



Polyphenol based adhesives for the production of agglomerate cork stoppers
Synthesis and applications

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Abstract:

In synthetic organic adhesives the emission of harmful substances is a serious problem, which is usually caused by the use of volatile organic solvents and evaporation of unreacted monomers. In the case of polyurethane based binders, they are formed by reaction of polyols with isocyanates, which derivate from non-renewable sources. The volatility in the price of these raw-materials, and the fact that they come from non-renewable sources, has made many companies seek for bio-based alternatives. In this particular case, since the objective is the production of agglomerate cork stoppers, which are used in contact with many different alcoholic beverages (wine, champagne, whisky, etc), there are a pressure in the consumer market to come up with bio-based adhesives which could be safe and without free monomers. With this objective in mind, the main goal of this study has been to develop one-component, thermo-curable adhesives based on natural sources, with solid contents between 50 to 60%, of which over 75% at 80% are adhesive components, and a viscosity between 500 and 4000 cP.

Tests carried out have shown good behavior of gelatin and polyethylenimine as crosslinking agents, as an alternative to formaldehyde in the polymerization process of polyphenolic tannins. Torsion tests were showed that we can observe torsion momentums similar to a polyurethane based resin, but has a maximum angle below expectations. Yet the development of this adhesive is not finished, and some of its characteristics may still be improved.

Keywords: Natural Binder, Tannins, Hexamine, Polyethylenimine, Gelatin, one-component, thermo-curable.

Introduction

^[1,7]Polyurethanes are composed by polyols and isocyanates. The types of isocyanates used in the production of agglomerated cork

binders are usually very volatile at room temperature. For this reason, they are a health hazard to people exposed to them. Additionally, both European and US legislation only allow for very low migration values of

isocyanate monomers to the beverages in contact with the cork stoppers, which lead to companies seeking bio-based alternatives to these polyurethane based binders.

Another important issue is the price of polyurethane raw materials, which oscillate according to the price of crude oil and refined products, as ethylene and propylene, in addition to being a derivative of non-renewable sources and a non-biodegradable material.

Many companies have been addressing the demand for alternatives such as the use of vegetable-based polyols, thus replacing their oil based counterparts. However this fact does not eliminate the problems caused by the use of isocyanates, the main promoters of urethane links.

This development had the objective of creating bio-based binders for the agglomeration of cork granules aimed at overcoming difficulties imposed by polyurethane based binders, thus allowing for the production of fully natural agglomerated cork stoppers. It was then decided that a tannin based binder could prove to be an excellent solution.

^[2]The condensed tannin molecules are made up of polymers or oligomers based on monomer units of flavonoid type and they can present several different structures.

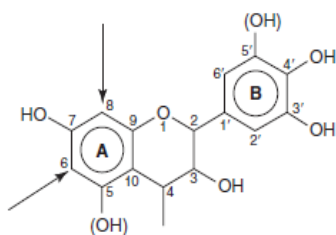


Figure 1- Flavonoid unit, constituted by resorcinol (ring A), and pyrogallol (ring B).

The most common chemical structure of the condensable tannins is 70% based on a resorcinol ring (A) and 25% present a structure in ring (B) catechol or pyrogallol, respectively. The remaining 5% are carbohydrates, gums, hydrocolloids and small fractions of amino acids.

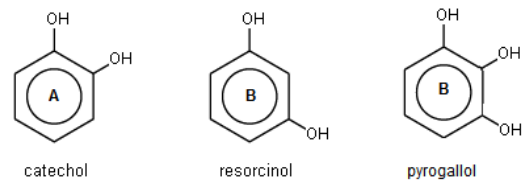


Figure 2- Structures of catechol, resorcinol and pyrogallol units.

The monoflavonoid units are linked by C-C bonds that can be degraded by hydrolysis. The interflavonoid connections are usually made through the strong nucleophilic centers in the ring, the carbons C₆ and C₈. In the case of pine bark extract, the pattern of condensation is usually accepted in this linear structure or C₆, C₈ links.

