reducing healing time would also reduce the costs.

Favourable pressure redistribution or pressure relief is dissipating concentrated constant point pressure over the as large area as possible. This is in connection with, for example, preventing bedsores for immobilized patients. When the bandage is applied on top the skin of the patient it lays in between the person and the flat surface of the bed. There will be places on the body which are more pressurized than others and in turn bedsores will be formed. If the material of the bandage has a good pressure relief it will spread this pressure over the larger area, thus easing the pain or otherwise preventing such displeasing wounds.

Every bandage contains a layer of adhesives. When producing adhesives for the medical purposes it is important to take into account certain properties. It has to adhere easily to the skin and be easily removed, have good absorption of fluids, good air permeability and be non-toxic. I am interested in how good balance of these properties is achieved. Adhesives in question are polymer blends, containing several components. One of the most commonly used adhesives in the medical industry is Styrenic Block Copolymer (SBC) - based. In this thesis I study four adhesive components: Elastomer, Tackifier, Plasticizer and Hydrocolloid - which are the ingredients found in Coloplast produced adhesives, by performing two different kinds of experiments. The pressure relief experiments; applying constant point pressure on top of the adhesive layer and measuring the pressure underneath it. To add a dimension to my data I have decided to use different thickness of the adhesive layer and look into how the pressure relief is dependent on the adhesive layer thickness.

The rheological experiments; collecting rheological data for supplementary information on the molecular structures and rheological behaviour. Seven different mixtures of the four adhesive components are studied. The mixtures were chosen on grounds of components included, availability and physical properties. I am interested to know how the ingredients in the mixtures influence they rheological behaviour and capacity for pressure relief. I present quantitative and qualitative analysis of the experimental data, theory pertaining to polymers, rheology and adhesives, and other relevant information as well as ideas ant thoughts for further work.

2 Theory

In this chapter the theoretical background relating to the experimental work is presented. Theory of rheology includes relevant general concepts and formulas and theory precluding to polymer rheology. Theory of polymers induces categorization of polymers and in depth description of the relevant polymer categories. Theory on adhesives includes general characterization of the adhesives and deeper presentation about synthesis, uses and ingredients for the relevant ones, as well as extends polymer theory

2.1 Rheology

Rheology is the science of deformation of matter under the effect of applied forces (external and internal). Deformation is defined as change of the shape and the size of a body due to forces applied. This change can be transient (reversible) or permanent (irreversible). Ability of a reversible change is described by *elasticity* - capacity of the material to store deformational energy and regain its original shape after being deformed. Ideal elastic bodies will instantaneously revert to they original state after the force acting upon them ends, thus deformation energy is recovered (Riedel et al. 2012). Irreversible change may also be described as *flow* and the ability of the material to resist flow is called *viscosity*. Ideal viscous bodies will not revert to they original position then the applied force is removed, thus deformation energy is dissipated and cannot be recovered (Ferry 1980, chapter 1). The goal of rheological measurements is to establish relationship between deformational force or $stress(\sigma)$ and the degree of deformation or $strain(\gamma)$ in the materials which are neither ideal elastic or ideal viscous but rather somewhere in between (Riedel et al. 2012). Such materials are called *viscoelastic* and they exhibit combination of elastic and viscous behaviour thus cannot be completely described by classical theories of elasticity and hydrodynamics. In order to understand viscoelastic materials we first must further familiarize with ideal solids and liquids.

2.1.1 Ideal Solids

Ideal Solids can also be referred to as Hookian solids, purely elastic or ideal elastic bodies. Such materials undergo a fully recoverable deformation, no flow occurs. Consider a cube made of material that behaves as an ideal solid, in figure 2.1 (black contour), which base is fixed to the surface. If a force F is applied to the top of the cube it will obey Hook's law of elastic deformation and will deform to a new position shown in the blue contour. This type of deformation is a shear deformation and is defined as deformation of a body in one direction only. Shear stress (σ) is expressed as a ratio between the force applied F



Figure 2.1: Sketch of deformation of Ideal Solid, black contour shows the initial shape and blue contour denotes a shape after constant force F is applied, du is the deformation which has occurred.

and the area of the top of the cube (figure 2.1) $A = l \times w$:

$$\sigma = \frac{F}{l \times w} = \frac{F}{A} \tag{1}$$

thus the unit of σ is $\frac{N}{m^2}$ or Pascal, *Pa*. It is a measure of internal forces acting within a (deformable) body.

Shear strain(γ) is expressed as a ratio of deformation du and the hight of the cube, h:

$$\gamma = \frac{du}{h} \tag{2}$$

 γ is simply a ratio between two length and therefore unit-less. It is a measure of deformation representing relative displacement of the particles composing the body to its reference length (Barnes et al. 1989).

For ideal elastic material stress is always directly proportional to strain ($\sigma \propto \gamma$) in small deformations and independent of the rate of strain, thus we can write Hook's law in such a form:

$$\sigma = G \times \gamma \tag{3}$$

where G is a constant of proportionality called shear modulus. It has a unit of Pa and describes overall resistance to deformation.

2.1.2 Ideal Liquids

Ideal Liquids can also be referred to as Newtonian liquids, purely viscous or ideal viscous bodies. Such materials will deform as purely elastic, but in this case the deformation will increase at a constant rate, thus the material will flow.

Now again consider a material that behaves as an ideal liquid, figure 2.2, in this case if the force is applied the material will again deform, but the deformation will continuously increase at a constant rate, in other words it will have a constant velocity, v in the direction



Figure 2.2: Sketch of deformation of Ideal Liquid, black contour shows the initial condition and blue contour denotes deformation after some time t a constant force F is applied, du(t) is then the deformation, at time t.

of the force applied. The rate of change of strain is referred to as *shear strain rate* or *shear rate* in short and it is a time derivative of strain:

$$\dot{\gamma} = \frac{\gamma}{dt} = \frac{du}{dt \times h} = \frac{v}{h} \tag{4}$$

It is most commonly denoted $\dot{\gamma}$ and has a unit of inverse time $\frac{1}{s}$. For ideal viscous materials stress is always directly proportional to shear rate ($\sigma \propto \dot{\gamma}$) and independent of strain itself, which is in accordance with Newton's law:

$$\sigma = \mu \times \dot{\gamma} \tag{5}$$

where μ is a constant of proportionality called viscosity. It has a unit of Pascal seconds Pas and describes the resistance to flow.

2.1.3 Viscoelastic materials

As mentioned before most of materials do not behave as purely viscous or purely elastic, nonetheless many solids and liquids approaches ideal behaviour for infinitesimal strain or rates of strain respectively, in such materials vicsoelastic anomalies often are negligible or of minor significance. If the solid/liquid is comprised of atoms/small molecules it is easy to see that forces relevant for the displacement is quite local in character, therefore the behaviour is predictable solely from knowing inter-atomic potentials or intermolecular interactions (Ferry 1980, chapter 1). In polymeric systems, not only the average volumes of the molecules are much grater than atomic dimensions, but they also are able to change contour shapes and its configurations, resulting in various long and short range interactions which are much more complex then interactions of small molecules. This complexity results in mechanical response which is dominated by viscoelastic phenomena even if both strain and rate of strain are infinitesimal (Ferry 1980, p. 1-4).



Figure 2.3: Sketch illustrating applied oscillatory Strain and resulting Stress for (a) Ideal Solid $\delta = 0$, (b) Ideal Liquid $\delta = 0.5\pi$ and (c) Viscoelastic material $\delta = 0.1\pi$

In other words viscoelastic materials combines solid-like and liquid-like characteristics. To illustrate this we could imagine a body made of a material which is not quite purely elastic, but rather solid-like viscoelastic. If we apply oscillatory strain $\gamma(t) = \gamma_0 \sin(\omega t)$ to such a body, the resulting sinusoidal stress would not be exactly in phase with strain as it would in ideal solid shown in figure 2.3 (a), but instead $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$, where $\delta > 0$. That means if such a body is constrained at constant deformation, the stress required to hold it diminishes gradually, or relaxes. In ideal liquids stress and strain are exactly 90° out of phase as shown in figure 2.3 (b). However, liquid-like viscoelastic material, while flowing under constant stress, recovers part of its deformation when stress is removed, which means that under oscillatory strain resulting stress would again be $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$, where $\delta < 90^\circ$. In viscoelastic materials part of the energy input is stored and recovered each cycle and part of it is lost as heat, resulting in $0 < \delta < 90^\circ$ as shown in figure 2.3 (c).

