

Kaunas University of Technology
Faculty of Mechanical Engineering and Design

Analysis of Rheological and Surface Properties of Adhesive Compositions for Hot Stamping Purposes

Master's Final Degree Project

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Kaunas, 2019



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Industrial Engineering and Management (6211EX018)

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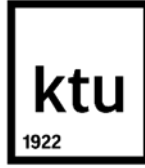
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Analysis of Rheological and Surface Properties of Adhesive Compositions for Hot Stamping Purposes

Declaration of Academic Integrity

I confirm that the final project of mine, Priyadharshini Shanthakrishnan, on the topic „Analysis of Rheological and Surface Properties of Adhesive Compositions for Hot Stamping Purposes“ is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

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Task of the Master's final degree project

Given to the student – Priyadharshini Shanthakrishnan

1. Title of the project –

Analysis of Rheological and Surface Properties of Adhesive Compositions of Hot Stamping Purposes.

(In English)

Terminiam pernešimui skirtų klijų reologinių ir paviršiaus savybių tyrimas.

(In Lithuanian)

2. Aim and tasks of the project –

Aim:

To evaluate and find out ways to improve the water based dispersion wettability to the surface of different types of multilayer films for hot stamping purposes.

Task:

1. To present an overview of hot stamping purposes techniques and environmentally friendly adhesives.
2. To evaluate the rheological behaviour of water based dispersion at constant shear rate and compare them with solvent based adhesives.
3. To evaluate the wetting properties of water based and solvent based adhesives in dependence of substrate nature.
4. To evaluate influence of surfactant on the surface properties of water based adhesive by measuring the wetting angle and surface tension.

3. Initial data of the project –

None

4. Main requirements and conditions –

Rheometer, Oven, Dynamic contact angle measuring device, Goniometer

Testing equipment: Brookfield viscometer DV II +PRO, Oven, surface tension measuring device (Data physics DCAT II), Goniometer, Image J software.

Testing materials: aluminum coated multilayer film for hot stamping with thickness of $h = 19 \mu\text{m}$, transparent hot stamping foil $h = 23 \mu\text{m}$ (III) and temper evident film $h = 34 \mu\text{m}$ (TE).

Surfactants: 96% ethyl alcohol (producer AB “Stumbras”) and nonanoic surfactant (producer JSC, MKDS innovation)

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Priyadharshini Shanthakrishnan. Analysis of Rheological and Surface Properties of Adhesive Compositions for Hot Stamping Purposes. Master's Final Degree Project, supervisor Assoc. Prof. Dr. Eglė Fataraitė-Urbonienė; Faculty of Mechanical Engineering and Design, Kaunas University of Technology.

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Summary

There are many environmentally friendly adhesive producers who produce various standards of adhesives for various applications. And they recommend using their products. It is not sure that these adhesives satisfy their needs. In this research suitable eco-friendly adhesive for hot stamping purpose from the producers was selected to improve their efficiency.

The rheological behaviour of solvent based, and water based dispersions at constant rotational speed of $D = 40, 60, 80, 100, 120$ and 140 rpm for 1 hour have been investigated. It was determined that due to the four times higher concentration of film forming material in water based dispersions significantly higher dynamic viscosity values compare to those of solvent based was found. Dynamic viscosity is dependent on rotational speed. Effect of rotational speed on water based adhesive viscosity changes has uneven character. At lower than 100 rpm rotational speed (60 and 80 rpm) during first $\tau = 10$ min of testing viscosity tend to decrease, while at rotational speed of 120 rpm and 140 rpm slight increase of viscosity was found. At rotational speed of $D=40$ and 100 rpm dispersions showed behaviour characteristic for Newtonian fluids.

The contact wetting angle relaxation of solvent and water based adhesives on the surface of aluminium coated and transparent hot stamping foil and tamper evident hot stamping foil have been investigated. Contact angle relaxation up to reaching constant (Young contact angle) value depends on the both adhesive and substrate nature. It was found that on both investigated hot stamping foil surfaces more intensive wetting angle shape changes were found during 2 first seconds, while for tamper evident film contact angle value gradually decreased. Young contact angle for solvent based adhesive was two time lower compare to the water based. Effect of surface nature on the Young contact angle value was found only insignificant.

In order to increase wettability of water based adhesive to selected substrates different amounts (0.27 vol. % , 0.51 vol. % , 0.81 vol. % and 1.35 vol. % to total amount of dispersion) of ethyl alcohol and commercial non anionic surfactant was added. It was determined that independently on substrate nature addition of ethyl alcohol and non-anionic surfactants decreases the initial contact angle, but increases Young contact angle compare to those of pure dispersion.

It was found that addition of surfactants results on the increase of the surface tension of dispersions. Higher effect using non anionic surfactant was found. Increase of amount of selected surfactants results on the decrease of surface tension relaxation duration.

Priyadharshini Shanthakrishnan. Terminiam pernešimui skirtų klijų reologinių ir paviršiaus savybių tyrimas. Magistro baigiamasis projektas, vadovė doc. dr. Eglė Fataraitė-Urbonienė; Kauno technologijos universitetas, Mechanikos inžinerijos ir dizaino fakultetas.

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Kaunas, 2019. 51 p.

Santrauka

Tirtos galimybės pagerinti vandens dispersinių klijų vilgymo savybes ant pasirinktų daugiasluoksnių polimerinių plėvelių paviršių.

Vertintos tirpiklių ir vandenių dispersinių klijų reologinės savybės esant pastoviam sukimosi greičiui $D=40, 60, 80, 100, 120$ ir 140 aps/min (poveikio trukmė $\tau=1$ val.). Nustatyta, kad dėl keturis kartus didesnės vandens dispersijos koncentracijos, jos klampa buvo ženkliai didesnė nei tirpiklinių klijų. Dinaminė klampa priklauso nuo sukimosi greičio, deformavimo trukmės ir medžiagos kilmės. Sukimosi greičio įtaka vandeninių dispersijų klampai yra netolygi. Esant mažesniai nei 100 aps/min sukimosi greičiui (60 ir 80 aps/min) per pirmąsias $\tau=10$ min klampa mažėjo, o esant 120 aps/min ir 140 aps/min sukimosi greičiui, klampa padidėjo. Deformuojant $D = 40$ ir 100 aps/min greičiu, dispersijos klampa nuo deformavimo sąlygų nepriklausė.

Tirtos tirpiklinių ir vandens dispersinių klijų vilgymo savybės ant aliuminiu dengtų ir skaidrių karšto įspaudavimo plėvelių bei savaiame susiardančių daugiasluoksnių plėvelių paviršiaus. Nustatyta, kad vilgymo kampo relaksacijos procesas iki pastovios (Jungo vilgymo kampas) vertės priklauso nuo klijų ir pagrindo kilmės. Nustatyta, kad intensyviausi vilgymo kampo vertės pokyčiai ant abiejų tirtų karštam įspaudavimui skirtų plėvelių paviršiaus pastebėti per 2 pirmąsias sekundes po kontakto sudaymo. Tuo tarpu, kai savaiame susiardančios plėvelės paviršiuje stebėtas tolygus vilgymo kampo vertės mažėjimas. Ši tendencija būdinga tiek tirpikliniams, tiek vandens dispersijos klijams. Jungo vilgymo kampo vertė tirpiklinių klijų atveju buvo du kartus mažesnė, nei naudojant vandens dispersiją. Paviršiaus kilmės įtaka Jungo vilgymo kampo vertei nežymi.

Norint pagerinti vandens dispersinių klijų vilgymo savybes ant pasirinktų substratų, į dispersiją buvo įmaišyta skirtingi kiekiai ($0,27$ vol.%, $0,51$ vol.%, $0,81$ vol.% ir $1,35$ vol.%) etilo alkoholio ar neanijoninės paviršiaus aktyvinimo medžiagos (PAM). Nustatyta, kad nepriklausomai nuo substrato kilmės, etilo alkoholio ir neanijoninės PAM panaudojimas, lyginant su gryna dispersija, sumažina pradinį vilgymo kampą, bet padidina Jungo vilgymo kampo vertes.

Ištirtas skirtingo kiekio etilo alkoholio ir PAM poveikis dispersijų dinaminio paviršiaus įtempio dydžiui. Nustatyta, kad pasirinkti priedai didina dinaminio paviršiaus įtempio vertę. PAM panaudojimo atveju nustatyta tendencija buvo ryškesnė. Priedų kiekio didinimas lemia relaksacijos proceso trukmės sumažėjimą.

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List of abbreviations and terms

Abbreviations:

AHS	–	Aluminium coated multilayer film for hot stamping
EA	–	Ethyl alcohol
THS	–	Transparent hot stamping foil
TE	–	Temper evident film
NAS	–	Nonanoic surfactants
SBA	–	Solvent based adhesive
VOC	–	volatile organic compound
WBA	–	Water based adhesive
C	–	Concentration, %
mPa.s	–	millipascal seconds, units
mN/m	–	milliNewton/metre, units
rpm	–	rotation per minute, units
D	–	rotational speed, s ⁻¹
s	–	seconds
γ	–	surface tension, units
η	–	viscosity, units
vol. %	–	volume percentage, units
θ	–	wetting angle, units

Introduction

Due to the amendment of Environment prohibition around the world and Green Label laws in the European countries demand of solvent free adhesives has increased. Production of ecolabels has become a mandatory due to the government ban in components as listed in Proposition 65 act, and volatile organic compound (VOC) substances in certain countries which are harmful to the environment and considered as hazardous substances to human. This has fastened the growth of solvent free adhesive industries over the past few years (1).

In order to put a solution to global warming, adhesive industries around the world are trying to bring an alternative product that does not produce hazardous substances. Due to the presence of VOC solvents in the solvent based adhesives which during the drying process generates green gases, chemicals that mix in the fog, ozone depletion substance and other gases that are hazardous to human health. There are a number of alternative solutions to replace one of them are water based adhesives (2).

Apart from the adhesive industry, solvent free adhesive also provides various benefits to other industries such as biomedical, biotechnology, nanotechnology, cosmetics and pharmaceuticals (3,4). Besides, water-based adhesives provide many advantages over solvent based adhesive i.e. they are environmentally friendly, easily available, water contains high surface tension which acts as an important property for wettability (5, 6, 7). Water based adhesives are the better alternative for the replacement of solvent based adhesive since water based adhesives are traditional ones. Moreover, water based adhesives can be obtained using the same procedure where solvent based adhesives are produced (8, 9, 10).

To achieve high quality of hot stamping/transfer of thin multilayer structures on the smooth substrate high quality adhesive layer is required, i.e. it must be smooth, even in thickness and exhibits excellent adhesion between substrates to be bonded (11). Surface wettability is one of most important factors ensuring good adhesion properties. Due to that both the liquid surface tension and the properties of the solid must be optimized to ensure suitable adhesion of the adhesive to the selected film (12). Wetting usually marked by the contact angle. One of possible ways to enhance wettability, i.e. to decrease surface tension between liquid and solid is application of surface active agents, so called surfactants. During thin coatings, in our case adhesive layer formation usually are used non-anionic surfactants, has no charge groups in its head (13).

The aim of this investigation is to evaluate and find out ways to improve wettability of water based adhesives on the surface of different types of multilayer films for hot stamping purposes.

Tasks for investigation:

1. To present an overview of hot stamping techniques and environmentally friendly adhesives.
2. To evaluate the rheological behaviour of water based dispersion at constant shear and compare them with solvent based adhesives.
3. To evaluate the wetting properties of water based and solvent based adhesives in dependence of substrate nature.
4. To evaluate influence of surfactant on the surface properties of water based adhesive by measuring the wetting angle and surface tension.

1. Literature Review

1.1. Methods of Polymer Coating Formation

There are various methods used for polymer coating formation. The method varies based on the application of type of substance and surface of the material. Depending upon the thickness of the materials, the polymer coating formation varies for different method. Some of the well-known methods used are immersion method, electrodeposition method, electrophoretic method, spin coating method, spray pyrolysis method and dip coating method.

Based on thickness, the suitable method which is widely used for nano meter thickness is immersion method whereas for millimetre thickness electrodeposition method is widely used, for several millimetres electrophoretic deposition method is used. Some of few methods are discussed below.

Electrodeposition is a technique used in the polymer coating process for the formation of polymer layer by layer method, also known as dip coating process. In general, it is a widely used technique for protecting metal against corrosion or providing an adding support to metal by means of adding grips to the surface or adding aesthetics. One of the most commonly used polymers widely in piping industries are PVC plastisol. Using this polymer during the process of electrodeposition it represents schematics of this process is presented in Fig.1 (22).

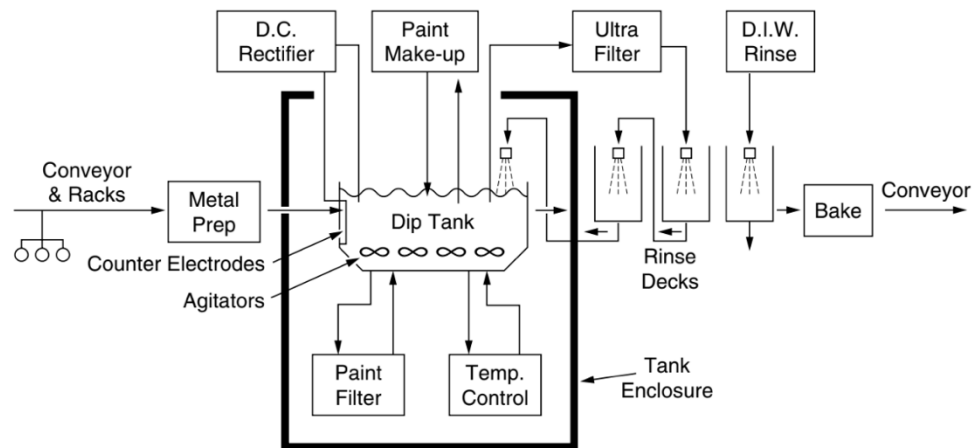


Fig . 1. Electrodeposition coating method (28)

Apart from being an advantage in the metal industry dip coating process is also used in the biomedical field for regenerating the bone tissue. It was known that one the important structure required for regeneration of bone tissue is scaffold, which is a porous engineering structure. It can be used alone or combined with cells for regeneration of tissue. Using dip coating process of a polymer coated bio glass scaffolds it is provided great support in regeneration (23). Characterization of ractopamine by Chen by using various methods of formation of ractopamine, which is widely used to decrease the fat content and increase the growth of muscles in the animals such as turkey, swine etc. by using electrodeposition method it was proven that it shows a significant growth (24).