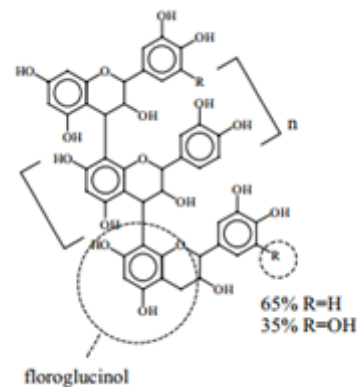


Figure 3- Structure of flavonoid units, comprising a standard linear condensation C4-C8 bonds

Tannin polymers may contain from 2 to more than 50 flavonoid units, thus providing very complex structures with different characteristics. Depending on their chemical structure and its degree of polymerization, the

condensable tannins may or may not be soluble in organic or aqueous solvents. However, it should be noted that the tannins are formed as a class of extremely complex and varied substances that share similar chemical properties.

Cross-link agents.

Hexamine, in basic environment, does not decompose directly into formaldehyde and ammonia, but through a very slow reaction step hexamine decomposes into amino-imino methylene bases.

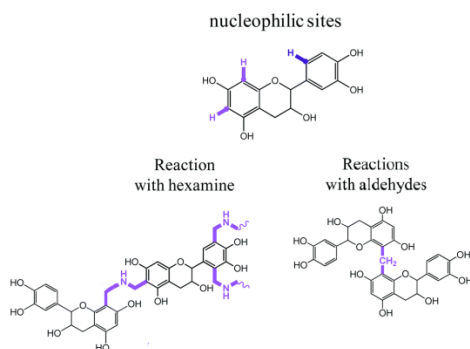


Figure 4- Condensation reaction of formaldehyde our hexamine with resorcinol.

The intermediate fragments of the decomposition of hexamine pass first through the formation of imines followed by their decomposition to imino-methylene bases (Schiff bases). The amino-imines formed behave as an amide that reacts with tannins leading to the formation of longer oligomers, by a polycondensation process. Through this fact, it's possible to consider, a very low or no formaldehyde emission by resins prepared.

Gelatin is a mixture of peptides and proteins produced by partial hydrolysis of collagen extracted from

skin, bones, and connective tissues of animals. Its chemical composition is, in many respects, very similar to that of the collagen. Its bio adhesive nature and non-toxicity to the human body makes gelatin a highly attractive catalyst for bio-binders.

Studies performed in recent years have shown various hydrophobic bonds between proteins and polyphenols. Polyphenols act as polydentate binding agents (binders with more than one attachment point).

It is assumed that the interaction between the vegetable tannins and polyamides result in forming peptide bonds between collagen and tannins.

Despite extensive investigations, the nature of the reactions between the proteins present in the gelatin and the tannins are still under discussion. The main reactions discovered between tannins and gelatins are: 1) Peptide reactions between the tannins and phenolic groups of the amino groups (NH) present in the gelatin protein; 2) ionic groups, such as amino group of lysine, the guanidyl group of arginine, and carboxyl residues of aspartic acid and glutamic acid; 3) The 3-hydroxyl groups of serine and hydroxyproline; 4) amine groups NH_2CO residues.

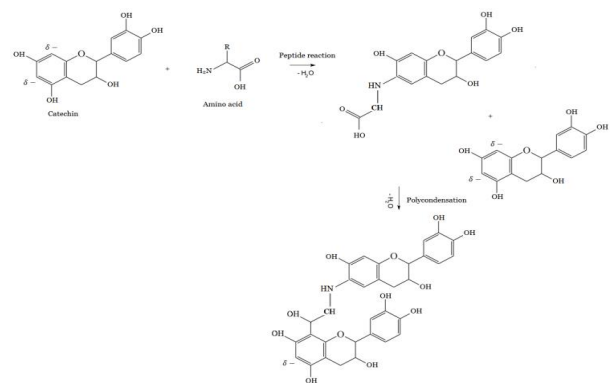


Figure 5- Possible reaction between Tannins and amino acid present collagen.

A number of studies favor the view that the primary linking group between tannin and collagen is CO-NH group.