Since the phase angle δ appears somewhere between elastic and viscous extremes by using trigonometric relationship we can conveniently separate stress signal into two components: elastic stress (σ') - which is in phase with strain and measure the degree to which the material behaves as an ideal solid; viscous stress (σ'') - which is in phase with rate of strain and is a measure of the degree to which material behaves as an ideal liquid:

$$\sigma(t) = \left(\frac{\sigma_0}{\gamma_0}\cos(\delta)\right)\gamma_0\sin(\omega t) + \left(\frac{\sigma_0}{\gamma_0}\sin(\delta)\right)\gamma_0\cos(\omega t) \tag{6}$$

In the limits for liquids ($\delta \rightarrow 90^{\circ}$) and solids ($\delta \rightarrow 0$) equation 6 is in accordance with equations 3 and 5, however in viscoelastic regime the coefficients of proportionality becomes a function of frequency (ω) (or alternately time) but not elapsed time (stress magnitude). Rewrite equation 6 in terms of coefficients:

$$\sigma(t) = G'\gamma_0 \sin(\omega t) + G''\gamma_0 \cos(\omega t) \tag{7}$$

we define storage (G') and loss (G'') moduli and the complex shear relaxation modulus $G^*(\omega)$ in terms of its real and imaginary parts:

$$G' = \frac{\sigma_0}{\gamma_0} \cos(\delta) \tag{8}$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin(\delta) \tag{9}$$

$$G^*(\omega) = G' + iG'' \tag{10}$$

Another useful parameter is loss tangent $(\tan \delta)$ which is a measure of the ratio of energy lost to energy stored during cyclic deformation:

$$\tan(\delta) = \frac{G''}{G'} \tag{11}$$

Until now viscoelastic behaviour is explained by means of shear deformation, however it need not be such a deformation.

Generally deformation at a given point can be specified by the strain tensor, which then represents the changes in dimensions and angles in the three Cartesian coordinates (see figure 2.4a).

$$\gamma_{ij} = \begin{bmatrix} 2\frac{\partial u_1}{\partial x_1} & \frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_2} & \frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3} \\ \frac{\partial u_2}{\partial x_1} + \frac{\partial u_1}{\partial x_2} & 2\frac{\partial u_2}{\partial x_2} & \frac{\partial u_3}{\partial x_2} + \frac{\partial u_2}{\partial x_3} \\ \frac{\partial u_3}{\partial x_1} + \frac{\partial u_1}{\partial x_3} & \frac{\partial u_2}{\partial x_3} + \frac{\partial u_3}{\partial x_2} & 2\frac{\partial u_3}{\partial x_3} \end{bmatrix}$$
(12)

Where $u_i = x_i - x_i^0$ the difference between final and initial positions of the respective plane. The rate of strain (γ_{ij}) and stress (σ_{ij}) can be defined with equivalent tensors. Where $u_i = v_i = \frac{\partial u_i}{\partial t}$ for the rate of strain, and components of stress describes the force (in *j* direction) per unit area acting on the face perpendicular to (*i*), see figure 2.4b. Suitably defined relationship between stress tensor and strain or rate of strain tensors can formulate relationships for different deformations. If both strain and rate of strain are infinitesimal and the time dependent stress to strain relationship can be described by linear differential equations with constant coefficients, as seen previously for shear deformation (see equation 7), we have linear viscoelastic behaviour. Such equations are called *constitutive equation* or alternatively, *rheological equations of state* (Ferry 1980, Barnes et al. 1989). Most strainghtforward examples are equations 3 and 5 for pure solid and liquid behaviours. Depending on the nature of deformation different coefficients of proportionality of constitutive equations are defined. These coefficients are often called elastic moduli. In viscoelastic materials moduli are functions of frequency (alternatively

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(a) Cartesian coordinates 1 2 and 3 (b) Components of the Stress tensor

Figure 2.4: Sketch illustrating cubical element and its 3 Cartesian coordinates and corresponding components of the stress tensor σ_{ij}

time, a periodic experiment at frequency ω , is equivalent to a transient experiment at time $t = \frac{1}{\omega}$) as shown previously for shear relaxation modulus. There are three different kind of deformations which are most common: tensile, bulk and shear. The simplest example is tensile deformation which occur when stretching or compressing the object along one of the axes, ability of the material to deform in such way is described by the *Young's modulus* (or sometimes just called elastic modulus), commonly denoted E. Bulk deformation occur when the object is subjected to uniform load from all of the directions, material capacity to deform in all directions is described by the *Bulk modulus*, commonly denoted K. Bulk modulus is an extension of Young's modulus in three dimensions. Similarly, as shown previously, *Shear modulus* defines materials ability to deform under shear stress, and it is denoted G.

Considering the directions and angles of such deformations the stress and strain tensors can be simplified. For example, for simple extension the only change in shape is occurring along the axis of applied stress, therefore the tensile strain is $\gamma_{ij} = \gamma_{11}$, for convenience practical tensile strain is defined as $\epsilon = \frac{1}{2}\gamma_{11} = \frac{\partial u_1}{\partial x_1}$, then the equation for tensile stress(σ_T) is:

$$\sigma_T(t) = \epsilon E(t) \tag{13}$$

In turn Young's modulus is defined as a ratio of tensile stress to strain:

$$E(t) = \frac{\sigma_T(t)}{\epsilon} \tag{14}$$

Bulk and Shear moduli are defined in a similar way with. Simple elongation experiments are easy to perform, however such deformation include both change in shape and volume, whereas shear is a deformation of shape at constant volume, which is convenient, since simultaneous changes in shape and volume make the behaviour more difficult to interpret on the molecular basis (Ferry 1980, p. 24-26). Bulk compression does not involve

changes in long-range molecular configuration or contour shape (only change in volume) and therefore differences between ordinary liquids or solids and polymeric materials are not as distinct as, for example in shear. Therefore when investigating the mechanical behaviour of polymeric materials, shear deformation experiments are most convenient. However, it is clear that the three moduli are not independent of each other. Provided deformations are small Young's and Shear moduli can be used interchangeably:

$$E(t) = 3G(t) \tag{15}$$

However, this equation is only valid if *Poisson's ratio* $\mu \approx \frac{1}{2}$, which is typical in polymeric systems. Physically it means that change in volume is negligible in comparison with the change in shape (in simple extension).

2.2 Polymers

Polymers are large molecules, composed from many repeating subunits called monomers and are produced through the process of *polymerization*. Polymers can be natural (also called biopolymers) or synthetic. Examples of biopolymers includes DNA, wool, amber, natural rubber and many others. Synthetic polymers are used to make paints, packaging films, clothing, household plastics, adhesives and many other common objects. One useful way to categorise polymers is by functional behaviour, diagram illustrating this is shown in figure 2.5. Two main categories are *plastics* and *elastomers*. Some plastics can be formed into *fibres* which, one could argue, is a category on its own due to different mechanical characteristics, however this is of little relevance in this case. Difference in mechanical characteristics between elastomers, fibres and plastic is shown in figure 2.6. This various mechanical behaviour is achieved by appropriate combinations of *crystallinity*, *crosslinking*, T_g and T_m (Odian 2004, p. 33).

Plastics represent very large group of polymers and range from highly flexible (typical elongation 20 - 800%) to rigid (typical elongation < 0.5 - 3%), have wide range of T_m and T_g and moderate to high crystallinity. Typical elastic modulus for such materials are 15 000 - 350 000 N cm⁻². On the other hand to be useful as a fibre a polymer must be very highly crystalline and contain polar chains with strong *intermolecular forces*. In turn fibres undergo only low elongations (<10 - 50%) and have characteristic T_g (intermediate) and T_m (200 - 300°C)(Odian 2004, p. 34-36).

In production of adhesives, polymers of importance are elastic polymers or elastomers. Such polymers, among other things, are necessarily viscoelastic and term rubber are often used interchangeably, however rubbers are preferred term for *vulcanizites*. elastomers are completely (or almost completely) *amorphous* and have low intermolecular forces, consequently they easily undergo very large, reversible elongations ($\leq 500 - 1000$ %) and

have low initial elastic modulus (< 100 N cm⁻²) which increases rapidly with increased deformation. Typical T_g is low, usually below 0°C. Elongations of flexible plastics can be similar to those of elastomers, however they differ in a way that only a small portion of it (approximately <20%) is reversible, hence plastics will retain the deformed shape after stress is removed (Odian 2004, p. 34-36).



Figure 2.5: Classification diagram of polymers, relevant ones in colour.