Since polymers are known for their cost effectiveness, easily processability and functionality they are being broadly used in electrical and electronic manufacturing industries as a major component

(25). For the manufacturing of hybrid polymer-semiconductor nanostructured material electrodeposition acts a bridge between two different thickness size since nanoparticles indicates similar distance measure by using $C_4H_6O_2$ nanocrystals along with stabilizing 1-thioglycerol shows significant increase in nanoparticles through electrodeposition (26). Certain modification on the aqueous monomer solution in an acid treated carbon nanotube without any help of an electrolyte by addition deposition to a non-conducting polymer like poly(o-aminophenol) show a slightly micrometre thickness on the non-conducting polymer (27).

Follow that, electrodeposition is a suitable method for various application, which not being restricted for limited applications. Apart from being widely used as coating for metal it is also used in various fields such as biomedical, chemical engineering etc. It shows incredibly great uses in metal industry for being an protection on most of the metals. By changing different fillers such as aqueous monomer and polymers solution, they provide a formation of polymer coating in various nanoparticles which is difficult form, because of their porous structure the above conditions have proven that using electrodeposition method there is a significant growth in the formation.

Porous roll Coating Method is one of the simplest method used in polymer coating techniques where coating is cured by electrobeam or ultraviolet light. Advantages of this method are less energy requirement, nonpolluting, more efficient, multiple process coating using silicone. The presence of non thermal substance helps in reducing the losses in production, heat profound substances can be used due to it low heat energy supply. Apart from the other benefits, this process is suitable for polymer films as well as paper. Schematic representation of this process is presented in Fig. 2 (28).

Another method used in the porous roll coating technique is the forward rolling process. This is process which contains liquid in between the roller moving opposite to each other and creates a pressure gradient which helps in formation of layer. The main thing that are needed for formation of coating is that roller contact angle is closer the stronger bond occurs; this issue is solved by means of unfold able roller in the coating system which prevents the difficulties of rubbing from each other (29).

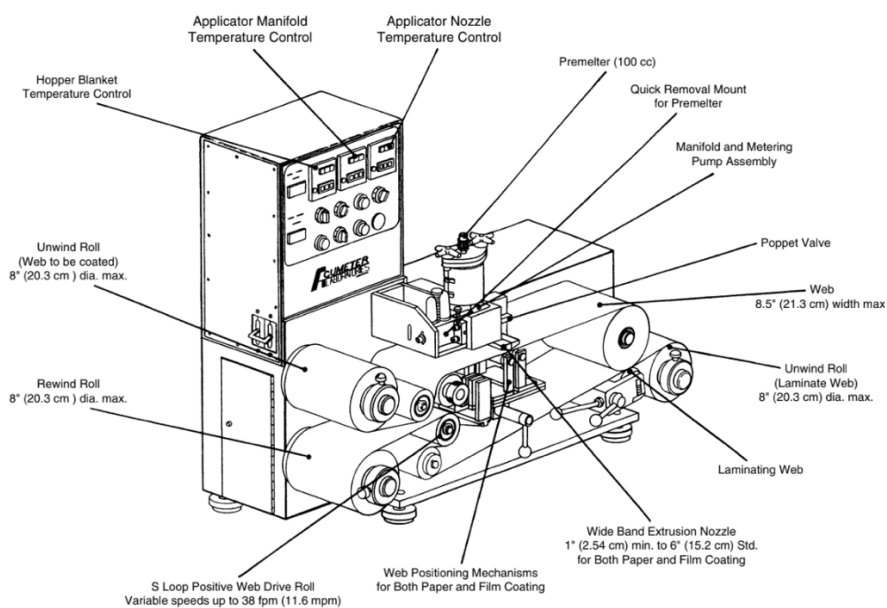


Fig. 2. Porous laboratory coater (28)

Bousfield explains how the rolling deformation takes place for different viscosity liquid. As a fluid used in between web initially by silicone oil as a medium it found that experimentally and theoretically show slight difference the thickness of film reduce as silicon oil is reducing which found inside the film (30).

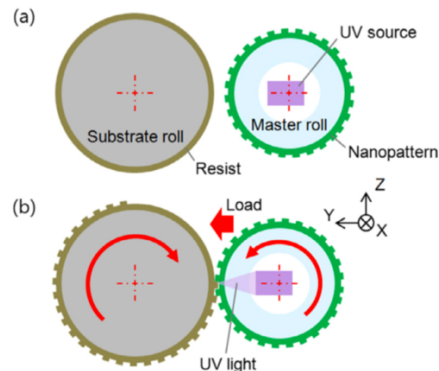


Fig. 3. Roll to roll concept of printing Nano imprint (30)

By changing the design of the rolling mechanism process as shown Fig. 3 by using different roller with nanopattern imprinted on them they show significantly better coating formation due to imprints (31). All the methods mentioned above are incredibly good for the manufacturing of polymer coating. Roll embossing process provides a solution to process microfluid chip in a cheaper way but also provides better quality in modifying the rheological properties of the substance. Whereas deformable roll coating process helps in reducing the risk factor of film thickness. Hence, it is known that by changing the contact angle of the roller in deformable method reduces a great risk of friction in between the roller, and in case of forward rolling method by changing the rheological and surface properties using different viscosity fluid, provides significant higher film thickness.

Embossing method is widely used for the both thermoplastic and non thermoplastic materials. Model varies on the condition of stress applied to surface. The efficient embossing system is obtained by balancing the heating based on the type of material and removal of given thickness and speed.

Hot embossing method (Fig. 4) can be applied for manufacturing micro-fluidic chip by using roller hot embossing. It is considered as the cost effective method compare to the lithographic processes and ion techniques. This is due to its continuous process of flexible sheets, film materials and possible mass production. Rheological properties of polymers used in this method show a change in viscosity and with non-Newtonian fluid it expresses higher shear rates whereas at lower shear rates it shows shear thinning (32).

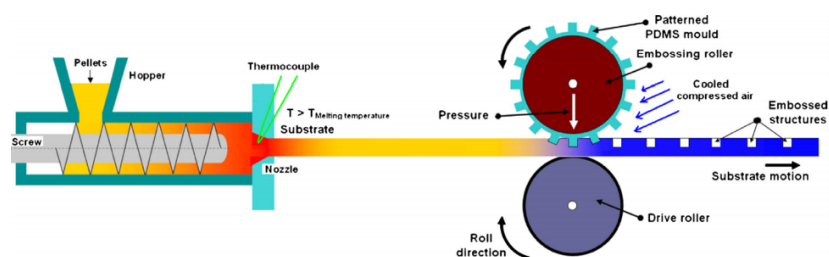


Fig. 4. Roll Embossing process (33)

Hot embossing method is mostly used in microstructures to bring accuracy and also they are cheaper to manufacture. So, they are commonly used in the biomedical, optoelectronics field for producing microlenses and microlens array (33). By changing the embossing parameters such as temperature, pressure and holding time required structures can be formed. After hot embossing process the process releasing the film from the surface requires demould force. Using Silicone mould this process provides easier way to remove them (34). All the methods used in embossing process provides great benefit to the manufacturing process by one way or other.

Being an advantageous method i.e. used in both type of plastics (thermoplastic and thermosetting plastic) they provide greater benefit for mass production hence they are cost effective. When there are modifications made in rheological and surface properties of material, they showed incredibly great performance when compare to previous ones.

Electrophoretic deposition is a key advantage of providing shape to objects but also provides a coating formation to metals thickness between micro meter to nano meter (35). For the manufacturing of poly (4-vinylpyridine-*co*-butyl methacrylate) when provided a change in surface properties by using trans-cinnamic acid in the process there is a significant growth in thickness from (0.5-15 micro meter) (36). When compared to the other coating techniques such spray coating or dip coating, they provide high throw power, high density and automation (37).

This method is widely used for polymer coating formation in metal industry. They are corrosive protection using cathodic electrophoretic deposition method anticorrosive coating of metal is formed with the help of urethanetriaizole as self-healing agent (38). Schematic view of this process is shown in Fig. 5.

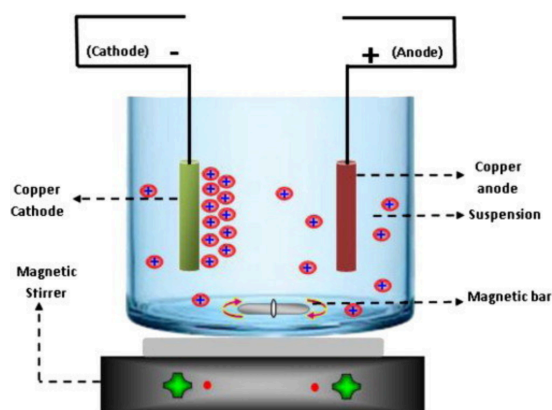


Fig. 5. Electrophoretic deposition process (39)

All the above method are incredibly good for manufacturing process despite of other methods electrophoretic method shows a life changing application that is anticorrosive and self healing process which in future would bring changes to anticorrosive coating.

1.2. Rheological and Surface Properties of Water Based Dispersions

All fluids have there on rheological and surface properties by nature some tend to perform better in their natural form, but others demand an external agent to perform certain condition. By modifying their rheological properties and surface tension they can provide solution of various problems.

In case of oil drilling process various external factors affect the process of continuation. This is due to the surface, rheological properties and the liquid use during this process. To overcome such problem bentonite substance is used in the wider the rheological properties of the interactive forces. This was formulated by a rheological modification done on the water based dispersion process. By using the surface active agent, the fluid properties can show shear thinning behaviour which in distant establishes dynamic viscosity. Hence, there is an increase in the concentration of the solution and improve the perform of the oil drilling process (50) .

Due to the presence of solvent which is harmful to the environment, solvent free adhesive are created. But solvent free adhesive requires an external agent to fulfil the characteristic properties required for coating process. Acrylic waterborne hybrid is a widely used solvent based material which is harmful to the environment. In order to bring a solution to these problems, zero presence of solvent and surfactant were used to produce the acrylic waterborne hybrid polymer. This is done by synthesizing the prepolymer with acrylic monomer to produce a solvent free and surfactant free adhesive (51).

A detailed investigation of waterborne polyurethane dispersion was conducted with changing the temperature, wavelength, shear stress incrementation. Obtained results indicate the environmentally waterborne polyurethane dispersion can provide wider benefits to the various application. It was found that there were changes taken place during the pre-neutralization and post neutralization process. Investigated solution showed viscoelastic behaviour, concentration variation were also found. Particles size distribution varied from the pre neutralization due to the post neutralization process (52). Preparation of waterborne polyurethane dispersion several functions were discussed. It is needed to understand the asymmetric nature and bifunctional characteristics of the liquid. In order to understand the nature of such type of dispersion various surfactants were added to create a solution to the functionally. The reaction chain of the compounds are shown in the Fig. 6 (53).

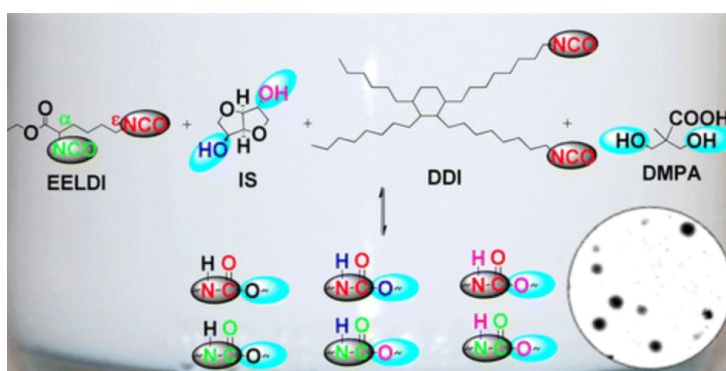


Fig. 6. Chain reaction polyurethane with the other compounds (53)

Synthetisation of polyurethane solution from fatty acid (diisocyanate) was done by cross linking it with different monomer. Obtained results shows excellent mechanical properties like high Young's modulus, high tensile strength, properties and they are provide exceptional anticorrosion properties (54).

The term “rheology” deals with substantial performance of substances that are under stress. It is used in four main categories, they are viscosity, rigidity, elasticity and plasticity. In case of coating, rheology of the liquid depends upon the consistency of the liquid and pressure applied to them. One

of the foremost characteristics is viscosity of the liquid, which helps in the fluid resistance. Viscosity is defined as shear stress per unit shear rate (40).

$$\text{Viscosity} = \frac{\text{Shear stress}}{\text{Shear rate}} \text{ (dynes / cm}^2\text{)} \quad (1)$$

where,

$$\text{Shear rate (D)} = \frac{\text{Velocity}}{\text{thickness}} \text{ (sec}^{-1}\text{)} \quad (2)$$

and

$$\text{Shear stress} = \frac{\text{force}}{\text{area}} \text{ (dynes sec/cm}^2\text{)} \quad (3)$$

Fluids with higher viscosity does not requires more time to flow when compared to the fluids with lower viscosity. Change in viscosity occurs only in case of Newtonian fluids like alcohol, air, water etc. whereas for Non-Newtonian fluids like ketchup, toothpaste does not obey the law of viscosity. Some of important characteristics of non-Newtonian fluids are discussed below:

Plasticity : In this type of fluids when there is pressure applied more than the yield point as shown Fig. 8, they behave like Newtonian fluids. Some examples are paint, gels etc. In case of paint they show zero viscosity or lower viscosity when brushed against wall but later when the pressure is increase, they tend to change their behaviour to Newtonian fluid. Another case, ink deposits in backside of the paper in some case this is due to the low yield point in the fluid. Fluids with higher yield tend to stay till their yield point.