Polyethyleneimine (PEI) can exist on linear form containing all secondary amines, in contrast to branched PEI which contains primary, secondary and tertiary amino groups. PEI is produced on an industrial scale, usually derived from their polycationic nature, finding many applications such as detergents, adhesives, water treatment agents and cosmetics, to name a few.

[6] This component has the ability to promote adhesion to wood laminates, cement and bricks.

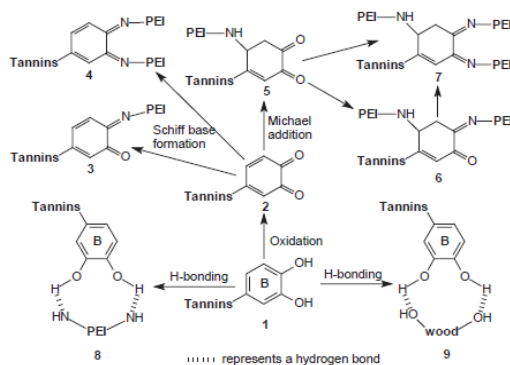


Figure 6- Possible reaction between PEI and condensed tannins.

Possible polymerization reactions occurring between the tannins and polyethylenimine include the following steps: a) The B ring of flavonoids units (1) is quite likely to suffer oxidation resulting in ortho-quinone (2); b) The ortho-quinone can react quickly with the amino groups of PEI, forming Schiff bases (3) and (4); c) The ortho-quinone (2) may suffer a *Michael reaction* to form one compound (5), which reacts with the amino groups of PEI forming Schiff bases (6) and (7).

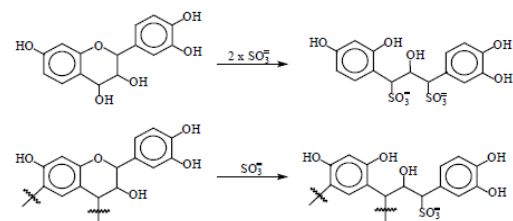
These reactions will lead to lower solubility of the three-dimensional networks formed between the PEI-tannins. The increase of polymerization leads to an higher viscosity of the solution. It is possible to observe weaker bonds by hydrogen bonding between the amino groups and hydroxyl groups, belonging to the group of the catechol units of tannin extracts flavonoids.

Because formaldehyde is a petrochemical based product, and also due to its high toxicity and low acceptance values in terms of free monomer, it was not used as an alternative to these crosslinkers.

Sulfitation, basic and acid hydrolysis process

[8,9] The adding of sulfite aims to decrease the viscosity of tannin extracts and to increase its water solubility.

The next figure shows the sulfite reaction of condensed tannins.



Fonte: Carneiro (2002)

Figure 7- Sulfite reaction of condensed tannins

The decreased viscosity and increased solubility are due to the following effects, caused by the sulfite process: a) Elimination of the ether group in the heterocyclic ring that is hydrophobic; b) Introduction of sulfonate groups and other hydroxyls in flavonoids units, increasing the hydrophilic character; c) Decrease in rigidity of tannin molecules, is

provoked by the decreasing of stereochemistry impediment through the opening of heterocyclic ring, resulting in an increase in the number of sites subjected to hydration; d) Hydrolysis of sugars and hydrocolloid gums and hydrolysis of interflavonoids.

The sulfitation promote the hydrolysis of carbohydrates and of the relatively high molecular weight hydrocolloid gums, and also the breaking of interflavonoid bonds (C4-C6 or C4 to C8) in the tannin polymer units, thereby increasing the amount of flavonoids per gram of compound.

One other method used to increase the solubility of the tannin extract is acidic or basic hydrolysis, being that the results obtained with these two methods are the same as in the case of sulfite. In order to get the biggest amount of flavonoids per compound gram, these processes should be used simultaneously. In acid hydrolysis, acetic anhydride or acetic acid is typically used and alkaline hydrolysis usually utilizes sodium hydroxide, most often under reflux.