Under normal conditions molecules forming the elastomer are randomly coiled. Upon stress the molecules will straighten out in the direction of the force and upon release molecules will return to they random compact position as shown in figure 2.8, hence rendering the material easily stretchable and elastic. However any macroscopic material is composed of very large number of polymers and any unrestricted relative movement of molecules will result in permanent deformation. Restriction of such movements can be achieved through cross-linking otherwise known as curing. Cross-link usually refer to ionic or covalent bonds between either monomers in the polymer or the polymers themselves. elastomers in which structural transformation is achieved by chemical cross-linking are thermoset elastomers (TSEs) (see figure 2.5) and are often referred to as rubber. To illustrate this figure 2.7 shows molecular structure of polyisoprene (natural rubber) after cross-linking. Sulphure cross-links are made through the process know as vulcanization. Elemental sulfur creates chemical cross-links between individual polymers, which allows



Figure 2.6: stress-strain plots for a typical elastomer, flexible plastic, rigid plastic, and fibre. Elastic modulus of a polymer is the initial slope of such a plot. Taken from (Odian 2004, p. 33)

for better durability. Materials become less brittle, deforms harder, since the cross-links restricts the molecules from moving independently, relative to each other, and consequently polymers snap in they original position, avoiding permanent deformation (see figure 2.8). Curing systems most commonly used for chemical cross-linking are sulfur systems, peroxides, metallic oxides, acetoxysilane and urethane cross-linkers (Odian 2004). Once cross-link is formed it is stable mechanically and thermally, hence this process is irreversible and once polymer is vulcanised it will stay in that state.



Figure 2.7: Schematic representation of two strand of polyisoprene after vulcanization with elemental sulphur, cross-links are created between the two strands.

A class of polymers known as thermoplastic elastomers (TPE) (see figure 2.5) do not require chemical cross-linking, structural transformation is achieved though physical pro-



Figure 2.8: Elastomer in the equilibrium state (A) and under stress (B), showing the stretching of individual molecular chains. The dots represent cross-links.

cess as a result of their two phase morphology, which can be described as a physical cross-linking. This is a consequence of morphological differences between the two blocks in the multi-block *copolymer*. One of the blocks is flexible and long and the other is rigid and short figure 2.9 shows such an arrangement. There are several types of TPEs which are shown in figure ??, however in this thesis I investigate styrenic block copolymer (SBC) based pressure sensitive adhesives (PSAs). As mention earlier in section 2.4 there are two common SBCs used in adhesive production:styrene-isoprene-styrene (SIS) and styrene-butadiene-styrene (SBS).



Figure 2.9: Schematic structure of Block copolymer

It is worth to mention that TPEs have important practical advantage over TSEs since there is no need for the additional chemical cross-linking reaction, which means that fabrication of objects is achieved on conventional equipment for thermoplastics. The transition from a molten polymer to a solid, rubbery product is much faster and takes place simply on cooling. There are significant advantages in recycle times, the ability to recycle



Figure 2.10: Classification diagram of Thermoplastic Elastomers

scrap, and overall production costs. However, thermoplastic elastomers generally are not as effective as chemically cross-linked elastomers in solvent resistance and resistance to deformation at high temperature (Odian 2004, p. 142).

2.2.1 Styrenic Block Copolymers (SBC)

Polystyrene is a typical rigid plastic although completely amorphous it has bulky rigid chains due to phenyl-phenyl interactions. Commercial polystyrene have *number average molecular weight* in the range of 50,000 - 150,000. It is good electrical insulator, has excellent optical clarity, possesses good resistance to aqueous acids and basis. Limitations include poor weatherability, brittleness, has poor impact strength due to stiffness of polymer chains. These problems can be decreased with suitable additives. Copolymerization and polymer blends are broadly used to increase usefulness of polysyrene. Copolymerization involves polymerizing a mixture of two monomers and the product contains both monomers in the polymer chain. It can be *alternating*, *statistical*, *graft* or *block* arrangement depending on the detailed chemistry of the specific monomers and reactions conditions, however only block copolymers are of interest in this thesis. Polystyrene can

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be useful not only as plastic but also as elastomer, copolymerization with butadiene and isoprene leads to elastomertic properties and are broadly used as common elastomers for commercial purposes. All the elastomeric styrene products are copolymers or blends; none are homo-polystyrene (Odian 2004, p. 303, 465).

Molecular structure of two SBCs SIS and SBS can be seen in figure 2.11. They both contain polystyrene as a rigid block in both ends of copolymer. Commercially produced SBCs contains short polystyrene blocks on each side of a long elastomeric block (isoprene or butadiene) x, z < y (trade names: Cariflex, Kraton, Solo-prene, Stereon). Di-block copolymers do not exhibit good elastomer behaviour, tri-block structure is needed for the elastic block to act as physical cross-link between two rigid ends (Odian 2004, p. 434).



(a) Molecular formula for SIS: Polystyrene-block-polyisopreneblock-polystyrene

(b) Molecular formula for SBS: Polystyrene-block-polybutadieneblock-polystyrene

Figure 2.11: Styrenic tri-block copolymers with rigid styrene ends (x,z) and elastic middle marts (y)

2.3 Polymer Rheology

Different regimes that occur in polymeric solutions can be described as dilute, semi-dilute and concentrated. In dilute solution polymer chains do not interact with each other and *viscoelasticity* is caused by properties of individual polymer molecules. When the total volume occupied by the molecules increase beyond the available space in solution it is said to enter semi-dilute regime. In such solution polymer molecules begin to entangle with each other and viscoelasticity is now also dependent on intermolecular interactions. For concentrated solutions the interactions between multiple polymer coils controls the rheological behaviour. Polymer melts are only comprised of the polymers themselves and are similar to concentrated solutions, hence the rheological behaviour is also dependent on the interactions between multiple coils.

Furthermore, rheology of the adhesive is influenced by polar functional groups, co-monomers, side chain length, cross-linking, molecular weight and molecular weight distribution.

To fully categorize a polymer macrostructure as well as the microstructure contributions must be known. The macrosructure can be categorised by *weight average molecular weight* (M_w) , number average molecular weight (M_n) molecular weight distribution $(M_{WD} = M_w/M_n)$ and branching (Benedek 2000).

In viscoelastic systems (i.e. polymer melts) the time scale or the frequency for witch shear force is applied is a significant factor. It determines the dominance of elastic or viscous behaviour. General rheological plots of polymer solution is illustrated in figure 2.12.



Figure 2.12: General curves of viscoelastic behaviour for shear deformation of polymer solutions as a function of frequency

This kind of data is useful since it can give insight into molecular structure and also help differentiate between thermoplastic polymer melts and polymers with cross-linked molecular structure. The cross-over between rubbery plateau and terminal region gives information about molecular weight distribution M_{WD} , which is also often called *polydispersity* and weight average molecular weight, M_w . The larger the M_w the lower the frequency at witch cross-over occurs. Similarly, the lower the M_{WD} the higher the values of G' at cross-over. At time scales of rubbery region polymer chains manage to come out of entanglements that give rise to tension between the coupling points and consequently elastic behaviour dominates. At high frequency cross-over up to transitional region and at the glassy region the ability of volume elements to irreversible change places starts to diminish and polymer is principally immobile, G' increases until is well above G'' at the glassy region. Elastic response suppresses viscous one. At frequencies from 0.01 to 100 Hz (which are the time scales of importance), non cross-linked thermoplastic polymer melts exhibits behaviour of terminal region, whereas cross-linked polymers rendered immobile by their cross-links exhibits behaviour of the glassy region(Schramm 1998).

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2.4 Adhesives

Generally adhesive is defined as a substance which when applied to a surface or surfaces of materials joins them together and resist separation. This type of assembly is called adhesive joint or adhesive bond (Nicholson et al. 1991, BSA, Pocius 2012). Materials in such a bond, other then adhesive itself, are called *adherents* or *substrates* (Pocius 2012). The first compound adhesive is believed to be used by prehistoric people as early 70 000 years ago in South Africa. The ability of stone age people to use and produce adhesive lead to innovation and development of new tools. More recent examples of adhesive use dates back to Babylonians (ca. 6000 years ago), archaeologist discovered evidence of the use of bituminous cement in statues of Babylonian temples (Pizzi & Mittal 2003). In 1991 the discovery of the "Tyrolean Iceman" or "Oetzi" who lived ca. 5200 years ago relieved the use of pitch, which is derived from tar by means of heating, for production of tools (Sauter et al. 2000). Later literature mentions of adhesive use was by Egyptians (ca. 1500 BCE), which reveal plant and animal glue was widely used for variety of tasks such as bonding and lamination of artefacts(e.g. weapons and furniture), wood gluing caskets, bonding of papyrus to clothing etc (Pizzi & Mittal 2003). Next great contributions to adhesive development comes from Greeks and Romans (ca.1 -500 AD) who developed the production of various kinds of animal glue. Wood veneering developed, Romans used wood glues as sealants for boats and ships, cement was used for building (Pizzi & Mittal 2003). About 1000 AD in Mongolia exceptional weaponry was produced, bows and arrows of laminated lemon-wood and bullhorns bonded with adhesives, which contributed to Genghis Khans extraordinary army power. By the same token Antonio Stradivarius (ca. 1700) musical instruments were exceptional because of the adhesive process used to laminate his specially treated woods (the process is still unknown today)(Nicholson et al. 1991, BSA). In 1690 first commercial glue plant was open in Holland which facilitated the widespread use of adhesives. Later the 20th century brought the plastic revolution with the production of Bakelite phenolic plastic in 1910, which started the era of synthetic chemistry. The synthetic resin adhesives were developed and with development of technology and chemistry followed the development of many different types and variations of adhesives (Nicholson et al. 1991, BSA). Even though people seemingly been using glue-like substances since the dawn of humankind the real progress in adhesives been made in the last hundreds years.