Pseudoplasticity : These types of fluid are more alike plastic fluid. The difference between them is there is no yield point. They show same characteristics in both plots (Fig. 7, Fig. 8) when comparing with plastic fluid. Viscosity reduce when there is decrease in the shear rate this phenomenon is known as shear thinning . Hence, by reducing the shear rate by increasing the force this in further increases the viscosity of the fluid. Moreover, higher viscosity more shear thinning.

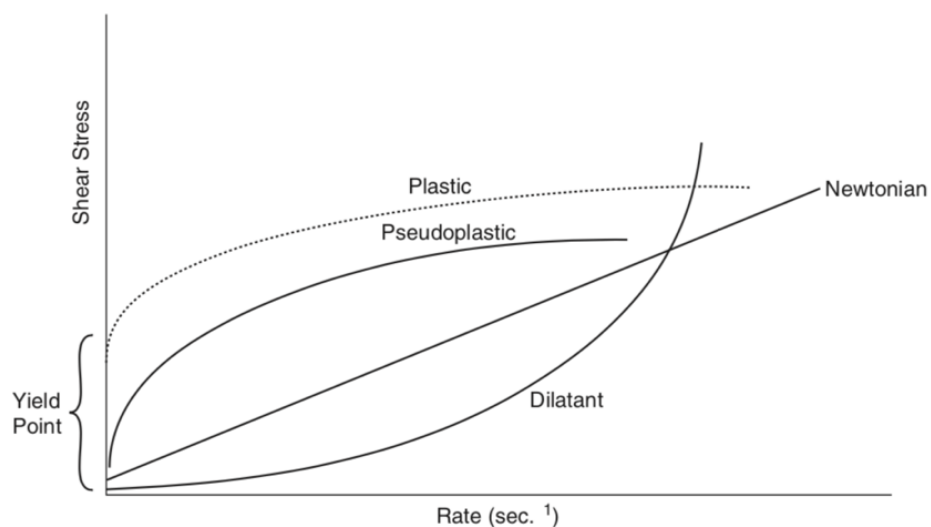


Fig. 7. Shear stress vs shear rate (28)

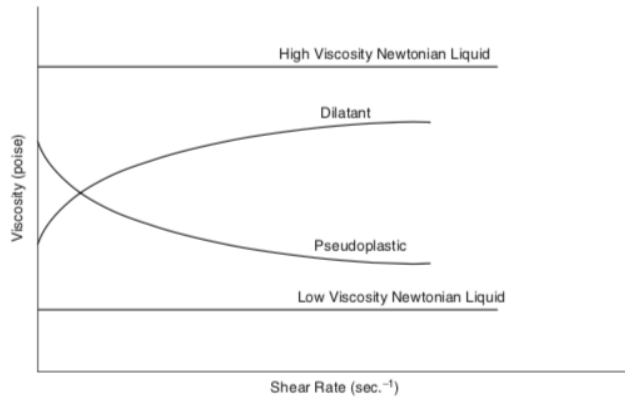


Fig. 8. Viscosity - shear rate plot (28)

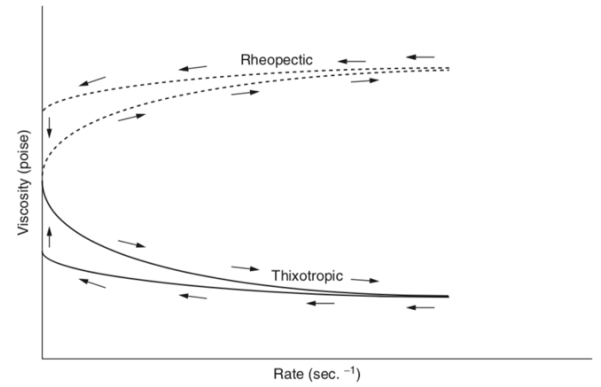


Fig. 9. Hysteresis plot (28)

Thixotropy : This is extensional characteristic of the pseudoplasticity for fluids. When shear thinning occurs but the shear rates reduces in a negligible amount this in further produces a hysteresis curve. For example, driplless paint this is due to thixotropy while brush, in the walls the paint remains to stay in the brush.

Dilatancy: This is also a characteristic of pseudoplasticity. When there is an increase in viscosity of fluids under a force this property is known as dilatancy as shown Fig. 9. For example, solvent based adhesive film present the roller coating process, when the roller applies more pressure in the process the solvent disappears/evaporates this results in increase in viscosity.

Rheopexy: When there is a decrease in viscosity and increase in the shear rate this phenomenon is known as shear thickening. This occurs during the rheopectic characteristic as shown in Fig. 9, an opposite of thixotropy. They are rare cases with occur in screen print process.

Temperature is an important factor during the measurement of viscosity, change in temperature affects the values. In some cases, few degrees are not much of a matter but for different material change in temperature affects the viscosity wider.

Fluid with higher viscosity are difficult to flow when compared to the fluids with lower viscosity ones. Hence, in order to increase the wettability of the fluid i.e. fluid fluency, solvents are added to the fluid. These substances decrease the viscosity and increases the wettability (28).

Below will be described several viscosity measuring techniques:

A device used to measure the rheological properties of the fluid are rheometer. Fig. 10 shows an example of rheometer. It is a device used to measure both viscosity and viscoelasticity of the liquids, solids and semi-solids (41).

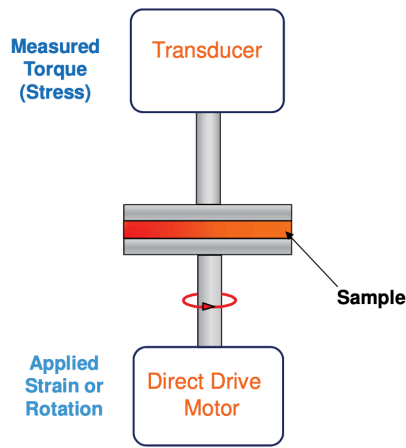


Fig. 10. Schematic diagram of dual motor rheometer (41)

Brookfield viscometer is a device used to measure the viscosity of the fluid. Its instrument that has higher precision than the viscometer. Since, viscometer can be used to determine the change in viscosity with shear rate. Fig. 11 represents schematic diagram of the Brookfield viscometer model (DV II + PRO).

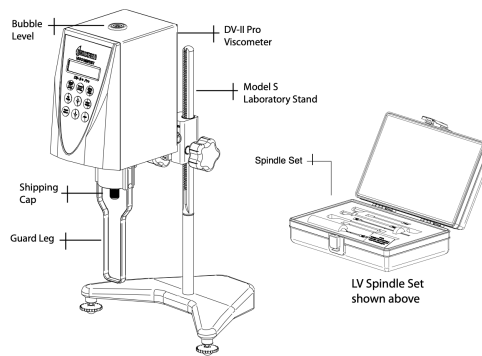


Fig. 11. Schematic diagram of Brookfield viscometer (DV II + PRO model) (42)

Ford cup is a device used to measure the flow time of the fluid. It consists of an orifice bottom and a cup filled with the liquid where the fluid transfer takes place and flow is measured. They are commonly used in the coating and paint industries (28). Fig. 12 shows a 200 model Ford cup apparatus.



Fig. 12. The Ford cup apparatus late 2000 model (43)



Fig. 13. The Zahn cup apparatus (44)

The Zahn cup is also a device used to determine the flow as shown in Fig. 13. The cup is dipped in an investigation sample and pulled out to determine the flow of liquid (28).

Understanding the characteristic of decorative material when embossing on the surface, yield value places an important role. It is shear stress value existing in the viscosity measurement. In other words, if yield value is the relatively low shear stress is also same that is produced under the deformation of flow. In case the yield values exceed the shear stress value it behaves like solid. In that case flow does not occur. For example, in case of printing the ink yield value plays a dominant role since the higher yield can make the ink flow and deposit poor layer on the material (28).

The term surface chemistry deals with the interactive between two matter. Matter can be of any phase; solid, liquid or gas. Liquids are made up of atoms and molecules when colliding with each other they exhibit forces. These collisions are known as surface tension. Surface tension is defined as force per unit length.

$$\text{Surface tension} = \frac{\text{Force}}{\text{Length}} \text{ (dynes/ centimetre)} \quad (4)$$

When a liquid is dropped on the surface forms a spherical shape. During that phase the liquid tend to move apart in the surface whereas solid counteracts the force below. Thus, creates an intermolecular force between the surface. When the surface is solid this type of inter action is considered as solid- liquid interaction. This is important in the coating of materials.

Surface tension of each fluid varies from one another. Fluid with lower surface tension tend to flow unevenly. This due to the poor spherical formation. This disadvantage can solve by interpolating with the forces. Whereas, the fluid with higher surface tension tend to form good spherical formation like water which can have high efficiency to flow over the surface.

When a liquid place on a surface it tends to form a spherical shape. Depending on the viscosity of the fluid the formation of shape occurs. Wetting occurs when the liquid is at zero degree in case liquid exceeds less than zero degree wetting does not occur. The angle between the surface and the semi sphere is known as contact angle as shown in the Fig. 14. Contact angle is the important property of solid liquid interaction. It characterises the wettability.

As shown the Fig. 14, non-wettability of the liquid occurs when the contact angle is 180 degree. When contact angle is more than 90 degree the liquid has poor wettability. When contact angle is less than 90 degree is considered as the low wettability. When contact is zero degree that case is considered as the perfect wettability of the fluid. In such case, fluid with the surface creating a perfect wettability condition.

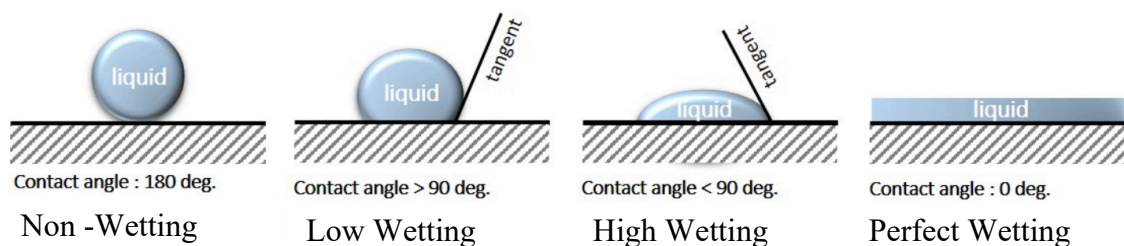


Fig. 14. Wettability of the fluid in dependence with contact angle (45)

Surfactants are the additional substance added to adhesives to modify their properties. Surfactants are known as surface active agents. The chemical structure of the surface active agents are designed in such a way that one group has capacity to be modified to liquid and other group has the tendency to lower the surface tension of the liquid. For example, water has a surface tension of 73 dynes/centimetre which relatively higher amount. Due to higher surface tension these sources have difficulty to bend, in such case surface active agent can be added to the liquid to lower the difference of surface tension and increase the wettability of the solution (47, 48, 49).

Hence, surface active agents are widely used in the adhesive industry to lower surface tension and to increase the wettability of the solution. They are also used in the coating process for certain type of materials, for example inks to increase the yield value. During the coating process when the non-wetting occurs that is creating a low surface tension of the liquid and surfactants are added to restrain their properties this is also known as wetting agents. Moreover, the amount of surfactants used is small and is more or less than one percent. Usage of bigger amounts surfactant can reverse the effect of the solution by increase the surface tension and creating a deviation in the surface properties. Fig. 15 shows surfactant reaction with oil.

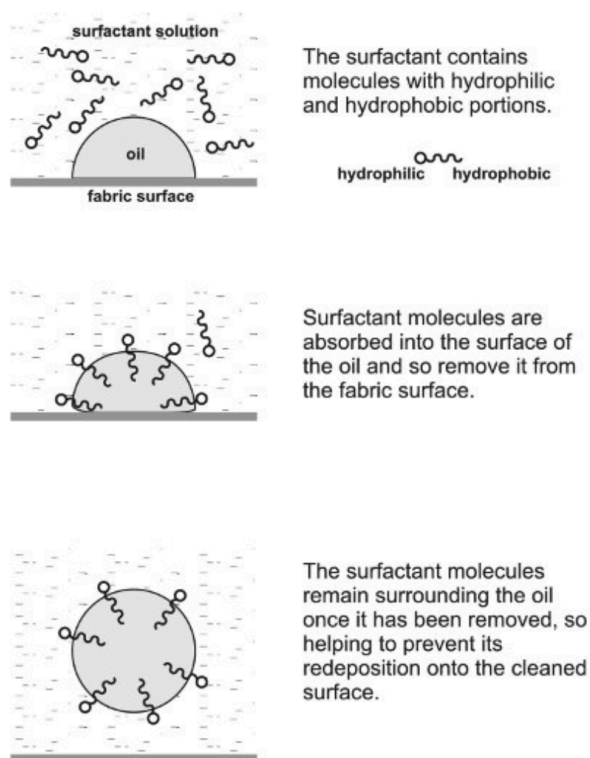


Fig. 15. Surfactant reaction with solution (oil) (46)

Some most commonly used surface active agents consider chemical groups with hydrocarbons, silicones and fluorenes. A smaller amount of silicon surfactants is used in the decorative industry to non-wetting for counter act the fish eye effect (28).