1. Experimental

2.1 Materials

Polyethylenimine (PEI) with average $M_w = 10\,000$ g/mol, tannins used in tests are quebracho extract from *Sanderma*, Gelatin from *Neogringidentes* (bloom indices of 105, 30 Mesh), and hexamine from *Quimidroga S.A.*

1.2 Preparation of tannin-PEI-Gelatin-Hexamine adhesives.

Formulation 1 consists in the dissolution of tannins in water at 50 °C.

Formulation 2 consists in a mix of gelatin and tannin powder, dissolution in water at 60° C and addition of the other components (sulfites, NaOH), hereafter designated by *Comp.*

Formulation 3 involves the adding of PEI to Formulation 1, with higher mixing speed and time.

Table 1- Formulations F1, F2 and F3

	F1 (m/m %)	F2 (m/m %)	F3 (m/m%)
Tannins	0,42	0,33	0,33
Water	0,46	0,46	0,46
Comp. 1	0,04	0,04	0,04
Comp. 2	0,05	0,05	0,05
Gelatin	—	0,09	—
PEI	—	—	0,09
Comp. 3	0,03	0,03	0,03
Total	1	1	1

Because of the high viscosity (Table 3), it was decide to proceed to a sulfitation of the tannic extract and gelatin, at reflux, for 30 min, pH 8, and a temperature of 90 ° C, with an increase in the content of sulfites to the stoichiometric amount required for the sulfitation of all poliflavonoids.

The Sulfitation with reflux, in basic environment, aims to increase the quality of the adhesive, considering the following aspects: 1. Breaking the interflavonoid-tannin connections, resulting in further movable monomer units, facilitating its dissolution. 2. The opening of the heterocyclic ring leading to higher flexibility. 3. The presence of a small quantity of hydrophilic hydrocolloid gums, is eliminated in the process by precipitation, promoting the reduction of the resistance in the mixture resulting in lower viscosity and higher solids content. 4. Sugars present in extract with low molecular weight, do not affect the viscosity of the solution.

Formulations A, B and C are produced by a reflux sulfitation process, with different quantities of Gelatins, and other components.

Table 2-Final Formulation, A, B, C.

	FA	FB	FC
Comp.	m/m (%)	m/m (%)	m/m (%)
Tannins	39,22%	39,22%	37,45%
water	37,58%	39,22%	37,45%
Comp. 1	1,96%	1,96%	4,87%
Comp. 3	2,94%	2,94%	3,37%
Gelatin	7,52%	5,88%	1,87%
Comp. 2	8,82%	8,82%	13,11%
Hexamine	1,96%	1,96%	1,87%
Total	100%	100%	100%

2.3 Methods for the characterization of adhesives

Viscosity

Viscosity data was measured using a Brookfield DV-E Viscometer at a temperature of $25 \pm 0,5^\circ\text{C}$.

Solids content

This method aims to determine the amount of binding material present in the adhesive solution and is based on evaporation, leading to a given mass of dried resin. It is assumed that a temperature of 105°C and time of 1 hour is sufficient for the removal of the volatile materials, but insufficient to cause changes in the solid constituents of the resin. This method is applied in duplicate, and the final result is the arithmetic average of both values obtained in each test.

Other key properties were evaluated such as: i) flexibility; ii) reactivity; iii) aggregation power; iv) stability.

We can measure these properties using the following tests:

- a) Boiling tests: iii);

- b) Gel time (it gives us gelation time, of the adhesive): ii);
 c) Torsion tests: i); ii);
 d) Stability tests: iv)

2. Results and Discussion

a) Boiling tests

Polymerization agents used, as already mentioned, were: PEI, gelatin, and hexamine.

The use of hexamine as a crosslinker between the flavonoids groups was demonstrated to be very effective with tannins in the production of adhesives for wood boards and plywood. However, due to its high reaction rate and low stability, the use of this catalyst, led to the manufacture of bi-component adhesives, where the mixing of the catalyst with the binder would have to be performed minutes before application.

The boiling tests did show that PEI and gelatin alone were not able to create the adhesive strength required for the application under consideration. As an alternative, hexamine was added to produce a more complete polymerization.