Consequently there are many different types of adhesive materials therefore specifying the type is required. One can specify the type of adhesive in many different ways, such as by their physical form e.g. *liquid adhesive, film adhesive, chemical properties e.g. epoxy, cyanoacrylate adhesives, materials bonded e.g. paper, wood, metal adhesives* or conditions of use e.g. *hot-melt, cold-hardening, solvent-based* (Pocius 2012, p. 1-14). These types

of categorisation is often most convenient when adhesive have to be used. However in research more systematic way of grouping is necessary.

Adhesives can be both organic and inorganic materials. There are many types of familiar inorganic adhesives such as cement or solder (Pocius 2012, p. 21), however in this thesis I will not be talking about such inorganic materials. Rather the adhesives discussed are entirely based on organic materials. Since there is such a great variety of organic materials and compounds saying that adhesive is of the organic kind does not really narrow it down. Another major way to specify adhesives in two groups is reactive and non-reactive adhesives. Reactive adhesives are those which achieves adhesion by the means of chemical reaction. There are two types of such adhesives, *multi-component* adhesives, which harden by mixing two or more components and consequently changes chemical composition leaving adherents intact, and *one-component* adhesive which requires outside energy source such as heat or radiation to harden via chemical reaction. Again in this thesis I am not concerned of such adhesives. Non-reactive adhesives can be further categorised by cure or application condition. Some examples of such types are *hot-melt* adhesive, which requires high temperatures while applying and solidifies upon cooling, *drying* adhesives which are solvent based or emulsion adhesives, cures by removal of solvent e.g. water, PSAs - which only requires pressure to adhere to the surfaces. PSAs are used in the medical industry as an adhesives for bandages and therefore are the focus of this thesis, next subsection describes such adhesives in depth.

2.4.1 Pressure-sensitive Adhesives (PSA)

In the last decades (since 1960) with the growing demand for technology application field of PSA has been very enlarged. For such products special recipes and technologies has been developed. It is used in wide variety of fields such as aerospace, automobile, wood products industries, home construction, manufacture of furniture and cabinets (especially for laminates), electronics including microelectronics for construction of integrated circuits and generation of electronic devices, medical industry for intimate care products, especially tapes for bandages and etc (Benedek 2000, Pocius 2012). PSA are adhesives witch has a permanent tack, which meant that they remain sticky when dried or cured, that makes them capable of bonding to surfaces simply by the application of light pressure which also makes products very convenient for consumer use.

The pressure sensitive Tape Council has defined pressure-sensitive adhesives as materials with the following properties (Pocius 2012, p. 273-274):

- A. Aggressive and permanent tack
- B. Adheres with no more than finger pressure
- C. Requires no activation by any energy source

- D. Has sufficient ability to hold onto the adherent
- E. Has enough cohesive strength to be able to be removed cleanly from the adherent

TACKIFIERS

Firstly, condition A "aggressive and permanent tack" requires the PSA to have *tack*. Tack can describe various phenomena (Pizzi & Mittal 2003, p. 824):

- wet tack ability of the adhesive to form a bond while still wet
- **green tack** ability of certain polymers (specifically rubbers) to bond to themselves for several hours after drying, even though the surfaces do not feel sticky
- **pressure-sensitive tack** ability of a dried film to bond firmly to surfaces under light pressure

Pressure-sensitive tack is the phenomenon of importance here, and from here on it will be referred to simply as tack. In the older rubber-resin systems tack arises from the presence of two-phase system. Disperse phase acts as viscous liquid that adheres to the surface while elastic phase provides strength and continuity to the system. However, modern systems can produce aggressive tack from a single component. Thus it is believed that tack can also stem from the viscoelasticity of polymers themselves, allowing them to conform to the adherent even in the dry state. Therefore, a fundamental requirement for tack is a glass transition temperature substantially below the application temperature to permit the necessary degree of flow (Pizzi & Mittal 2003, p. 825). Polymers of such abilities are called *Tackifiers*. Tackifier is one of the key ingredients when producing a PSA.

ELASTOMERES

Secondly, conditions D and E requires a delicate balance of properties such as cohesion and tack since it has to have "ability to hold onto" and "be removed cleanly" of the substrate. Cohesion is achieved with another key ingredient to PSA -an elastomer. An elastomer is a viscoelastic polymer, with weak intermolecular forces, thus having high relative failure strain. Elastomers are amorphous, existing above their glass transition temperature, therefore considerable segmental motion is possible (see section ??). An elastomere is a base ingredient to the PSA. The majority PSA are produced with three types of base elastomer (Pocius 2012, p. 275-277):

Natural Rubber Natural rubber (NR) is poly(*cis*-isoprene) and is obtained as a natural latex from the Hevea rubber plant. The chemical structure is shown in figure 2.13. It was the first material to gain the widespread use as a basis for PSA. Advantages

of such elastomer is low cost and high peel strength, however its disadvantage is that it has an unsaturated bond in the backbone (see figure 2.13), making it easy to cross-link, hence it would become yellow and brittle.

- Acrylates 2-ethylhexyl acrylate and iso-octyl acrylate are two primary acrylates, these examples can be seen in figure 2.13. These type of polymers usually do not require tackifier to be made into PSA. Pressure sensitive characteristics usually results from the inherent physical properties of the polymer. These type of elastomers are considerable more expensive than natural rubber, however have outstanding shelf-life.
- **Block copolymers** Typical block copolymers have A-B-A block structure of isoprene with styrene or butadiene with styrene, examples shown in figure 2.13. they are less expensive than acrylates, but unsaturation in the B block which, as to natural rubber, gives them oxidative instability and short shelf-life.
- Other elastomeres There are several other types of PSA, which are used for more specific tasks. A few examples are silicone, poly(iso-butylene), polyvinyl ethers, and polybutadiene based PSA (examples shown in figure 2.13). Silicones have inorganic backbone but are surrounded by organic groups, they must be tackified and crosslinked to have sufficient PSA performance. Silicone-based PSA are by far most expensive. Poly(iso-butylenes) are resistant to oil and have low moisture permeability, however they are difficult to cross-link (thus exibit poor shear properties) and have limited shelf-life. Polyvinyl ethers are used as blend of high and low molecular weight polymers and font need to be tackified. Polybutadienes have simultanious low glass transition temperatures and good electrical properties and its mostly used in electrical tapes (Pocius 2012, p. 276).

NR-based and Acrylate-based PSA usually need to be cross-linked to meet all the requirements for PSA mentioned above. Block copolymer-based PSA obtains its cohesive strength through phase separation which acts as a physical cross-link rather than chemical one (Pocius 2012, p. 286).