Rheological properties are very important during coating process. Levelling is one of the most difficult procedure to carry out, since it is based on the surface chemistry and rheology. During the

coating process there are several steps to be carried out. Some of them are spraying on the film, coating of adhesives on the layer etc. All the procedure requires to level out the surface and create even layer. Levelling depends on the factors such as surface tension, surfactant, thickness of the coating, contact angle, yield value and viscosity. It is defines in the ratio as expressed below:

$$a_t = a_0 * \frac{\exp(const \sigma h^3 t)}{3 \lambda^4 \eta} \quad (5)$$

where

a_t = height of the coating ridge, millimetre

λ = distance between the ridges, millimetre

t = the time required for levelling, seconds

h = coating thickness, millimetre

η = viscosity coating

σ = the surface tension of the coating, mN/m

Using the above equation levelling can be improved by increasing the duration, and height is powered to three times. This explains that increasing the coating thickness to thrice can increase the levelling properties. Apart from that in some cases where the yield value is greater than the levelling value required this expression can be used to improve the properties of the levelling.

$$T_{max} = \frac{4 \neq ah}{3} \quad \text{or D (coating ridge depth)} = \frac{3}{4 \neq ah} \quad (6)$$

where,

t = the time required for levelling.

h = coating thickness

a = amplitude of coating ridge.

In order to overcome the yield value factor as shown in the Equation 6 it is required to the shear stress of the liquid by increasing the surface tension, wavelength and coating thickness therefore the shear stress increases. Because, yield value will always affect the shear value of the liquid this in default form thixotropy phenomenon.

It is critical to perform the levelling due to the yield value factors since the factor can create low wettability properties. If the yield value is more than the maximum shear wettability will not occur. Another case if the surface active agents are added in minimal amount levelling will not takes place (28).

2. Comparative Overview of Hot Stamping techniques and Adhesive Industry

Hot stamping is conventional method for embossing the design on to the materials. It is widely used in various applications such as labels in varieties of products like wine bottles, corks etc., luxury articles packing, food industry, pharma industry etc. Adhesives used in this technique are heat sensitive which serves in between the layers to bond the material (14, 15).

Hot stamping is a process which uses pressure and temperature to bond the structure with layer adhesive with the substrate. This results in producing the design on the surface. Some of the technique used are rotary stamping method as shown in Fig. 16 and Fig. 17. Equipment uses a rolling heated die over the heat sensitive adhesive to emboss the print, vertical stamp method which uses vertical stamp to move in up and down strokes to emboss the design as shown Fig. 16. In the Rolling method the heated die rolls continuously to emboss the constant moving design, clamshell method or cylindrical method (16).

The process is carried out by a heated die at certain temperature, a heat sensitive foil that is placed in between the die and substrate and residing time where the die and foil comes in contact with each other. Main factors that are required for hot stamping are the pressure, temperature and residing time.

Main tools used in this process are the carrier with generally made of polyester substance with act as medium to transfer the coating from a heated die. Once the carrier transfer is made due to the pressure the die moves the foil where the substrate moves the temperature. The hot stamping foil contain multiple layers in which the die embosses the decorative coating (16).

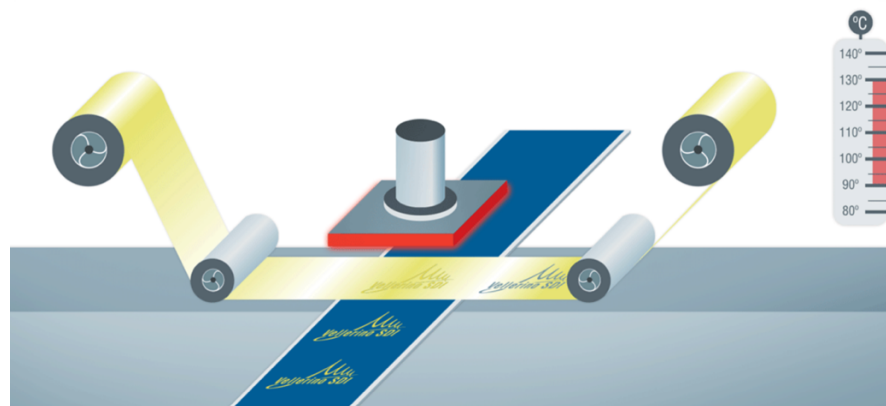


Fig. 16. Hot stamping technique for flat surface method (16)

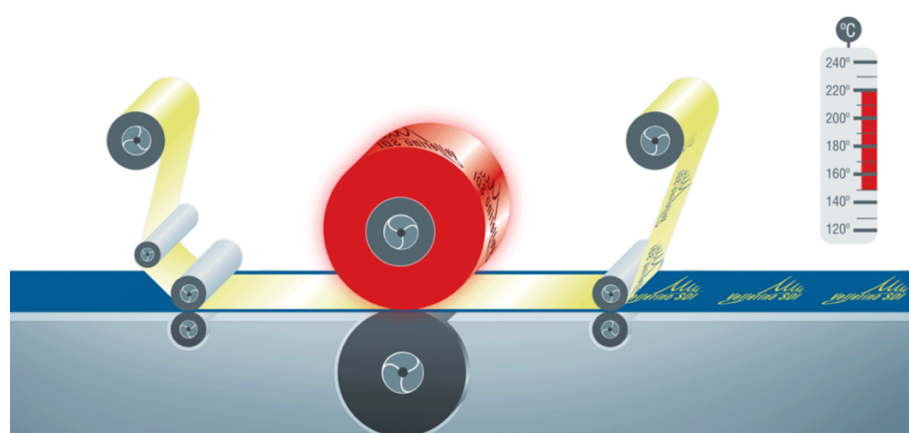


Fig. 17. Hot stamping technique for rotary method (16)

Various adhesives are used in this process but due to the environmentally friendly goals created by global warming most the companies are replacing the solvent based adhesive to solvent free adhesives some of the companies and their types of adhesives are discussed below.

JSC “ MKDS Innovation” produces non anionic surfactant which has commercial concentrated solution with 50-60% of diethylene glycol and less than 6 percent of no anionic surfactant (17). “Henkel” company’s emulsion is based on organic binder which mostly consists of polyvinyl alcohol which non-ionic biodegradable material which distributed to water Fig. 18 shows the sample adhesive packed in the box (18). “Caswell adhesives” company uses 600 varieties of PVA based adhesives as a base with various standards (19).

“Limited liability company(LUX-X)” produces bio adhesives that are produce from animal and vegetable wastes. This type of adhesive contains casein content which glue based substance when dissolved in water produces an alkaline solution with protein content. They are used in the alcohol labels present in the bottle as shown Fig. 19 (20). TGP(the glue people) company manufactures water based adhesives with polyvinyl alcohol with 50% concentration with D2 grade as shown in Fig. 20 (21).



Fig. 18. Henkel adhesive (17)



Fig. 19. LUX-X company's finished sample (20)



Fig. 20. TGP 50% concentration water based adhesive (21)

“Bond tech” water based adhesives producer manufactures varieties of water based adhesive such as white glues. The general form of water based adhesive used for various applications such as ATM cards, packing industry, adhesion for ultraviolet papers, assembly of products , coating the clay etc. They also have dextrin. Adhesive made from the vegetable consists of starches, which is a natural polymer. They are produce Water based adhesives in form of casein which is animal based protein have been around 4000 years, old technology used for bonding the paper and other packing (55).

“Conversion technologies” International company produce water based adhesives up to a curing temperature of 176⁰ C with 60 millimetres of maximum thickness with two method curing using the room temperature and drying the adhesive in hot air for quicker procedure. Some of their clients are Kimberly Clark, IAC, Ford, General motor, SAUDER, Visteon and Uniroyal (59). “Chemionics Corp.” produce water based adhesives with a standard of ISO 9001:2015 with no VOC substance present in them. They also produce other water based adhesives such dextrin, foam adhesive and latex based adhesives. They are producing them in various customisable colour used for various applications such as coating the films, bonding the layers (56).

“Celanese corporation manufactures” water based adhesives for the various food packing industries, bonding woods, bonding fabric material, films etc. They use a wide range of polymer for the adhesives and produce environmentally friendly adhesive for food packing industry(57). “Fraboadesvi”, Milan is very large producer of adhesive with motto of “ water is our element and sun is our energy” and produces water based adhesive in ISO standards for more than 50 years (58).

“Adhesive Direct UK. LTD” is an adhesive producer of water based and solvent based adhesive for various applications such construction, wooden assembly, paperboard. Their waterborne dispersion consists of Dextrin, Starch and polyvinyl acetate etc (60). “NANPAO” company produces water based adhesives uses neoprene as a major substance with 3 to 5 minutes curing condition at temperature of 55⁰ C. Main features of this adhesives are high heat resistance, good oxidation resistance and better adhesion properties. Viscosity of water based adhesive is between 2000 to 3500 centipoises (61).

“Tailored chemical products, INC” produces water based and solvent based adhesives. They also produce water and solvent cements for construction purposes, water based adhesive with high viscosity for packing industry and starch containing water based adhesive i.e. dextrin (62). “Applied adhesives” produces water based adhesive and their main components are starch (dextrin), emulsion and natural resins. They are specially manufactured for roll coating, injection moulding and layers.

There are many environmentally friendly adhesive producers who produce various standards of adhesives for various applications. And they recommend using their products. It is not sure that these adhesives satisfy their needs. The next step of this research is to find a suitable eco-friendly adhesive for hot stamping purpose from the producers and to improve their properties, so that they provide better efficiency.

3. Materials and Research Methodology

3.1. Materials

Three types of multilayer films have been selected: aluminum coated multilayer film for hot stamping (there and after - AHS) with thickness of $h = 19 \mu\text{m}$, transparent hot stamping foil (there and after THS) $h = 23 \mu\text{m}$ (III) and tamper evident film $h = 34 \mu\text{m}$ (there and after -TE). Fig 21 shows the structure of multilayer film selected for the experiment.

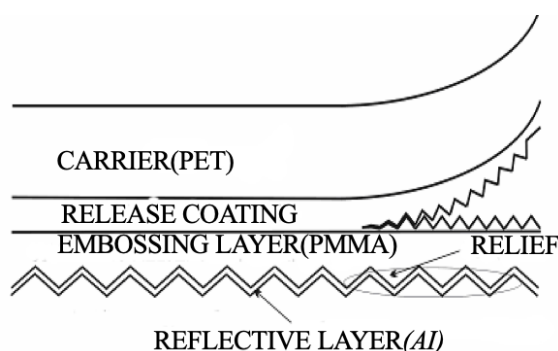


Fig. 21. Structure of multilayer film (28)

Commercial water born adhesive 125WB (Centro Grafico DG S.p.A, Italy) and commercial solvent based adhesive TC-03 (Centro Grafico DG S.p.A, Italy) were used.

In order to modify surface properties two types of surfactants was selected: 96% ethyl alcohol (EA) (producer AB “Stumbras”) and nonanoic surfactant (NAS) (produced by JSK, MKDS Innovation). Amounts of 0, 0.27, 0.54, 0.81, and 1.35 vol.% of surfactant to total amount of dispersion was added.

3.2. Research Methodology

3.2.1. Determination of Dynamic Viscosity at Constant Shear Rate

Rheological properties of water based, and solvent based adhesives were evaluated using Brookfield DVII + PRO rheometer apparatus as shown in Fig. 22. Initially, the rheometer was turned on and standard mode was selected and Autozeroing process was done by removing the spindle and resetting it. Then, the glass container was filled with 100 ml of investigated fluid was added in the rheometer and spindle (LV 61) Spindle was turned on. After every 10 minutes rotational speed was increased to 40, 60, 80, 100, 120, 140, 160, 180 and 200 rpm. The test was performed at temperature of $20 \pm 3^{\circ}\text{C}$ and the viscosity values were fixed.

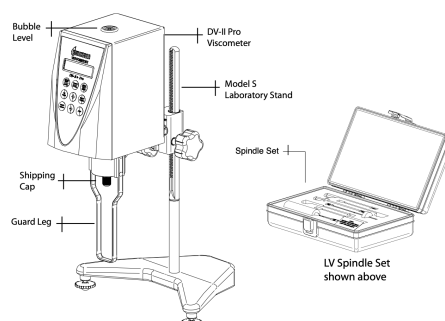


Fig. 22. View of Brookfield viscometer DV II + PRO viscometer (42)

3.2.2. Contact Angle Measurement

Contact angle measurements were conducted using goniometer equipped with digital camera. Droplet of investigated solution/dispersion was deposited on the surface of multilayer film. Contact angle relaxation process on the substrate surface was fixed by digital camera. Contact angle relaxation measurement was carried out by investigation of fixed digital images during 6 seconds after their contact with substrate. Fig. 23 shows the schematic diagram of contact angle measuring using goniometer. The stable state was assumed as Young contact angle. Measured value was assumed as average of 3 measurements. Image J software were used to measure the contact angle.

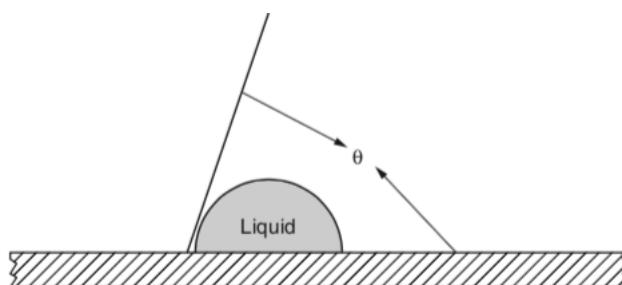


Fig. 23. Measurement of contact angle (28)

3.2.3. Dynamic Surface Tension Measurement

Surface tension measurements were carried out using dynamic contact angle meter and tensiometer DCAT 21 as shown in Fig 24, manufactured by Data Physics Instruments GmbH, Filderstadt (Germany). Initially, the Wilhelmy plate PT11 which is made of platinum iridium was burned using the blow torch to avoid presence of foreign substances.