Formulations 2 and 3 have shown the following results, where the observed viscosity is high. The addition of a plasticizer (component P) could help to solve this problem, reducing viscosity to acceptable levels for the required application.

Table 3- Viscosity diminution due to use of plasticizer. The percentages of plasticizer refer at total mass of the adhesive.

Formulation	Plasticizer		
	1	2	3
Viscosity (cP)	5870	7073	13000
Solids (%)	47,65	45,36	51,51
% Comp. P	–	3%	10%
Viscosity (cP)	–	2556	3575

Boiling tests were performed, submerging the cork stoppers in boiling water, in order to determine its binding capacity of the various formulations. The following results were obtained, wherein X represents the time at which cork started to disintegrate:

Table 4- Boiling tests to different formulations, H-10% of hexamine per gram tannic extract, H_{1/2}-5% of hexamine per gram tannic extract.

Time of boiling	30 min	1h	2h	3h
Formulation 1-H		X		
Formulation 2	X			
Formulation 3	X			
Formulation 2-H _{1/2}			X	
Formulation 3-H _{1/2}			X	
Formulation A		X		
Formulation B		X		
Formulation C		X		
Formulation A-H				
Formulation B-H				
Formulation C-H				

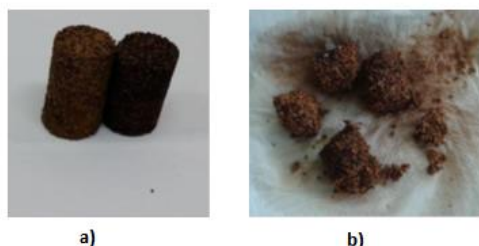


Figure 8- Cork stoppers after boiling tests: a) cork stopper with good aggregation without deformation of its shape *approved; b) completely disaggregated cork * X.

With the stoichiometric amount of hexamine on Formulation 1 (consisting of only tannic extract), the cork stopper produced endured about 1 hour in boiling water, ensuring that the adhesive had a reasonable degree of polymerization. The use of gelatin and polyethylenimine allowed the decrease the hexamine amount to half of the stoichiometric quantity, giving the cork stoppers a better degree of polymerization and improved elasticity. After 3 hours of boiling, they did not present any visible desegregation.

It was considered, as criteria for approval, that the cork stoppers should endure at least one hour of boiling. The analysis of the results in Table 4 allow for the conclusion that the use of hexamine permitted a more complete and effective polymerization, being that the stoppers held for about 2 hours of boiling in each case (Formulations 2 and 3).

Sulfitation with reflux in basic environment.

This production method has helped to considerably increase the solids content, at the same time decreasing the viscosity of the adhesive.

In the production of formulations A, B and C tannin extracts were used along with gelatin, which suffered sulfitation, and hydrolysis in basic environment. There was obtained the following results of these formulations:

Table 5- Viscosity analysis of solid content of formulations A, B, C (FA, FB, FC)

Results	FA	FB	FC
Solid content (%)	59,0	57,0	58,4
Viscosity (cP)	3860	956	510,6
Adhesive material (%)	48	46	40

It is observed that the use of gelatin considerably increases the viscosity. This is due to the fact that gelatin is produced by the controlled hydrolysis of collagen, composed of insoluble fibrous proteins. Comparing formulations B and C, it can be seen that there was an increase of solid content, with a reduction in viscosity. This is due to the decreased mass concentration of gelatin.

b) Gel-timer

Analyzing the gel times at 115-125°C of the different formulations allows for the conclusion that increasing the concentration of gelatin produces lower gel times.

Table 6- Gel timer's at different formulations.

Catalyst	Gel time (min)		
	FA	FB	FC
5 % Hexamine	10,41	13	17,15
10 % Hexamine	10,19	12,3	14,55

It is also noted that the resin gelation time decreases with the increase of hexamine concentration. However, the difference between the gelation times with more or less hexamine is accentuated by the decrease of the gelatin content present in the binder. Observing this fact, it can be concluded that gelatin catalyzes the polymerization reaction.

c) Torsion tests

Torsion tests were applied to analyze the aggregation strength of the cork stoppers.