BALANCE OF PROPERTIES

For production of sufficient PSA it is critical to choose the correct ratio of its components¹, since all of the five characteristics must be fullfilled. Achieving this balance is the main goal of the formulator. Desirable properties are quick "wetting" (tack), enough resistance to peel and enough shear to hold on. Figure 2.14 shows the general characteristics for the

¹acrylates does not necessarily need to mix with a tackifier due to inherent characteristics of the polymer (Pocius 2012)



Figure 2.13: Basis Elastomers, taken from (Pocius 2012, p. 274)

elastomer (NR-based) to tackifier ratio for the three properties mentioned (Pocius 2012, p. 296). Certain classes of teckifiers work better with certain elastomers. For example with block copolymers, aromatic tackifiers with high melting point in small quantities stiffen the product, which improves its heat and shock resistance whilst aliphatic tackifiers of low melting point improve tack and low-temperature flexibility. In general, tackifiers with solubility parameters similar to those of the elastomer selected (if block copolymer selected than mid block phase(Benedek & Feldstein 2009, p. 102)) are most likely to perform sufficiently (Pizzi & Mittal 2003, p. 828). Figure 2.15 shows the schematics of microphase-separated block copolymer-based PSA, with a compatible tackifier. Number of other ingredients can be added to the mixture such as plasticizers or softeners for flexibility, stabilizers or antioxidants, especially in products containing unsaturated bonds, thickeners or thixotropes may be used to alter rheology, fillers, curing agents, solvents, biocides, pigments and other additives for customization of product features (Benedek & Feldstein 2009, p. 47). If plasticizers are added their compatibility with adherent have to be considered to ensure no transfer of the adhesive as well as compatibility with elastomer (for copolymer, plasticizer must be compatible with diene mid-block rather then the polystyrene end, in figure 2.15 plasticiser should lie in the same area where the

tackifier is)(Pizzi & Mittal 2003, p. 830). When formulating a PSA specific application must always be kept in mind in order to choose the most fitting ratio of constituents.



Figure 2.14: Diagram of the relationship of performance properties to the elastomer-to tackifier (ruber-to resin) ratio in a NR-based PSA. Note that the highest value of each performance property is not obtained at the same ratio. Optimum performance of a PSA is obtained with the best balance of properties that is required for application intended. Cross-linking is assumed to be constant. Taken from (Pocius 2012, p. 296)



Figure 2.15: Schematic drawing of a microphase-separated block copolymer-based PSA. Plasticizer would be were tackifier is. Taken from (Benedek & Feldstein 2009, p. 102)

2.4.2 Production of PSA for Bandages

In this thesis I investigate tri-block copolymer(SIS) based PSA, from here on adhesive will refer to this specific type unless stated otherwise. Major application of such adhesives are tapes, which may be classified according to the application area, such as packaging electrical or medical (Benedek & Feldstein 2009, p. 832). I am interested in medical applications, and in this section I will try to specify requirements for production of such

tapes and in turn products including them. In this case I am considering bandages, since that is the area where this tape is used.

There are several criteria for production of PSA for bandages:

- 1. Adhesion must stick to the skin
- 2. Removal have to be easy to remove from skin and do not leave residues or sores
- 3. Toxicity materials must be non toxic or hypo-allergic
- 4. Fluid Handling must be able to absorb or permeate wound exudate and sweat
- 5. Cohesion

Criteria 1, 2, 5 were already discussed in some detail in section 2.4.1. Tack, peel and shear balance should be such that it adheres to the skin and stays on until removal, which should not inflict pain or other uncomfortable sensation as well as adhesive should stay intact upon removal. Criteria 3, 4 arises because the bandage have to be applied to skin and be in contact with a person for extended period of time. As mentioned in previous section the key two ingredients in PSA are elastomer and tackifier, however usually (and in this case necessarily) additives are included in order to enhance particular features or add properties that is required for specific applications.

Adhesives for intimate healthcare are delicate products, hence often require many ingredients thus it is inevitable that it has to be a polymer blend. Polymer blends are compositions of chemically different polymers. They can be homogeneous if the components are compatible and mix at molecular level, and heterogeneous or incompatible if the components are present in separate phases, in such case the minor component is usually dispersed in a matrix of the dominant component(Sadiku-Agboola et al. 2011)(*Understanding Rheology of Thermoplastic Polymers* n.d.). In case of adhesives for Coloplast bandages besides the elastomer (SIS) and tackifier (aliphatic) there are two additives present:*plasticizer* and *hydrocolloid*. Plasticizer is added in order to improve flexibility of the adhesive tape since the surfaces where it should be applied (skin) have curved and irregular surfaces. Both tackifier and plasticizer are compatible with elastomer and mix homogeneously. Hydrocolloid is added in order to solve the problem of fluid handling. Hydrocolloids are incompatible and mix heterogeneously with other ingredients.

3 Materials

For the general description of adhesives refer to section 2.4. In this section the adhesive mixtures used for the experiments will be described. One of the more known and popular "Coloplast" products is bandage brand "Compeed". "Compeed" are small bandages for small blisters and sores, for example on the lips or feet. Because of usage for less severe wounds and sores it is small sized and is made only from PSA layer and some microfilm. It has only a few parts and it can be considered as a simple example of bandage. Main components of PSAs are described in detail in sections 2.4.1 and 2.4.2.

The possible components of 'Coloplast' adhesives are: elastomer, Tackifier, Plasticizer and Hydrocolloid (see section 2.4).

Elastomer used in Coloplast products is block SIS. Plasticizer and tackifier both mix homogeniously with elastomer and are both hydropgobic, hydrocolloid are hydrophilic and mix heterogeniously with the other ingredient. the adhesives are polymer melt.

'Compeed' adhesive includes all of these components and is used as a starting point, then minor variations to the adhesive mixtures are done to investigate the influence of various additives. Seven different adhesive mixtures are tested for the purposes of this thesis. I call all of the test materials for adhesive mixtures, when in fact it is not entirely accurate. In section 2.4 I have defined adhesives as PSAs, which then in fact necessarily requires tackifier (except for acrylates) and not all of the samples include that. The word mixture is also a little misleading, all of the samples are polymer melts, however not all of them are mixtures, for example number 5 is actually just SIS. However for all intensive purposes I will call these samples adhesive mixtures or just mixtures. Descriptions of mixtures used in the experiments are listed below and summarised by ingredients in table 1.

- mixture 1 Standard "Compeed" adhesive, used for most sold Compeed products and contain the four main ingredients. it is opaque in colour
- mixture 2 Same as mixture 1, but without hydrocolloid, appearence is less opaque than 1, but very similar
- mixture 3 Same as mixture 1, but contains 20 % more hydrocolloid, than mixture 1.
- mixture 4 Same mixture, but without hydrocolloid. SIS used for this adhesive has a lower molecular weight, it is very sticky and quite transperant.
- mixture 5 The pure tri-block copolymer used in mixture 1, opaque

mixture 6 Only contains the tri-block copolymer and plasticizer

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mixture 7 Adhesive similar to mixture 4 with hydrocolloid but with no plasticizer. So instead of plasticizer, a large amount of mineral oil has been added, which makes the adhesive very soft

Table 1 is an overview of ingredients for the seven mixtures.

Table 1: Adhesive mixtures described by their constituents, (+) if it is present in the mixture (-) if it is excluded, special changes/substitutions described in parenthesis. Lower molecular weight of polymer indicated by $(\downarrow M)$ additional material indicated by percentage.

	Polymer	Tackifier	Plasticizer	Hydrocolloid
Mixture 1	+	+	+	+
Mixture 2	+	+	+	—
Mixture 3	+	+	+	+ (+20%)
Mixture 4	+ (↓M)	+	+	_
Mixture 5	+	_	—	—
Mixture 6	+	_	+	—
Mixture 7	$+$ (\downarrow M)	+	– (+ mineral oil)	+

4 Methods

In this section I will describe the methods and materials used to obtain the data. In this projects I use two types of data, the pressure dissipation trough the layer of the specific adhesive which is presented in subsection 4.1 and rheological measurements made with parallel plate rheometer are presented in subsection 4.2. Pressure measurements are made by "Tekscan Pressure Measurement System 7.60-13I" device and rheological data are collected on Haake RS600 and Haake RS6000.

4.1 Pressure measurements

In this subsection the method of preparing and measuring samples for the pressure relief experiments with some raw data examples and description of the equipment will be presented. The chemical composition of the samples and the preliminary preparation can be found in section 3. The information about the device is taken from the device manual produced by manufacturer.

4.1.1 Device and Data

The measurements for the pressure relief are made by the "Tekscan Pressure Measurement System 7.60-13I" device, which is capacitive tactile sensor. The information about the device is taken from the device manual produced by manufacturer. It uses electrical property capacitance, that is the ability of the object to store electrical charge, to measure pressure applied. A simple example of two electrodes with some area separated by the distance d is shown in figure 4.1. If air gap decreases capacitance C goes up. The sensor pad is build by separating the electrodes using a proprietary compressible dielectric matrix, which acts like a spring. The electrodes are arranged as orthogonal overlapping strips. A distinct capacitor is formed at each point where the electrodes overlap (see figure 4.2). By selectively scanning a single row and column, the capacitance at that location, and thus the local pressure, is measured.