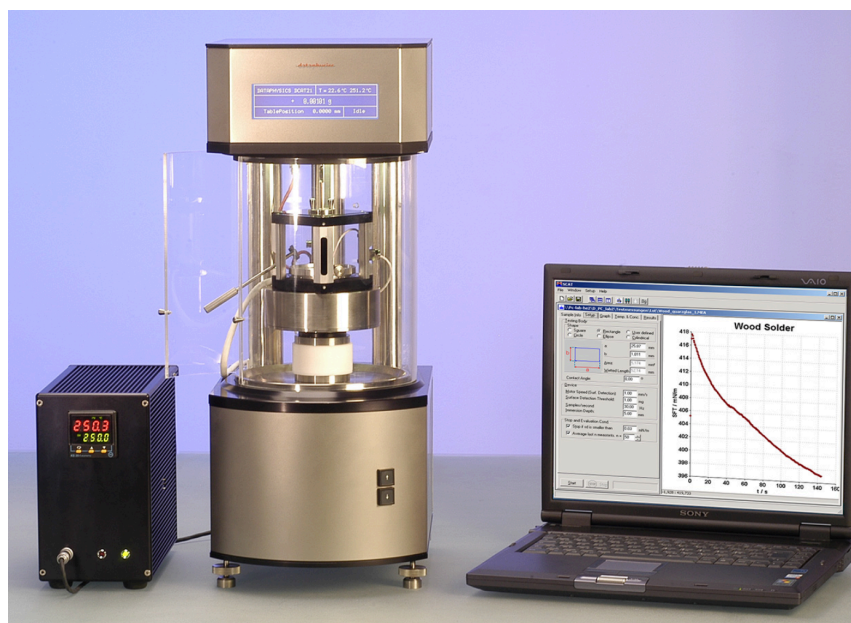


Fig. 24. Data physics DCAT II apparatus (35)

Then, the sample was placed inside the apparatus as shown in Fig 26. Following procedure presented in Fig. 25 the surface tension of the samples was measured. The surface tension was calculated using the Equation. (8, 9, 10) derived from Fig. 27 .

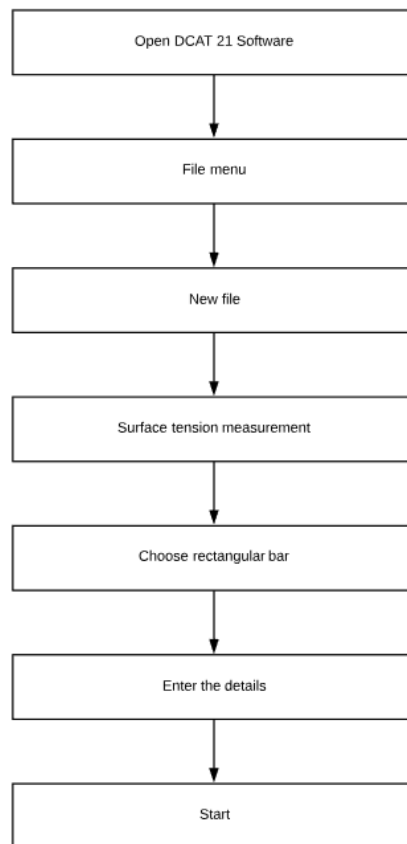


Fig. 25. List of steps to measure the surface tension of the investigation samples

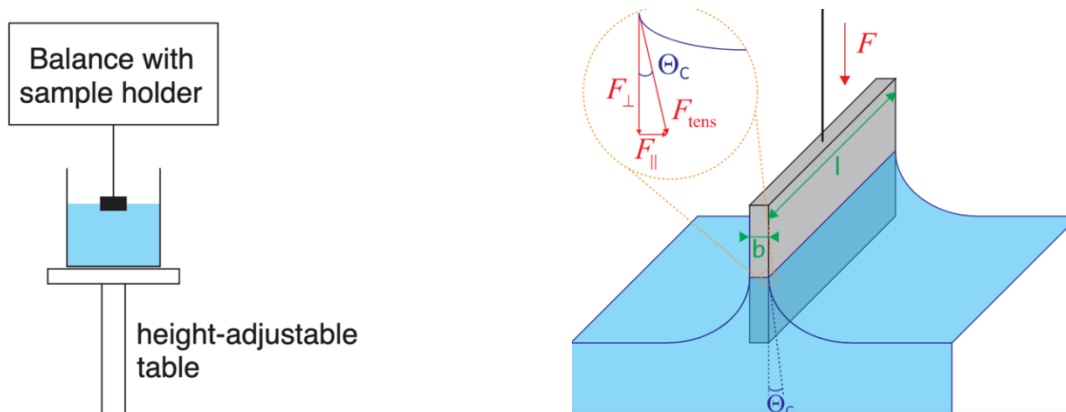


Fig. 26. 2D view of the plate inside the sample (33) **Fig. 27.** Wilhelmy plate in contact with the sample (33)

where,

$$F_{\perp} = F_{\text{tens}} * \cos\Theta_c \tag{8}$$

$$F_{\parallel} = F_{\text{tens}} * \sin\Theta_c \quad (9)$$

$$\sigma = \frac{F_{\text{tens}}}{L} = \frac{F_{\perp}}{L * \cos\Theta_c} = \frac{FG}{L * \cos\Theta_c} \quad (10)$$

$$L = 2b + 2l \quad (33).$$

where,

b = thickness of the plate, millimetre;

l = length of the plate, millimetre;

Θ_c = deviation angle, degree.

3.2.4. Determination of Solution Concentration

Express method for determination of solution concentration was used. Initially, plates were weighed (M_1) and reading was noted. Using micropipette, the solution was dropped in one of the plates in the centre and they were closed using the other one and weighed (M_2). The steps were repeated for three times with three different pairs of plates at two different adhesives. Then, they were placed in the ovens with two distinct temperatures 70 °C for solvent based and 100°C for water based. After 30 minutes the plates were drawn from the oven and they were weighed, and the readings were noted (M_2). Finally, this step was repeated for every consecutive 10 minutes until the plates show a constant mass. Using the Equation 7 the concentration of the liquid was calculated.

$$K = \frac{M_2 - M_0}{M_1 - M_0} \times 100 \quad (7)$$

where,

K = Concentration of the solution, % ;

M_0 = initial mass of the plates, g;

M_1 = mass of the plates with solution, g;

M_2 = final mass of the plates, g.

4. Results and Discussions

4.1. Comparison of Rheological Properties of Water Based and Solvent Based Adhesive at Constant Shear Rate

It is known that for solutions in organic solvents and water based dispersions non-Newtonian behaviour under shear conditions are characteristic. During selection of optimal technological regimes for thin adhesive layer formation using roll coating technique and to ensure smooth and even in thickness layer formation it is important to understand mechanism of materials behaviour under rotational conditions.

Dynamic viscosity of solvent based adhesive concentration of $C=10\%$ and water based dispersion concentration of $C=39\%$ was determined at different rotational speed. Obtained results for solvent based and water based adhesive respectively are presented in Fig 28 and Fig. 29.

In Fig. 28 viscosity changes of solvent based adhesive during 1 hour at rotational speed of $D=140$, 180 and 200 rpm are presented. Due to low concentration solution shows quite low viscosity values. They are not higher than 17 mPas. It seems that viscosity is high dependent on rotational speed value. At rotational speed of 180 and 200 rpm decrease of viscosity with increase of rotation duration was found, while at rotational speed of 140 rpm slight increase of viscosity from 10 to 13.3 mPas was obtained. Interesting to state, that after 10 minutes of testing, viscosity of solution at rotational speed of 140 and 180 rpm reaches the same value and is equal to 13.3 mPas. Different changes made was found for solution at rotational speed of 200 rpm. After decrease of viscosity at first 10 testing minutes from 10 to 6 mPas, plateau of viscosity till 40 minutes is characteristic. After that viscosity started to decrease. Seems, that viscosity after 60 min at 200 rpm are more than 7 times lower than those found for solutions at 140 and 180 rpm.

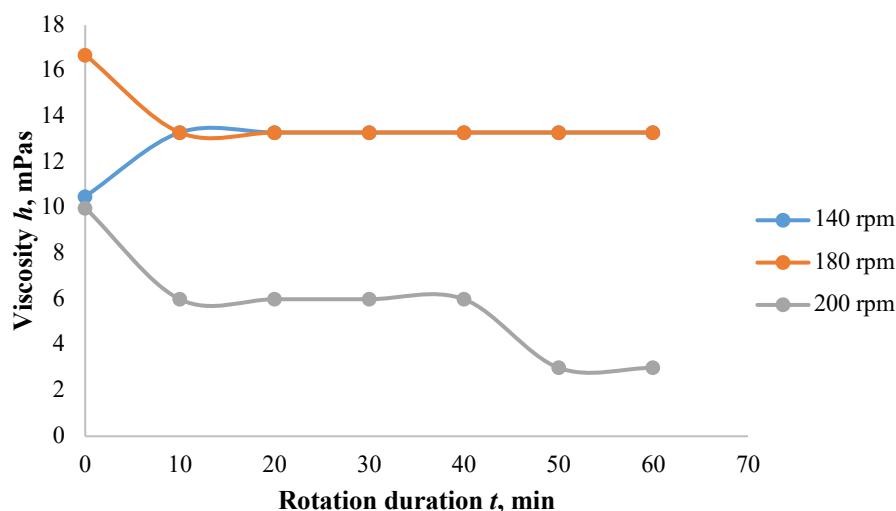


Fig. 28. Influence of constant shear rate duration on the viscosity of SBA

Higher viscosity values compare to those of solvent based adhesive, were found for water based dispersion (Fig. 29). That is mainly due to 4 fold higher concentration of film forming material in water medium compare to those of solvent base. At rotational speed of 40 and 100 rpm no viscosity changes during all testing period was found. In this case dispersion behaviour was similar to the Newtonian fluid, when dispersion behaviour is independent to the external forces. At higher than

100 rpm rotational speed after 10 minutes of testing slight increase of viscosity was found after what they remain constant during rest period of testing. While at rotational speed of 60 and 80 rpm investigated dispersion shows decrease of viscosity from 70 down to 60 mPas and from 67.7 down to 60 mPas at rotational speed 60 and 80 rpm, respectively. The reached viscosity value is the same as those obtained for dispersion at rotational speed of 120 rpm and 40 rpm.

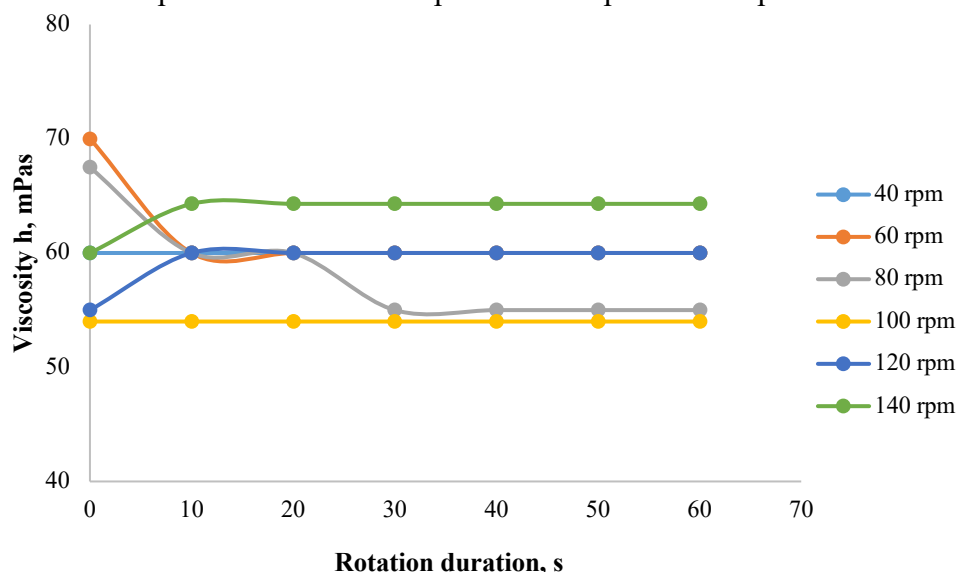


Fig. 29. Influence of constant rotational speed duration on the viscosity of WBA

Obtained results showed that water based adhesives due to the higher concentration of film forming material shows significantly higher viscosity values compare to those of solvent born. Effect of shear rate on viscosity changes has uneven character. At lower than 100 rpm rotational speed (60 and 80) during first 10 min of testing viscosity tend to decrease while for rotational speed of 120 rpm and 140 rpm slight increase of viscosity was found.

4.2. Comparison of Wettability of Water based and Solvent Based Adhesives.

Methodology of evaluation of wettability of water based and compare it with the solvent based adhesives on different substrates, process of adhesive droplet relaxation on the three selected films have been investigated. Wettability of water based, and solvent based adhesives were performed as explained in chapter 3.2.2. Three types of multilayer films have been selected: aluminum coated multilayer film for hot stamping (AHS) with thickness of $h = 19 \mu\text{m}$, transparent hot stamping foil (THS) $h = 23 \mu\text{m}$ (III) and tamper evident film $h = 34 \mu\text{m}$ (TE).

As it was mentioned in the previous chapter 3.2.4 concentration of the solution was determined. Obtained results show that water based dispersion was $C=39 \%$ and concentration of solvent based adhesive was found equal only to $C=10 \%$. Evident that due to high concentration of water adhesive usually it is difficult provide high wetting angle value.

Obtained digital images of contact angle views are presented in Table 1 and Table 2. Table 1 shows the digital visualisation of water based adhesive and Table 2 shows the digital representation of solvent based adhesive and how they vary during the entire relaxation process. Obtained images shows that initial contact angle of water based adhesive independently on the substrate nature tend to decrease to 30 degree for AHS, and TE and 12 degree for THS.

After 1 second water based adhesive shows one degree of decrease for AHS, 5.3 degrees for decrease for THS and 16 degree of decrease for TE. After 2 seconds AHS show less a degree of decreases in contact angle, THS shows decreases of 2.5 degree of contact angle and TE shows one degree of decrease in contact angle. Eventually, there was no major significant decrease of contact angle during next few seconds. The young contact angle values are 46.56 degrees for AHS, 43.16 degrees for THS and 47.74 degrees for TE films.