This test consists of applying rotational force on the stoppers, in which a piece of material suffers traction and the other piece is compressed. This stress application leads to the angular deformation of the cork stopper.

The implementation of this test allowed for the observation of some of the features which the adhesive offers, including the aggregation strength and mechanical elasticity of the stopper.

Compared with standard cork (polyurethane based), the test subjects demonstrated good torsional moments, but low values of maximum angle (half of the observable value in the standard cork). This mechanical property allows the conclusion if the stopper has the essential characteristics for a good compression, permitting an easy insertion in bottles or its extraction without breaking the cork. The flexibility of the cork stopper is associated with two parameters, the type of binder and the grain size used in its manufacturing process.

It is advised the testing of various types of cork stoppers in order to verify the influence of cork granulate size in maximum angle obtained as well as the effect of the use of a plasticizer in order to increase the binder's flexibility after curing.

M_t - Torsion moment

θ_{max} - Maximum torsion angle.

Table 7- Comparative table of characteristics of corks made in the laboratory (D = diameter, L = length).

Cork	L (mm)	D (mm)	weight (g)	density (Kg/m ³)	M_t (N.m)	θ_{max}
Standard cork	45,5	25,92	6,1	254	2,67	52°
A2	44,99	26,01	5,7	238	2,15	27°
A3	44,65	25,96	5,1	214	1,57	20°
A4	44,87	25,91	5,7	240	1,90	16°
B2	44,98	25,88	5,6	238	2,55	20°
B3	42,83	25,77	6,6	296	2,52	15°
C2	45,38	25,99	5,7	235	2,00	25°
C3	44,43	25,62	5,5	241	1,96	23°
C4	45,15	25,84	5,5	233	2,67	21°

d) Stability

Stability tests were performed with samples of the final formulation adopted, which is an average between formulations A and B. Samples, prepared with various hexamine catalyst concentrations, were placed into an oven at 60°C. Daily viscosity measurements were made in order to observe the evolution of stability. Depending on the degree of tannins

polymerization, the viscosity of the solution will increase overtime.

It is possible to greatly increase the lifetime of the adhesive if the product is used in a bi-component mode, with the catalyst being added to the solution just before it is with the cork granules.

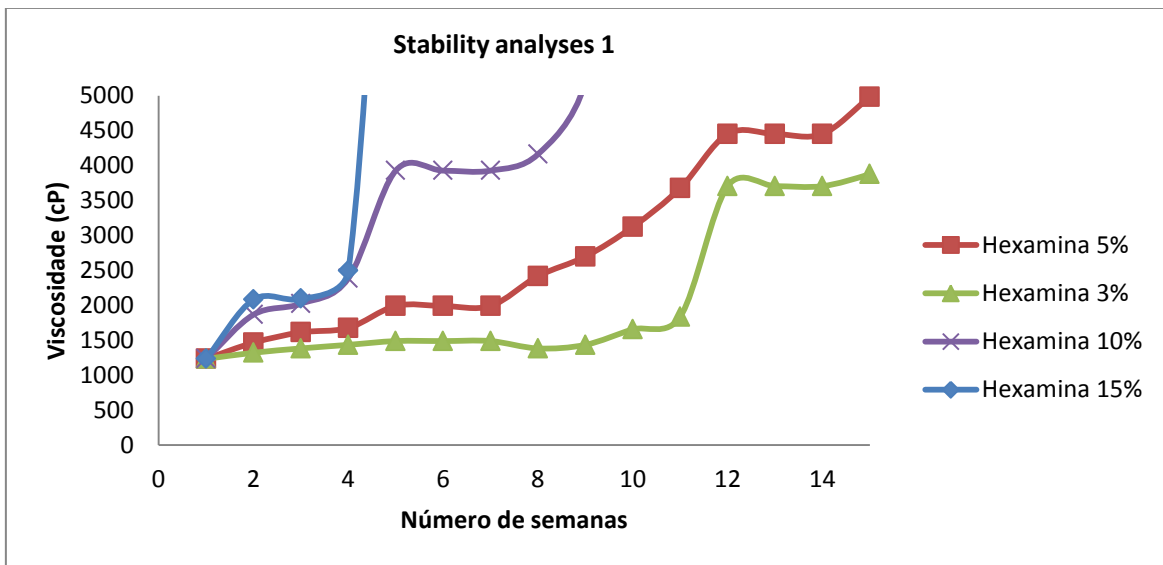


Figure 9- Stability analyses until 5000 cP.