Figure 4.1: Capacitance



Figure 4.2: electrode arrangement in the sensory pad



Figure 4.3: Sensory pad of pressure measuring system

A sensory pad show in figure 4.3 consist of a (27.3×27.3) mm plate with 1936 capacitors/detectors which are arranged in 44 rows and 44 columns. Row and column spacing is 0.635 mm, each detector then correspond to an area of 0.403 mm². The output of the data is 44 × 44 matrix with local pressure readings in Pa. Raw data can be illustrated by a matrix and a contour plot can be made directly from the matrix values. This is shown in figure 4.4. The example below shows contour plots of two samples one dissipates pressure better then other, which can be impatiently seen from these two plots, all the other things being equal. (25×25)

After data is collected all the further analysis is done with MATLAB R2017a software.

4.1.2 Sample Preparation

All the samples are prepared by the same method. The adhesive mixtures are prepared beforehand (see section 3). In order to test the pressure relief of different adhesive mixtures different thickness of samples are prepared. 10-30g of adhesive is weighted and put under



(a) Example data matrix, with pressure values in Pa (only non-zero part of the matrix)



(b) One of the softer materials (mix- (c) One of the harder materials (mixture 4) at thickness of 1.46 mm ture 6) at thickness 1.50 mm

Figure 4.4: Examples of the raw data, in the quantitative and qualitative matter, all measured after 15 min.

the heat press with a setting of chosen specific thickness. Afterwards a layer of soft and flexible microfilm (15 μ m Poly-urethane film) is applied on both sides of the adhesive in order to avoid it sticking to the measuring device. Then the samples are cut into a 25 × 25 mm squares and the specific thickness of each sample is measured with electronic thickness measuring device.

4.1.3 Measurement

One end of sensory pad is connected to a computer and the other end is fastened to the metal block. The sample is put on sensory pad. Second metal block which weighs 1085.5 g. and has a small round sliver sticking out in the center of it of 8 mm in diameter, crude sketch of it is shown in figure 4.5. When this block is put on top of the sample only the round slice is in contact with the sample. Following sample contact with the block pressure data is collected by the computer. Data on all of the samples is collected every minute for fifteen minutes. Some samples were tested up to 60 min and one sample





of each mixture were tested overnight in order to determine appropriate time. Figure 4.6 shows area versus time, for 3 different adhesive mixtures. As it can be seen area is not constant, however it tends towards a constant after some time. The example of soft mixture (4) comes to the constant area almost immediately, which makes it almost time independent, however mixture 6 (which represent the harder samples) have a rapid increase in area in the beginning of the experiment until around 300 seconds passes, at which points the increase becomes slower. Adhesive 1 have a slow linear increase all the way through experiment which is still such after 12000 seconds (not shown on the graph, however data is available). In order to perform time independent experiments, one time frame had to be chosen, from the analysis of such data like shown in figure 4.6 900 seconds (15 min.) was chosen for all of the following experiments. Raw data as shown in figure 4.4 at t = 15 min. is used for the analysis.



Figure 4.6: Change in area trough time under experiment for 3 different adhesive mixtures 1, 4, 6 all of the sample thickness approximately 2 mm.

4.2 Rheological measurements

In this section the method for the rheological measurements will be presented. Sample preparation, measuring device and examples of raw data are included. As before the crude sample preparation is explained in section 3.

4.2.1 Rheometer

Rheological measurements are made by Haake RS600 and Haake RS6000 rheometers. Rheometer is a laboratory device used for measuring rheological properties of the material (see section 2.1). It applies a shear force to a sample and measures deformation, or in other words, it measures relationship between stress (σ) and strain (γ). Both constant and oscillating stresses can be applied to test steady-state and time dependent flow, respectively. In such way the fundamental flow properties of the material can be studied. There are several kind of different shear rheometers, such as Pipe or Capillary, Cone and Plate, Rotational Cylinder and Parallel Plate (P-P). In this thesis I am using a Parallel Plate rheometer. The crude skech of such a rheometer can be seen in figure 4.8. It is chosen because this type of rheometer is good for testing samples exhibiting dominant elastic response and having high molecular-weight, for example rubber polymers and rubber compounds (Schramm 1998). The sample is placed in the gap which can be varied from 0.2 - 3 mm. stress is applied as a sinusoidal time function

$$\sigma = \sigma_0 \sin(\omega t)$$

and the resulting time dependant strain is measured. Test of oscillating stresses are often named "dynamic tests". In this thesis I perform dynamic testing on the samples to test time-dependent rather than steady-state flow. Dynamic testing requires one to sweep and assigned frequency range. Stress frequency is stepwise increased and complex shear modulus (G*) and phase angle (δ) are measured at each step (see figure 4.7). This data have be transformed into viscous and elastic components, which is done automatically by rheometer software (for mathematical equation for these transformations see section 2.1).

4.2.2 Sample Preparation and Measurement

Adhesive samples are pressed under heat press with a 1 mm thickness setting, several round samples of 20 mm in diameter are cut for each adhesive type, the specific thickness of each sample is measured before hand and the gap size is chosen (≈ 0.1 mm), temperature is chosen to be 32° C, since it is an average human skin temperature. The sample is placed between the two plates the top plate is lowered until the normal force (F_n) is above 0 N indicating contact. Applying F_n to the sample the deformation perpendicular to force occurs, and this effects the shear modulus, therefore ideally it should be just



Figure 4.7: Dynamic testing: a decline in δ /frequency - curve marks the increase in viscous and corresponding decrease in elastic behaviour of sample tested (taken from Schramm (1998), p. 127)



Figure 4.8: Sketch of the Parallel Plate Rheometer

above 0 N, but its very difficult to achieve since the sample can have small irregularities on the surface. All the samples were tested under different (F_n) ranging 1-100, most of the samples shows no significant difference in the output data, albeit samples for mixtures 1 and 3 shown observable fluctuations. All of the samples were tested in the interval of 0-10 for F_n , where no difference in data was observed.

The strain amplitude (γ_0) is defined as a ratio of total deformation to the initial dimension of the sample: $\gamma_0 = \frac{\Delta L}{L}$. It is set to be $\gamma_0 = 0.01$, for low deformation. This is because linear viscoelastic range is limited to amplitude range for witch G^* is constant. In theory of viscoelasticity the relevant equations are linear differential equation and coefficients of time differentials are constant (material constants). Outside of this range presents one is presented with non-accountable deviations in the data. Under these conditions the sample is deformed to the point that internal temporary bonds of molecules or aggregates are destroyed, shear-thinning takes place and a major part of the energy is lost as heat (Schramm 1998). As a consequence before every experiment stress sweep is done, to make sure that the strain amplitude is suitable, figure 4.9 illustrates this. Equations 6 and 7 in section **??** shows the relationship between stress and strain amplitude.



Figure 4.9: Change of G^* in stress amplitude sweep (taken from Schramm (1998), p. 133)

For the purposes of this thesis frequency sweep is done for frequencies (0.001 - 100) Hz. Different quantities such as time (t), frequency (f), complex viscosity (μ^*), complex shear modulus ($G^* = G' + iG''$), stress (σ), strain (γ), temperature (T) and normal force (F_n) are logged in the output file and can be easily acceded for further use In this case I am interested in the shear modulus G^* , examples of the raw data for G' and G'' can be seen in figure 4.10. In both 4.10a and 4.10b there are some irregularities at the very high frequencies, which is most likely because of exiting linear range.

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(b) Lower molecular weight adhesive, no Hydrocolloid

Figure 4.10: Examples of raw data for shear modulus (G' and G'') as an output

5 Results and Analysis

In this section I will present results and analysis for the data obtained throughout my experiments. Rheological and pressure data have been collected for all of the seven mixtures. Table 1 in section 3 represents the adhesive mixtures in terms of their ingredients.

5.1 Pressure Measurements

Multiple samples were tested for seven different adhesive mixtures as described in section 4.1.

The same force of 10.65 N is applied on all of the samples, the contact area was measured to be 30.6 mm^2 , hence pressure (denoted P) at the contact is

$$P = \frac{F}{A} = \frac{10.65\text{N}}{30.6\text{mm}^2} = 3.47 \cdot 10^5 \text{Pa}$$

Pressure is measured in the matrix of points so it can be seen how it is distributed as shown in the section ??. At the contact between metal block and the sensory pad all of the points experience the same pressure, which equals $3.47 \cdot 10^5$ Pa. There are roughly 75 contact point between the pad and the metal block, which means that at each point pressure is about 4600 Pa, which is then the upper limit for the pressure at any point in the matrix.

However when the material is put between the sensory pad and the metal block, pressure at sensory pad is dissipated over the larger area (denoted A), which is then lowered at every point and new points becomes under pressure, this describes the phenomenon which I call pressure relief. It is intuitive that the thicker the material between the sensory pad or skin and the pressure source the greater is the pressure relief. However it is also largely dependant on the material. In this thesis I am concerned with polymer based adhesive ability to relieve pressure. The ability of viscoelastic materials to undergo deformation is related to pressure relief, which will be discussed in next section.