In case of solvent based adhesive, the initial contact angle decreased about 13 degree for AHS, 10 degree for THS and 5 degree for TE. The contact decreases gradually during next few seconds. After one second solvent based adhesive shows decrease of 4 degrees for AHS, 9 degree for TE and 10 degree for TS. After 2 seconds they show 2 degrees for AHS, 6 degree for TE and 5 degree for TE. The young contact angle values are 25.7 degrees for AHS, 21 degrees for TE and 25 degree for TE.

Results shows that the least young contact angle was achieved by TE film for 21 degrees for solvent based whereas the highest young contact angle was achieved by THS for 43.16 degrees for water based adhesive. Results showed that water based adhesive shows twice higher young contact angle value when compared to the solvent based adhesive. From this it was understood that solvent based adhesive provides good wetting angle when compared to water based adhesive.

Obtained results are presented in Fig. 30 and 31. For water based adhesive it was found that drastic decrease of wetting angle value during first second after drop contact with the surface. For hot stamping foils this decrease was found about 30 degrees, i.e. wetting angle value decreased from 82.4° till 51.6° and from 84.8 till 54.7 degrees for AHS and THS respectively. While for temper evident film decrease was not so intensive. After 1 second of contact it was decreased from 80.7 down to 68.9 degrees.

Obtained changes of wetting angle value indicates that after 2 seconds of contact, changes of wetting angle values become insignificant and after 5 seconds equilibrium was reached and wetting angle values of 47.7, 46.6 and 43.2 for TE, AHS, and THS film was found. Obtained values indicates that selected dispersion shows good wetting ability of the selected surfaces. It was interesting to compare obtained results with commonly used solvent based adhesives.

Contact angle changes between solvent based adhesive droplet and surface of selected films are presented in Fig. 31. It is evident that just after deposition contact angle values are significantly lower compare to those, obtained after WBA drop deposition and are lower than 60 degrees. Increase of duration after droplet deposition results on the gradual decrease of contact angle value and after 5 seconds it falls down to 20-25 degrees. Follows that for solvent based adhesives contact angle value is more than twofold lower than those for water based adhesive.

Table 1. Digital images of contact angle for WBA

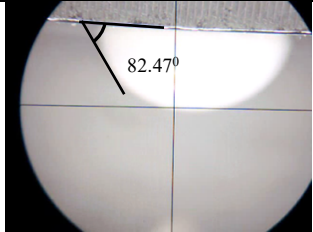
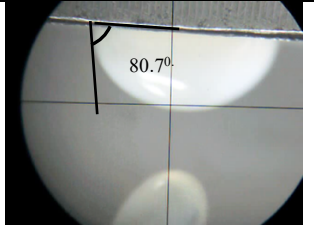
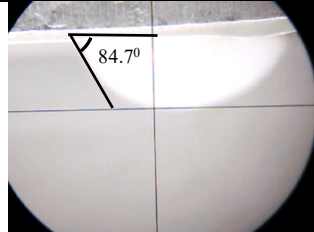
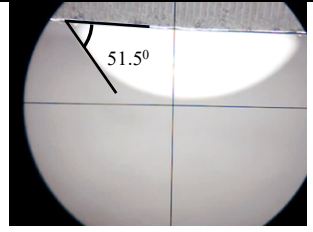
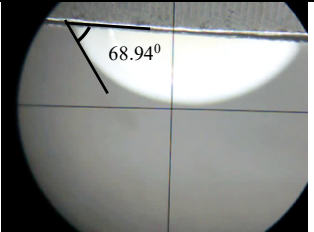
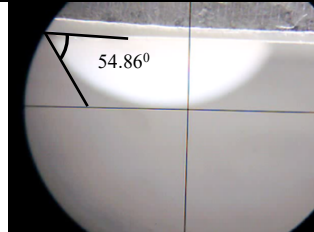
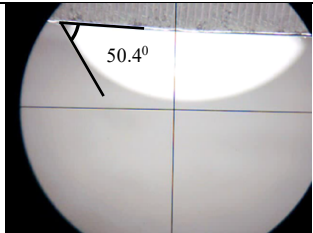
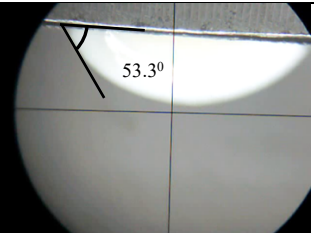
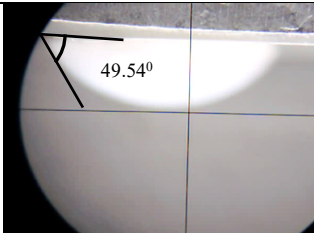
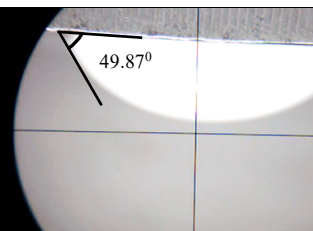
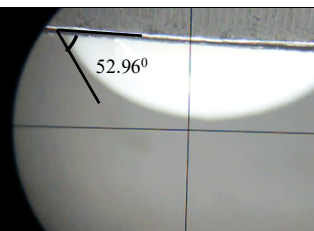
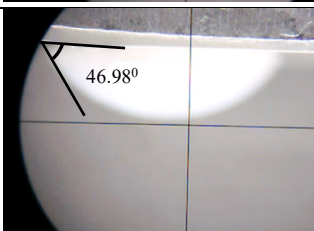
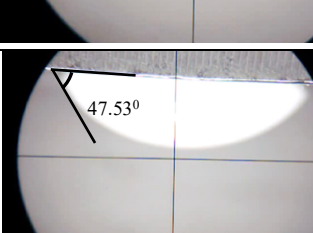
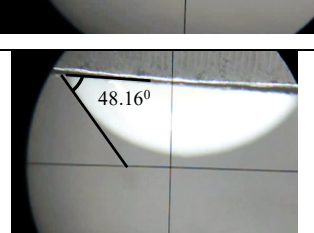
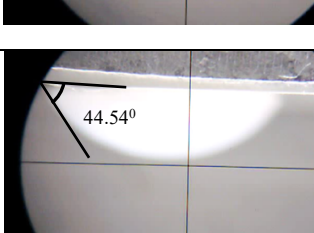
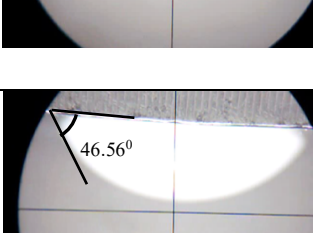
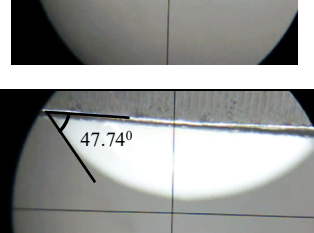
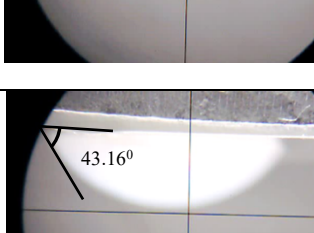
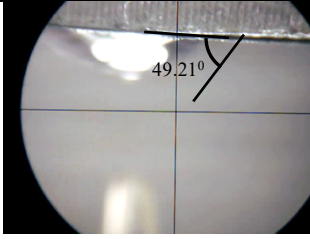
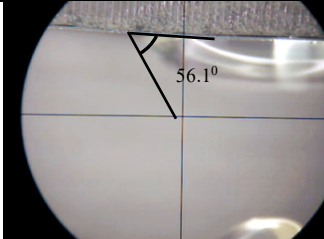
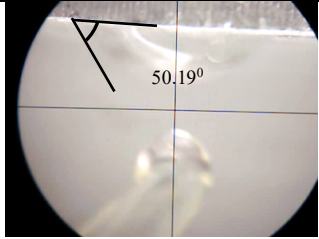
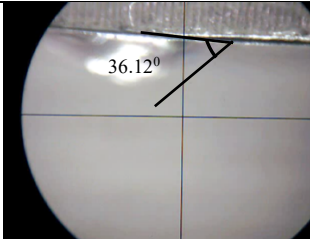
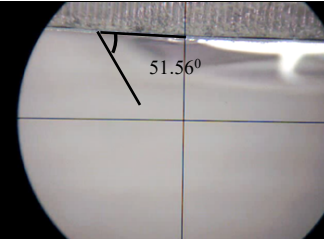
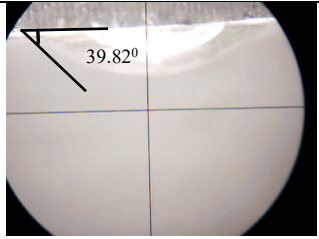
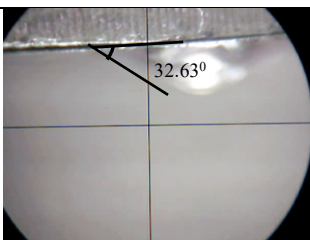
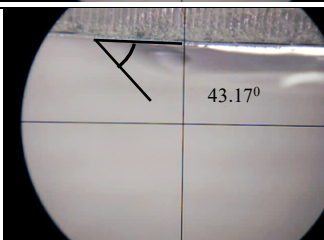
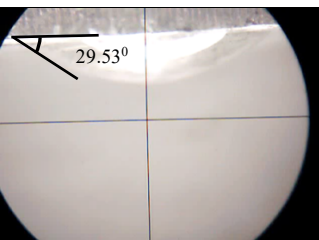
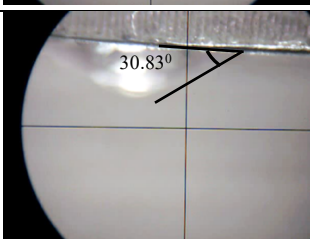
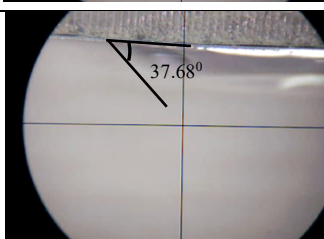
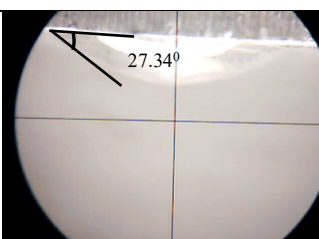
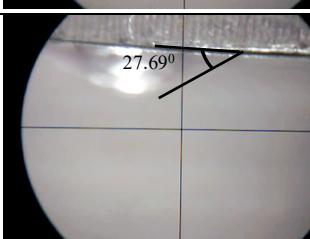
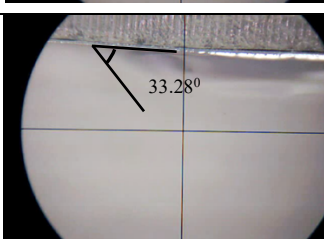
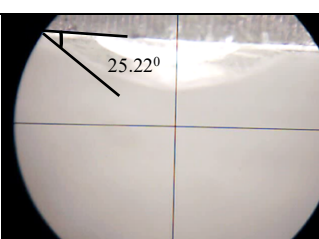
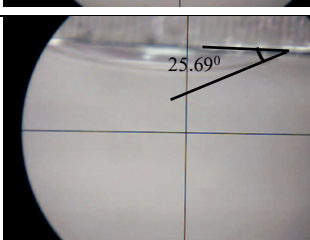
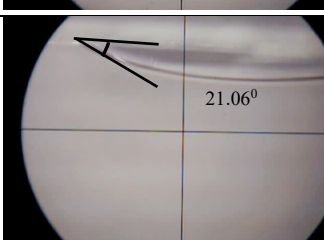
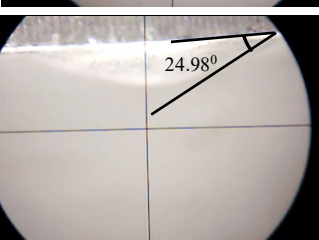
Duration after droplet coated with surface (τ)	Types of multilayer films		
	AHS	TE	THS
0	 82.47°	 80.7°	 84.7°
1	 51.5°	 68.94°	 54.86°
2	 50.4°	 53.3°	 49.54°
3	 49.87°	 52.96°	 46.98°
4	 47.53°	 48.16°	 44.54°
5	 46.56°	 47.74°	 43.16°

Table 2. Digital images of contact angle for solvent based adhesive

Duration after droplet coated with surface (τ)	Types of multilayer films		
	AHS	TE	THS
0	 49.21°	 56.1°	 50.19°
1	 36.12°	 51.56°	 39.82°
2	 32.63°	 43.17°	 29.53°
3	 30.83°	 37.68°	 27.34°
4	 27.69°	 33.28°	 25.22°
5	 25.69°	 21.06°	 24.98°

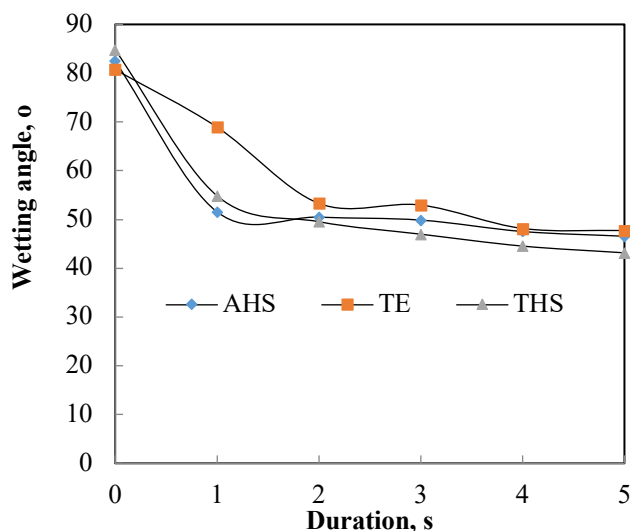


Fig. 30. Water based adhesive droplet relaxation in different multilayer films

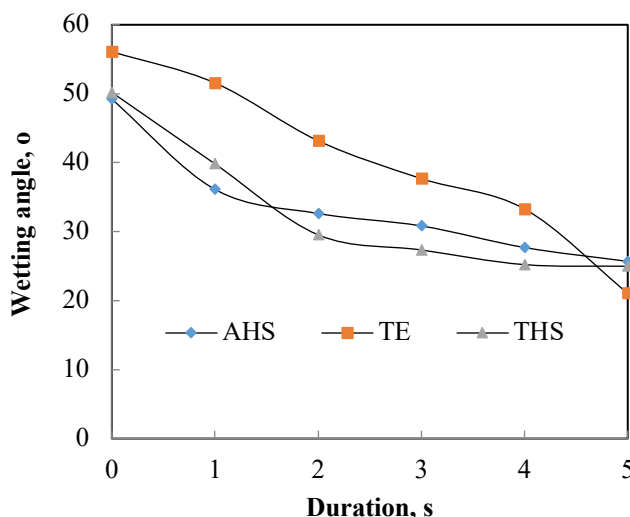


Fig. 31. Solvent based adhesive droplet relaxation in different multilayer films

Obtained results shows that in order to increase wettability of water based adhesive to selected substrates different amounts (0.27 vol. % , 0.51 vol. % , 0.81 vol. % and 1.35 vol. % to total amount of dispersion) of ethyl alcohol and commercial non anionic surfactant was added. It was determined that independently on substrate nature addition of ethyl alcohol and non-anionic surfactants decreases the initial contact angle, but increases Young contact angle compare to those of pure dispersion.