As would be expected, increasing catalyst concentration produces a decrease in the pot life of the adhesive. Whereas the limit viscosity for application in the study is 5000 cP, and considering the results obtained previously, an adhesive with 5%

hexamine remains in valid conditions for 15 weeks (4 months), while the addition of 10% of hexamine represents a validity of 9 weeks, which corresponds approximately to 2 months storage.

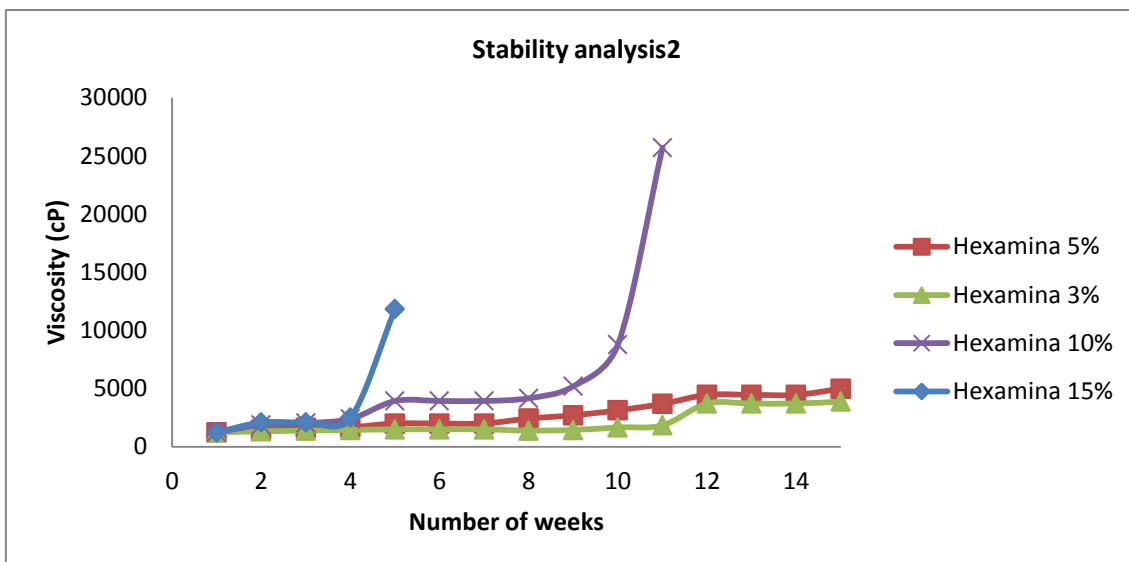


Figure 10- Stability analyses until polymerization of 10 % hexamine concentration in adhesive

Outside the technical specification limits, we can see that pot life until the gelation point is much higher. For example, the binder with 10% of hexamine takes 11 weeks to complete total polymerization.

3. Conclusion

It was possible to develop an adhesive that allows for the production of agglomerated cork stoppers which resist about 3 hours boiling, with torsion moments resembling those of polyurethane based cork stoppers and with relatively low viscosity (1000 -3000 cP), considering the high solid content (57%-59%).

The pot life obtained is at least 4 months, similar with the polyurethane adhesives used in this type of applications.

However, the maximum angle is too low, considering the standard cork stoppers, and the gel time is somewhat higher than that of a polyurethane binder, which is between 3 and 5 minutes. ^[10]With,

more research it might be possible, to overcome the mentioned difficulties. Recent studies showed that use of DMC (dimethylcarbonate), as a polymerization agent and one diamine with an hydrocarbon (hexamethylenediamine) allows for the increase of the distance between the main polymerization units which are esterified and very low spatial mobility, thus improving the elasticity of the adhesive.

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