In this experiment I have tested multiple samples of different thickness (denoted h) to see how the pressure is changed throughout the matrix. Figures 5.1 and 5.2 shows the contour plots of the area under pressure of adhesive mixtures 4 and 6. It is obvious that these two materials relieve pressure very differently, since the four chosen h are approximately the same, the only difference is the material itself. P of mixture 4 is lower throughout the area and the area is larger in each instant. These data also confirms the intuition that the thicker the material the greater the pressure relief. We can also see that the highest pressure is in the middle, which makes sense since it is dissipating away from the source.

In order to compare such data more conveniently the cross-section can be examined. Figures 5.3, 5.4 and 5.5 show pressure at row cross-section through maximum pressure



Figure 5.1: Contour plots for the Mixture 4 at 4 different thickness at time of 15 min.

point for different thickness for all of the seven mixtures. The maxima (denoted r_{max}) of these is an indication how well the material relieve pressure, however the length (l) is also an indication of dissipation of pressure, it is related to the area $A \approx = \pi l^2$, since it is approximately circular. r_{max} and A then both can be considered a measure of pressure relief, the larger the area swept and the lower maxima, the better the relief.

From the figure 5.3 it can be seen that at h = 0.4 mm in most instances the larger the r_{max} the smaller the length, which would suggest that these two measures are equivalent, however if we look at the thicker samples of h = 0.7 and h = 1.5 this do not hold for all of the mixtures. In addition it is clear that the difference in the relief is more prominent for the thicker samples, since there is more material to change the pressure distribution. To examine this further I plot A versus r_{max} for all of the *h* (see figure 5.6a). The relationship between these two quantities seems to be independent of the material, since all of the points seem to fall on the same curve suggesting that the measure of A and r_{max} are interchangeable. This graph looks a lot like exponential function, I can plot $\ln(A)$ versus $\ln(h)$ to see if that is the case.



Figure 5.2: Contour plots for the Mixture 6 at 4 different thickness h at time of 15 min.

Now I make linear fit for the ln functions shown in figure 5.7a together with the data. This actually show a distribution rather than one line. The previously considered hypothesis that the relationship between A and r_{max} is independent of the material seems to be false and in reality the materials dissipate pressure with significant difference. Such graph could be very useful to distinguish which material is better at pressure relief, however if I convert the fit back to power function $A(r_{max})$ in the following way:

$$\ln(A) = a\ln(r_{max}) + b \tag{16}$$

$$A(r_{max}) = r^a_{max} \cdot e^b \tag{17}$$

(18)

where a is slope and b is y-intercept and look at it again (figure 5.7b) it can be seen that these fits are really bad and do not actually contain any useful information. For this reason I proceed looking at these two variables separately.

Figures 5.8b and 5.8a show thickness plotted against both the area and the maxima respectively. Firstly, we see from figure 5.8a that the data for r_{max} is quite irregular



Figure 5.3: P [Pa] at the cross section through the maximum point, where $h \approx 0.4$ mm

as the apparatus is highly sensitive and r_{max} is only one point in the matrix. Figure 5.8b shows that area data is more regular. Area values are combined of many points thus are less sensitive to fluctuations. To make the data more regular I apply MATLAB 'smoothingspline' function to both sets of data.

Secondly we observe that none of these two data sets are completely linear. However if we zoom in figure 5.8b we can see that for thickness interval [0.4, 1.5] it can be approximated as linear. To make such fit I disregard the data points above h = 1.5. For the linear fit for figure 5.8a I use all of the data points.

Table 2 lists all the slopes for h(A) and $h(r_{max})$ as well as some values for A and r_{max} for three specific thickness. Figures 5.10, 5.11 5.12 and 5.13 shows plots $(h(A) \text{ and } h(r_{max}))$ for the different pairs of mixtures for purposes of qualitative analysis by comparison of these mixtures. For example mixtures 5 and 6 can be compared to see the effects of plastisizer on the abilities to relieve pressure (see table 1).

Figure 5.9 shows the smoothed data and the fitted linear functions $h(r_{max})$ and h(A).



Figure 5.4: P [Pa] at the cross section through the maximum point, where $h\approx 0.7~{\rm mm}$



Figure 5.5: P [Pa] at the cross section through the maximum point, where $h\approx 1.5~{\rm mm}$



Figure 5.6: Data plots for r_{max} and A for all of the seven mixtures

Table 2: Values for the slopes of linear fits $h(r_{max})$ and h(A) along with some values for A (in mm²) and r_{max} (in Pa) for h = 0.4, 0.7, 1.5 calculated from the functions

Slope	$h(A) \cdot 10^2$	$h(r_{max}) \cdot 10^3$ ·	h = 0.4		h = 0.7		h = 1.5	
Siope.			A	r_{max}	A	r_{max}	A	r_{max}
Mixture 1	3.50	-5.99	43.6	592	52.1	542	75.0	408
Mixture 2	1.25	-3.66	37.4	582	61.4	500	125.6	281
Mixture 3	4.01	-6.79	45.2	541	52.7	497	72.6	379
Mixture 4	0.98	-4.71	38.9	495	69.4	432	150.9	262
Mixture 5	4.97	-4.19	43.8	604	49.9	533	65.9	342
Mixture 6	6.98	-3.57	44.0	729	48.3	645	59.8	422
Mixture 7	0.40	-2.34	41.6	566	117.5	438	318.2	96



(b) A versus r_{max} and $A(r_{max})$

Figure 5.7: Data plots for r_{max} [Pa] and A [mm²] and the fitted functions, for all of the seven mixtures



(b) $A \ [mm^2]$ versus $h \ [mm]$

Figure 5.8: Data plots A, h and r_{max} for all the seven mixtures



(b) Data and h(A) the data from the interval 0.5 - 1 mm. is used to generate the fit, since that best represents near linear regime

Figure 5.9: Data and fitted functions h(A) and $h(r_{max})$ for all the seven mixtures



Figure 5.10: Plots of h(A) and $h(r_{max})$ for pairs of mixtures 1, 3 and 1, 7



Figure 5.11: Plots of h(A) and $h(r_{max})$ for pairs of mixtures 3, 4 and 1, 4



Figure 5.12: Plots of h(A) and $h(r_{max})$ for pairs of mixtures 1, 4 and 2, 6



Figure 5.13: Plots of h(A) and $h(r_{max})$ for pair of mixtures 5 and 6

5.2 Rheological Measurements

The data is collected as described in section 4.2. Figures 5.14 and 5.15 show the plots for G' and G'' and table 3 list numerical values for some of the data points throughout the frequency range. Figures 5.17 and 5.18 are separate plots of G' and G'' for all the seven mixtures.

Another quantity to look at is $\tan(\delta)$. $\tan(\delta)$ is a ratio of energy lost and stored during cyclic deformation or in other words measure of the internal friction of the material. It is defined as

$$\tan(\delta) = \frac{G''}{G'}$$

if G' < G'' than $\tan(\delta) > 1$ and the sample can be said to be more viscous than elastic and vice versa. The plot of $\tan(\delta)$ versus frequency can be seen in figure 5.16.

This figure indicates that mixtures 4, 2, 1 becomes more viscous than elastic at 0, 5 and 10 Hz respectively. A ll of the other mixtures exhibits elastic response throughout the whole frequency range.



Figure 5.14: Plots of G' and G'' for mixtures 1, 2, 3 and 4

If we look at the figure 5.14, the shapes of these curves indicates that 5.14a, 5.14b and

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5.14c is at rubbery plateau region (refer to section 2.3 figure 2.12) and 5.14d seems to be right at the high frequency cross-over point between rubbery and transition regions.

Mixtures 5 and 6 (figures 5.15a and 5.15b respectively) show rheological behaviour expected from cross-linked thermoplastic polymer melts (refer to section 2.3), which is expected, since mixture 5 is a tri-block copolymer (SIS) and 6 is mixture of a copolymer and a plasticizer. Although they are not chemically cross-linked, tri-block copolymer rubbery isoprene mid-block acts as a kind of physical cross-link, thus exhibiting rheological properties similar to vulcanizites.

From figures 5.16 we see that 5 has lower $\tan(\delta)$ and G'' than 6, but G' is higher, this is due to plasticizer, which is to be expected, since it is used to increase flow or in other words, soften the material. In addition G'' is said to coincide with number of cross-links along the original chain (Schramm 1998), which means that the way plasticizer works is by decreasing the effects or interfering with the physical cross-links in the tri-block copolymer. Figure 2.15 in section 2.4.1 illustrates arraignment of tri-block copolymer and plasticizer.