4.3. Influence of Surfactants on the Wetting Properties of Water Based Adhesives

From the modified water based additives, as discussed in chapter 3 the influence of surfactant on three different films and their contact angle are discussed below.

Obtained results tend to the decision to find out ways to improve wettability of selected dispersion by different amounts of EA and NAS additives as surface active agents. Influence of these additives on the contact angle changes just after deposition and young's contact angle are presented in Table

3.

From the influence of EA on AHS results show that initial contact angle decreased about 10 degree compare to pure substance. After initial second with 0.27 vol. % AHS contact angle decreased to 5 degree, 0.54 vol. % for 10 degree, 0.81 vol. % for 9 degree and 1.35 vol. % for 4 degrees. After 1 seconds with 0.27 vol. % AHS contact angle decreased to 6 degrees, 0.54 vol. % for 4 degree, 0.81 vol. % for 2 degree and 1.35 vol. % for 3 degrees. After 3 seconds with 0.27 vol. % AHS contact angle decreased to one degree, 0.54 vol. % for 2 degrees, 0.81 vol. % for less than degree and 1.35 vol. % for 2 degrees. After 4 seconds with 0.27 vol. % AHS contact angle decreased to less than degree, 0.54 vol. % for 1.5 degrees, 0.81 vol. % for one degree and 1.35 vol. % for 4 degrees. Obtained results show that amount of surfactant influences the contact angle of the adhesives in during the entire relaxation process. The young contact angle value are 57.55 degrees, 51 degrees, 55.67 degrees and 54.8 degrees for 0.27 , 0.54, 0.81 and 1.35 vol% of EA surfactants respectively. Obtained results shows the addition EA reduces the initial contact angle value but increases the young contact angle value.

From the influence of NAS on AHS, results show that initial contact angle decreased on average of 5 degree compare to pure substance. After initial second with 0.27 vol. % AHS contact angle decreased to 10 degree, 0.54 vol. % for 12 degree, 0.81 vol. % for 4 degree and 1.35 vol. % for 5 degrees. Comparing it with EA results shows contact angle decrease during the first second with the influence of NAS. After 1 seconds with 0.27 vol. % AHS contact angle decreased to 9 degrees, 0.54 vol. % for 4 degree, 0.81 vol. % for 2 degree and 1.35 vol. % for 2 degrees. After 3 seconds with 0.27 vol. % AHS contact angle decreased to 4 degree, 0.54 vol. % for 2 degrees, 0.81 vol. % for 4 degrees and 1.35 vol. % for 3 degrees. After 4 seconds with 0.27 vol. % AHS contact angle decreased to less than degree, 0.54 vol. % for 3 degrees, 0.81 vol. % for one degree and 1.35 vol. % for 2 degrees.

From the influence of EA on THS results show that initial contact angle decreased about 10 degree compare to pure substance. After initial second with 0.27 vol. % THS contact angle decreased to 9 degree, 0.54 vol. % for 9.6 degree, 0.81 vol. % for 9 degree and 1.35 vol. % for 4 degrees. After 1 seconds with 0.27 vol. % THS contact angle decreased to 8.3 degrees, 0.54 vol. % for 6 degrees, 0.81 vol. % for 7 degree and 1.35 vol. % for 4 degrees. After 3 seconds with 0.27 vol. % THS contact angle decreased to 3 degree, 0.54 vol. % for 2 degrees, 0.81 vol. % for less than degree and 1.35 vol. % for 1 degree. After 4 seconds with 0.27 vol. % THS contact angle decreased to less than degree, 0.54 vol. % for 1 degree, 0.81 vol. % for less than one degree and 1.35 vol. % for 3 degrees. Obtained results show that amount of surfactant influences the contact angle of the adhesives in during the entire relaxation process. The young contact angle value are 50.28 degrees, 53.87 degrees, 52.92 degrees and 50.06 degrees for 0.27, 0.54, 0.81 and 1.35 vol% of EA surfactants respectively.

From the influence of NAS on THS, results show that initial contact angle decreased on average of 8 degree compare to pure substance. After initial second with 0.27 vol. % THS contact angle decreased to 11 degree, 0.54 vol. % for 12.3 degrees, 0.81 vol. % for 7.92 degrees and 1.35 vol. % for 4 degrees. After 1 second with 0.27 vol. % THS contact angle decreased to 3 degrees, 0.54 vol. % for 4 degree, 0.81 vol. % for 4 degree and 1.35 vol. % for 3 degrees. After 2 seconds with 0.27 vol. % AHS contact angle decreased to 3 degree, 0.54 vol. % for 3 degrees, 0.81 vol. % for 2

degrees and 1.35 vol. % for 2 degrees. After 4 seconds with 0.27 vol. % THS contact angle decreased to 4 degree, 0.54 vol. % for less than one degrees, 0.81 vol. % for 2.6 degrees and 1.35 vol. % for 5 degrees. Obtained results show that amount of surfactant influences the contact angle of the adhesives in during the entire relaxation process.

Table 3. Influence of wetting agent amount on the initial and Young contact angle values

Film type	AHS		TE		THS	
Additive amount vol%	EA	NAS	EA	NAS	EA	NAS
Initial contact angle ($\tau = 0$)						
0	82.4		80.7		84.8	
0.27	88.74	72.31	79.26	75.67	70.26	77.8
0.54	70.66	73.61	72.54	70.84	65	63.7
0.81	74.34	71.84	77.31	74.38	69.45	67.33
1.35	78	75.9	68.15	71.44	66.52	69.84
At $\tau = 1$						
0	51.56		54.6		53.32	
0.27	75.5	61.04	65.42	68.55	63.67	56.18
0.54	60	67.38	63.37	61.33	58.79	58.33
0.81	65.3	65.44	62.44	62.56	58.88	60.56
1.35	74.16	62.46	61.84	61.06	57.04	62.88
At $\tau = 2$						
0	56.1		56.18		55.13	
0.27	69.85	56.22	59.47	58.91	60.473	53.27
0.54	58.57	57.35	58.89	57.59	56.2	55.46
0.81	60.52	60.58	57.4	58.84	56.4	57.45
1.35	65.73	62.46	56.54	57.97	54.33	58.3
Young contact angle ($\tau = 5$)						
0	46.7		47.6		43.2	
0.27	57.5	52.66	50.28	55.31	54.4	48.45
0.54	50.59	50.59	53.87	52.88	55.51	51.47
0.81	55.67	54.28	52.92	54.72	53.31	51.88
1.35	54.8	53.77	50.06	51.49	48.82	52.78

From the influence of EA on TE results show that initial contact angle decreased about 19 degrees compare to pure substance. After the initial second with 0.27 vol. % TE contact angle decreased to 9 degree, 0.54 vol. % for 2 degree, 0.81 vol. % for 8 degree and 1.35 vol. % for 5 degrees. After one second with 0.27 vol. % TE contact angle decreased to 2 degrees, 0.54 vol. % for 5 degree, 0.81 vol. % for 3 degree and 1.35 vol. % for 2.5 degrees. After 2 seconds with 0.27 vol. % TE contact angle decreased to 3 degrees, 0.54 vol. % for 2 degrees, 0.81 vol. % for 2 degrees and 1.35 vol. % for 3 degrees. After 4 seconds with 0.27 vol. % TE contact angle decreased to 4 degrees, 0.54 vol. % for 1 degree, 0.81 vol. % for one degree and 1.35 vol. % for 1.6 degree. Obtained results show that amount of surfactant influences the contact angle of the adhesives in during the entire relaxation process. The young contact angle value are 54.42 degrees, 55.51 degrees, 53.31 degrees and 48.82 degrees for 0.27, 0.54, 0.81 and 1.35 vol% of EA surfactants respectively.

From the influence of NAS on TE, results show that initial contact angle decreased on average of 10 degree compare to pure substance. After the initial second with 0.27 vol. % TE contact angle decreased to 17.4 degrees, 0.54 vol. % for 8 degree, 0.81 vol. % for 7 degree and 1.35 vol. % for 4 degrees. After 1 second with 0.27 vol. % TE contact angle decreased to 4 degrees, 0.54 vol. % for 3.8 degrees, 0.81 vol. % for 3 degree and 1.35 vol. % for 3 degrees. After 2 seconds with 0.27 vol. % TE contact angle decreased to 3 degree, 0.54 vol. % for 3 degrees, 0.81 vol. % for 3 degrees and 1.35 vol. % for 4 degrees. After 4 seconds with 0.27 vol. % TE contact angle decreased to 2 degrees, 0.54 vol. % for 2 degrees, 0.81 vol. % for 3 degrees and 1.35 vol. % for 3 degrees. Obtained results show that amount of surfactant influences the contact angle of the adhesives in during the entire relaxation process.

It is evident that increase of additive content results on the significant decrease of contact angle values just after droplet deposition. Unfortunately, results indicate that for final contact angle value addition of selected additives results on the decrease of wettability, i.e. Young's contact values increase compare to those of unmodified compositions.

4.4. Effect of Surfactants on the Dynamic Surface Tension of Water Based Adhesives

Wetting properties evaluation results tend to the suggestion that selected additives changes surface properties of adhesives. Next task was to investigate influence of selected surfactants on the dynamic surface tension of adhesives. Obtained relaxation curves are presented in Fig. 32-40 and relaxation duration is summarized in Table 4.

It is evident (Fig. 32-34) that for all investigated compositions is characteristic drastic decrease of surface tension during first 10 seconds, after what process is starting to go more slowly up to reaching equilibrium.

From the results presented in Table 4. It is evident that edition of selected additives results on the decrease of relaxation duration. That can be one of reasons why values of Young's contact angle after addition of additives was found to increase.

Summarized final dynamic surface tension values for investigated compositions are presented in Fig. 35. The pure form of water based adhesive with surface tension value was found of 29.067 ± 0.029 mN/m.

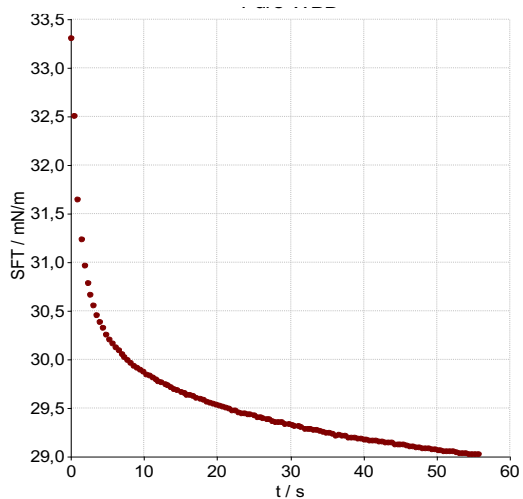
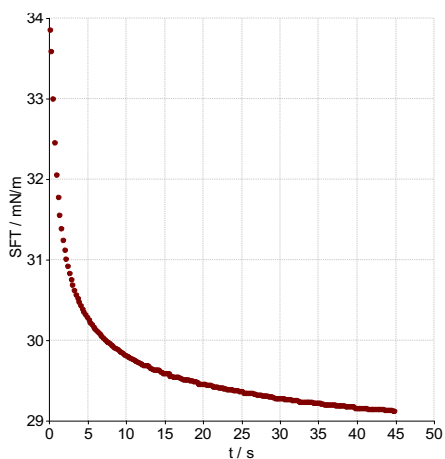
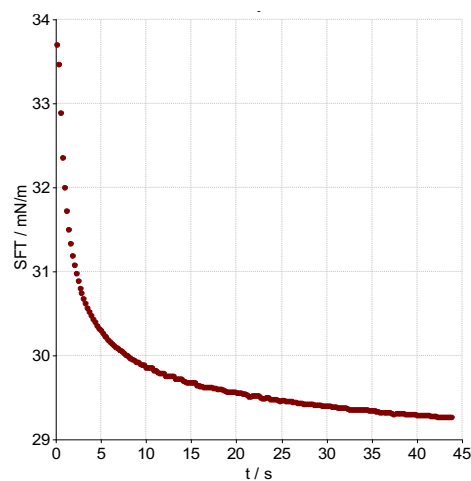


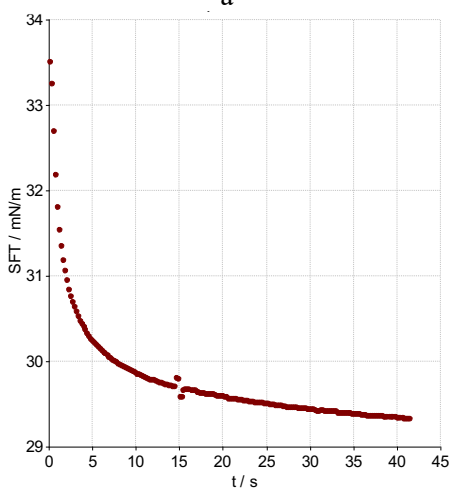
Fig. 32. Surface tension measurements for pure WBA



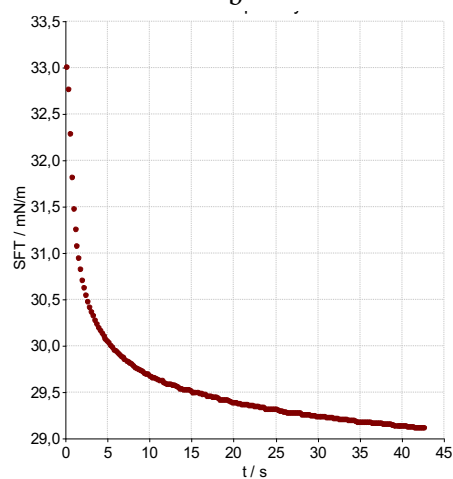
a



b



c



d

Fig. 33. Surface tension measurements for WBA with 0.27 (a), 0.54 (b), 0.81 (c) and 1.35 (d) vol. % of EA

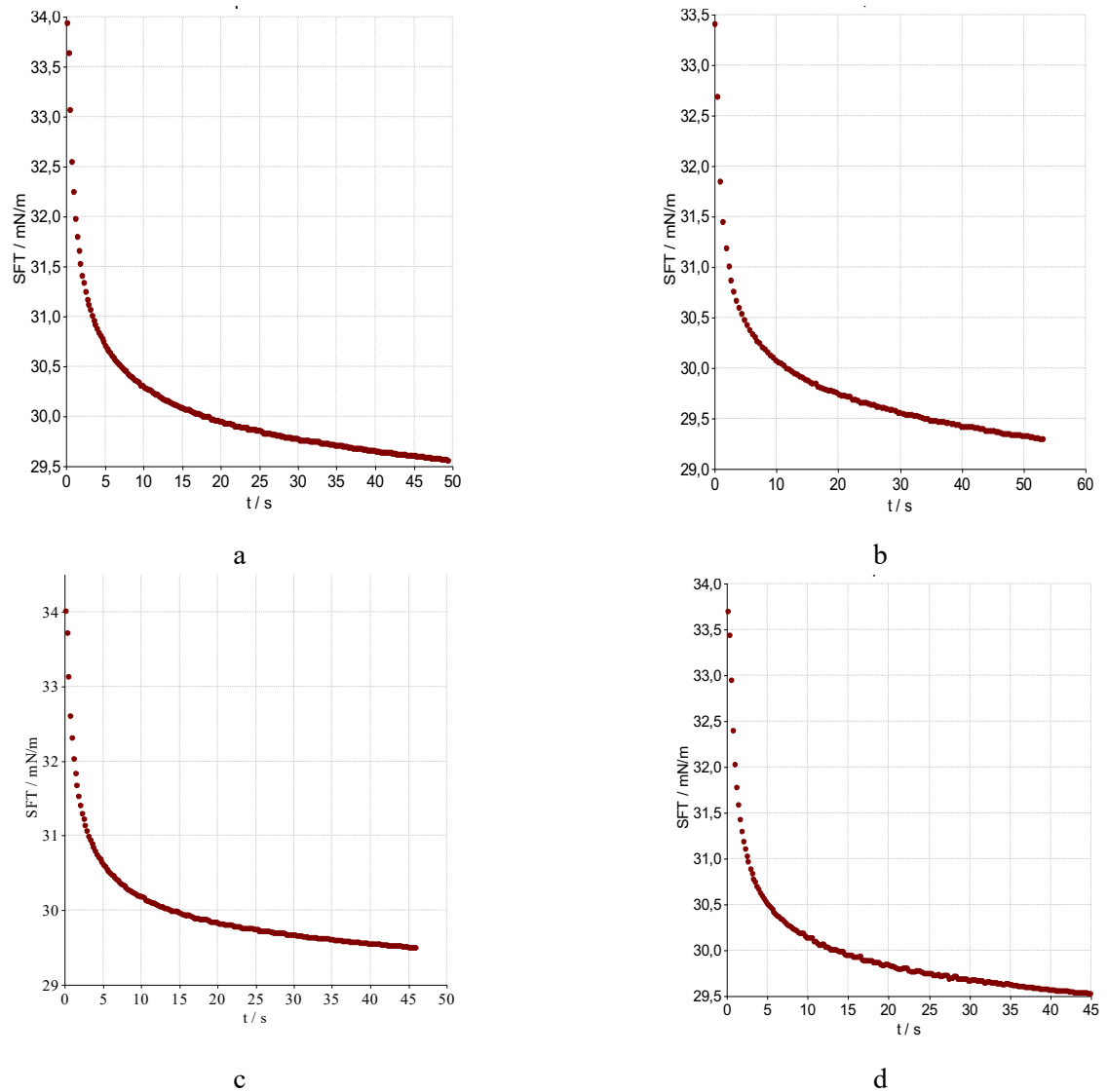


Fig. 34. Surface tension measurements for WBA with 0.27 (a), 0.54 (b), 0.81 (c) and 1.35 (d) vol. % of NAS

Table 4. Relaxation duration of surfactant

Surfactant amount vol. %	Relaxation duration, s	
	EA	NAS
0	56	56
0.27	45	50
0.54	44	53
0.81	42	46
1.35	43	45

Obtained results for modified water based adhesive shows least surface tension variation in 1.35 vol. % of EA with 29.160 ± 0.030 mN/m as shown in Fig 33 (a), with maximum variation in 0.27 vol. % of NAS with 29.604 ± 0.030 mN/m in Fig 34 (a). Comparing the results of adhesive influence with EA surfactant, results shows that relaxation duration has decreased. In Fig. 33(a)

shows 0.27 vol. % of EA that initial surface tension value has increased to 0.05 mN/m comparing with pure WBA, but relaxation duration has decreased to 10 seconds.

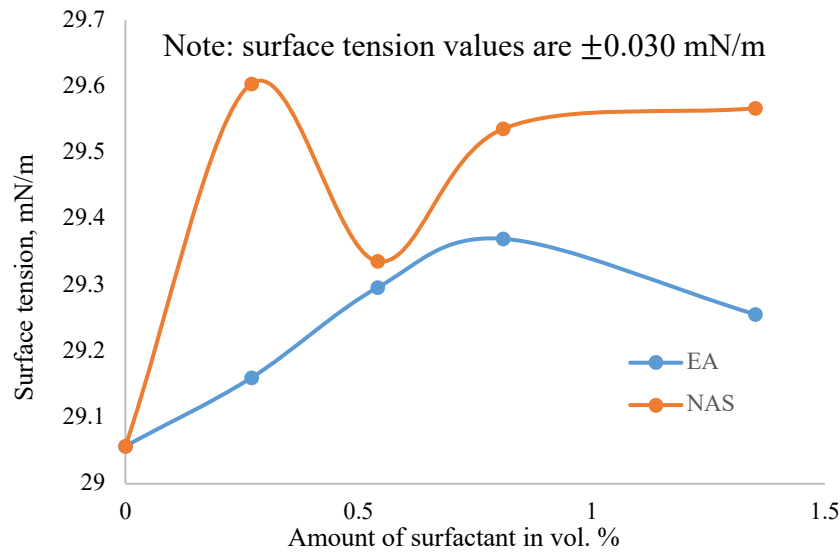


Fig. 35. Surface tension of WBA vs Amount of surfactants

From Fig. 33 (b), the initial surface tension value has decrease to 0.01 mN/m and relaxation duration to 1 second comparing with 0.27 vol. % of EA. This shows the addition of 0.51 vol. % amount of EA surfactant influences the surface properties. Fig. 33 (c) shows 0.81 vol. % of EA with WBA surface tension values has decreased to 0.01 mN/m compared to 0.54 vol. % and relaxation duration has decreased to 2 seconds. This shows that there is an influence of surfactant with reduces the surface tension and relaxation duration. Fig. 33 (d) shows surface tension measurements of 1.35 vol. % of EA with WBA. Obtained results shows that surface tension has decreased to 0.03 mN/m compare to 0.81 vol. % and relaxation duration has increased to 2 seconds. Comparing with all the surface tension measurements 1.35 vol. % of EA shows the least surface tension. Due to the high concentration percentage of water based adhesive the surface tension is higher compared to solvent by adding more one percent of surfactant, surface tension can be reduced. This can improve the wettability of the adhesives.

Surface tension measurement values of 29.604 ± 0.030 mN/m 0.27 vol. % of NAS with WBA. Obtained results show that surface tension has increased to 0.04 mN/m and relaxation duration has decreased to 4 seconds. Fig. 34 (b) shows surface tension measurements for 0.54 vol. % of NAS with WBA. Obtained results shows that surface tension has decrease to 0.05 mN/m, but relaxation duration has increased to 2 seconds. Fig. 34 (c) shows the surface tension measurement of 0.81 vol. % of NAS. Obtained results show that surface tension has increased to 0.04 mN/m and relaxation duration has decreased to 5 seconds compared to 0.54 vol. %. Fig. 34 (d) shows that 1.35 vol. % of NAS. Results show that surface tension has decreased to 0.03 mN/m and relaxation duration to 1 second compared to 0.81 vol. %.

Fig 35 shows the total change of surface tension value over amount of surfactant volume in percentage. From this it can be concluded that usage of surfactant has to be limited to modify the properties adding high amounts of the surfactants reduces the surface tension compared to lower amounts. Addition of 1.35 vol. % of EA shows better results where compared with others.

Conclusions

The evaluation of water based adhesives was carried out and ways to improve the wettability of water based adhesives on the different multilayer films for hot stamping purposes were done.

1. An overview of water based adhesives present in the market have been discussed. There are many environmentally friendly adhesive producers who produce various standards of adhesives for various applications. And they recommend using their products. It is not sure that these adhesives satisfy their needs. The next step of this research is to find a suitable eco-friendly adhesive for hot stamping purpose from the producers and to improve their properties, as a result they provide better efficiency.
2. The rheological behaviour of solvent based, and water based dispersions at constant rotational speed of $D = 40, 60, 80, 100, 120$ and 140 rpm for 1 hour have been investigated.
 - 2.1. It was determined that due to the four fold higher concentration of film forming material in water based dispersions significantly higher dynamic viscosity values compare to those of solvent based was found.
 - 2.2. Dynamic viscosity of solvent based adhesives is high dependent on rotational speed value. It was found impossible to fix dynamic viscosity of solvent based solution at low rotational speed ($D = 40, 60$ and 80 rpm). At rotational speed of 180 and 200 rpm decrease of viscosity with increase of rotation duration was found, while at rotational speed of $D = 140$ rpm slight increase of viscosity from $\eta = 10$ mPas to $\eta = 13.3$ mPas during first 10 min of rotation was determined.
 - 2.3. Viscosity of solvent based adhesives after rotation for 60 min at 200 rpm are more than 7 times lower than those found for solution at rotational speed of $D = 140$ and 180 rpm.
 - 2.4. Effect of rotational speed on water based adhesive viscosity changes has uneven character. At lower than 100 rpm rotational speed (60 and 80 rpm) during first $\tau = 10$ min of testing viscosity tends to decrease, while at rotational speed of 120 rpm and 140 rpm slight increase of viscosity was found. At rotational speed of $D = 40$ and 100 rpm dispersions showed behaviour characteristic for Newtonian fluids, i.e. rotation duration had no influence on the viscosity of dispersion.
3. The contact wetting angle relaxation of solvent and water based adhesives on the surface of aluminium coated and transparent hot stamping foil and tamper evident hot stamping foil have been investigated.
 - 3.1. It was found that process of contact angle relaxation up to reaching constant (Young contact angle) value depends on the both adhesive and substrate nature.
 - 3.2. It was found that on both investigated hot stamping foil surfaces more intensive wetting angle shape changes were found during 2 first seconds, while for tamper evident film contact angle value gradually decreased. This mode was found for both water based and solvent based adhesives.
 - 3.3. During 1 second of contact for hot stamping foils decrease of contact angle value was found about 30 degrees, i.e. wetting angle value decreased from 82.4° till 51.6° and from 84.8 till 54.7 degrees for aluminium coated and transparent hot stamping foils respectively. For tamper evident film decrease was not so intensive. After 1 second of contact it was decreased from 80.7 down to 68.9 degrees.

- 3.4. Young contact angle for solvent based adhesive was two time lower compare to the water based. Effect of surface nature on the Young contact angle value was found only insignificant.
4. In order to increase wettability of water based adhesive to selected substrates different amounts (0.27 vol. % , 0.51 vol. %, 0.81 vol. % and 1.35 vol. % to total amount of dispersion) of ethyl alcohol and commercial nonanoic surfactant was added and wettability of modified dispersion have been investigated.
- 4.1. It was determined that independently on substrate nature addition of ethyl alcohol and nonanoic surfactants decreases the initial contact angle but increases Young contact angle compare to those of pure dispersion.
- 4.2 Effect of surfactants on initial contact angle depends on the substrate nature. Most significant initial wettability improvement for transparent hot stamping foil was found using ethyl alcohol. For aluminium coated hot stamping foil non-anionic surfactant was more effective and for tamper evident film the effect of surfactants nature was found only insignificant. Increase of surfactant amount results on the decrease of initial contact angle value.
- 4.3. The effect of surfactants and substrate nature on the Young contact angle value was found dependant on the surfactant and substrate nature. In dependence of substrate nature and surfactant amount Young contact angle was increased in $\theta = 5-11^\circ$.
5. The influence of different amounts of ethyl alcohol and commercial non-anionic surfactant on the surface tension of dispersion have been investigated. It was found that addition of surfactants results on the increase of the surface tension of dispersions. Higher effect using nonanoic surfactant was found. On the other hand, increase of surfactants content results on the decrease of surface tension relaxation duration.

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