As mentioned before mixtures 1, 2 and 4 flow the best at high frequencies, which can also be seen from the plot of loss modulus (figure 5.18). The cross-over for mixture 4 occurs at 0.7 Hz, which is two orders of magnitude lower than mixtures 1 and 2 (8 Hz and 7 Hz, respectively) and three orders of magnitude lower than mixture 3 (70 Hz).

Mixture 4 is the comprised of the same ingredients as mixture 2 except its weight average molecular weight, M_w of the elastomer is lowered which means that there are more di-block copolymer present in the mixture. Lowered M_w should move the low frequency cross-over point toward the higher frequencies, but as we see from the data high frequency crossover point is moved the other way (relative to mixture 2). This is than means that the rubbery region is reduced. This happens because of the reduced entanglements among the polymer molecules in the melt.the size of this region depends highly on the molecular weight between the entanglements or cross-links, only the polymer that are sufficiently long can form entanglements.

Mixture 1 is a standard Compeed adhesive with all the standard ingredients described in section 3 and mixture 2 is the same except for absence of hydrocolloid. In this case hydrocolloid seems not to have any influence on internal friction (since the curves in 5.16 can be assumed to overlap), which makes sense since it is inhomogeneous and do not interact at the molecular level with elastomer, tackifier and plasticizer mixture. It is dispersed in the polymer matrix as a minor component of polymer blend.



Figure 5.15: G' and G'' for mixtures 5, 6, and 7

Figures 5.14a and 5.14b although G' and G'' cross at the same frequency the modulus of mixture 1 is higher. If we assume that the curves follow the same shape, which is quite a safe assumption, than the low frequency cross-over would have the same difference in modulus values. That means that molecular weight distribution M_{WD} (mixture1) $< M_{WD}$ (mixture2). However it is not the case, the only difference between these two adhesives is hydrocolloid, it seems that hydrocolloid have an effect of decreasing M_{WD} and increasing values of G' and G'', which is not actually possible. The only way to decrease polydispersity is to break down the longer molecules to the size of all the short ones, which would increase flow considerably. whereas here we

Mixtures 1 and 3 differ in the amount of hydrocolloid, which seems to have a noticeable effect. G' and G'' are increased throughout the whole frequency spectrum. the addition of hydrocolloid increases G' throughout the whole frequency spectrum.

The tackifier effect is immediately obvious, the only two mixtures which do not have tackifier are 5 and 6, and these are the only ones which behaves like a cross-linked thermoplastic polymer melts.

If we compare mixtures 1 and 7 in figure 5.17 and 5.18 that both storage and loss moduli

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are decreased considerably. Everything is shifted towards lower values of G. Mixture 7 is more elastic than viscous in all of the frequency range, does not cross over, but the values are quite low. The difference in mixtures 1 and 7 is that plasticizer is exchanged with mineral oil and it has lower molecular weight M_w and in turn M_{WD} since there is probably more di-block copolymer present. The flow properties in usually increased by lowered molecular weight, since di-block copolymer do not have the plysical cross-links in its structure. Mineral oil replacing plasticizer, but it has the same purpose which is to increase viscous flow, adding these two together makes for elastic but very soft material.



Figure 5.16: $tan(\delta)$ versus frequency [Hz] for all the seven mixtures



Figure 5.17: G^\prime [Pa] versus frequency [Hz] for all the seven mixtures



Figure 5.18: G'' [Pa]versus frequency [Hz] for all the seven mixtures

Table 3: Values of G' and G'' for all of the seven mixtures for some specific frequencies ranging from high (68 Hz) to low (0.0068 Hz).

G/				Fre	quency [F	Iz]		
Mixture		68.1300	6.8130	2.1540	1.0000	0.2154	0.0681	0.0068
	1	1937000	392300	187300	119900	60840	46180	48780
	2	465100	73020	31820	19300	8975	6623	7518
C''	3	702200	168200	109100	93130	81280	81680	100200
	4	661700	129400	62980	39590	16240	8911	2978
[ra]	5	39900	27360	25020	22460	18840	18320	14640
	6	55980	43640	39280	35310	27970	24350	21380
	7	12070	7040	4332	2932	1314	830.30	620.90
	1	1230000	429500	329600	291000	242100	216700	162200
	2	190400	66880	50950	44820	37280	33630	27880
C'	3	701300	489700	444500	414900	355800	309300	197300
	4	347500	92860	52830	36830	19900	13630	7946
[ra]	5	335100	300200	288100	279200	263800	251700	237100
	6	350600	279400	246900	228400	199000	181200	151500
	7	30330	19450	15700	14230	12750	12210	11630

6 Disscusion

The four ingredients in the typical Coloplast produced adhesive are SIS, plasticizer, tackifier and hydrocolloid. For the medical adhesive these four ingredients have to be balanced so the adhesive can be applied not only on the healthy skin but also around sores and ulcers. In this thesis I investigate these ingredients and they affects on the overall adhesive mixture by testing their ability to relieve pressure and some supplementary rheological measurements. Pressure relief is very important in the medical bandages because of possible bedsores and ulcers. The desirable effect is evenly distributed pressure throughout the whole bandage even if it is being applied at one point. Of course this could be achieved with the material which is near ideal solid, however it is not possible because it would be very hard non-deformable bandage. Pressure relieve is only one of the several criteria which are desirable for purposes of medical adhesives.

Mixture 1 is one of the adhesives Coloplast have in production for the brand "Compeed", and it is a good adhesive for the purposes it is produced for. From table 2 slopes of h(A)and $h(r_{max})$ are relatively steep, which means that it does not handle pressure well, the dissipation is minimal with increased thickness, however if we remove hydrocolloid from this mixture, which is mixture 2, the abilities to relieve pressure increases substantially. Since the hydrocolloid do not mix homogeneously with the other ingredients it seems that suspended particles in the matrix make it harder for molecules to move within the melt. This is also supported by looking at the pressure relief of mixture 3, which contains increased amount of hydrocolloid. Pressure relieve becomes worse than for mixture 1. However slopes of A are not s steep as for mixtures 5 and 6 (see table 2) meaning that the area still increases better than for cross-linked polymers which are virtually immobile. Although mixtures 1 and 3 are able to relieve some pressure, we can conclude that hydrocoloid in the mixture makes material harder to relieve pressure. The interesting case is mixture 7 which contains hydrocoloid however exhibits very good properties for pressure relieve. If we look at its G values (figure 5.15c and table 3) we can see that G'' at the high frequencies (bonding frequencies) relative to mixture one, is very low (12 kPa), which mean that this mixture will not adhere to the substrate surfaces. High loss modulus is required for adequate bonding (to have tack) and on the other hand at the de-bonding frequencies (low frequencies) the elastic behaviour of the adhesive is required, which is more adequate in the case of mixture 7, it would have cohesion for peel. Mineral oil been known to increase the rate of the local rearrangements of the polyisoprene (Benedek 2000). If that is the case it could lower the molecular weight, and than hydrocolloid would not have the same effect as in predominantly tri-block melt.

From figure 5.9 we know that the best pressure relieve is shown by mixtures 2, 4 and 7, although mixture 5 seems to not be that bad in $h(r_{max})$ which means that it does distribute pressure in one direction better than the other. If we look at bonding (loss modulus) and debonding (storage modulus) frequencies in table 3 for these 3 mixtures (high frequency for storage modulus and low frequencies for loss modulus) only mixture 2 seems to qualify for good adhesive properties - cohesion at peel and adequate adhesion at contact.

7 Conclusion and Further Thoughts

From my experiment I can conclude that is is very difficult to achieve good balance of properties if you take into account good pressure relieve, even with increased thickness of the adhesive layers the relieve is often poor. It is possible to make adhesive materials with good ability to relieve pressure, but as a trade off is adhesion or cohesion is lost, soft materials which has high flow properties are often better at relieving pressure, however loss of elastic properties affect cohesion of the system and too much flow will deform materials irreversibly. Mixture 2 was shown to have best qualities for adhesive with good pressure relieve, but even that it was lacking in hydrocolloid, which was shown to reduce the ability for pressure relieve substantially. two parameters were defined for quantitative survey of pressure relieve ($A r_{max}$) and shown to not be equivalent. Linear models were made for the thickness of material and the parameters. for further investigation these two parameters could be connected to one model, however further experimental work is needed. Also experimental work with varying amount of hydrocolloid (small increase for different samples) added to adhesive mixture 2 would be interesting to perform in order to find a better adhesive mixture for bandages.

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