UNIVERSITY POLITEHNICA OF BUCHAREST

Doctoral School of Applied Chemistry and Material Science

COMPOSITE MATERIALS BASED ON THERMOPLASTIC AND THERMOREACTIVE RESINS WITH LOW ENVIRONMENTAL IMPACT

-SUMMARY-

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Abbreviations

AS – stearic acid
ATH – aluminium tryhidrate
$CaCO_3$ – calcium carbonate
DINP – diizononyl phthalate
DOTP – dioctyl terephthalate
EOO – epoxidized olive oil
EOO_AA – polyol obtained from epoxidized olive oil with acetic acid (AA)
EOO_DEA - polyol obtained from epoxidized olive oil with diethylamine (DEA)
EOO_EtOH - polyol obtained from epoxidized olive oil with ethanol (EtOH)
HCl – hydrochloric acid
HMH – hydromagnesite and huntite
LOI – limiting oxigen index
MDI - 4, 4’ methylenediphenyl diisocyanate
OO – olive oil
pbw – parts by weight
pcs- pieces
phr – parts at 100 part resin -PVC
PVC – polyvinyl chloride
SC – calcium stearate
SPF – flexible polyuretane foams
S. Ref. – reference foam
VO1 – calcium carbonate 1 μm
VO2 – calcium carbonate 2 μm

1. Introduction

There are currently two major global trends in composite materials.

The first trend is to replace composites based on thermoreactive matrices with composites based on thermoplastic matrices. This is because composite materials based on thermoreactive matrices are not biodegradable, constituting an important source of environmental pollution. The use of thermoplastic matrices eliminates this shortcoming, the composites being totally recyclable (both manufacturing waste and end-of-life products) and are processed by high productivity methods characteristic of plastics: extrusion, injection, vacuum forming, etc.

It should be noted that the physical-mechanical properties of composites are like those obtained from thermoreactive polymeric matrices, and many of the plastic materials used are currently obtained from plant precursors due to "green chemistry".

The second trend is to obtain composites based on heat-reactive resins (required in certain applications) and at least one of the components is obtained from renewable raw materials and not from fossil raw materials.

The same trend is manifested in the case of polyurethane foams, a fact demonstrated by the significant number of studies in the literature, based on the synthesis of polyols from vegetable oils.

This doctoral thesis is in line with the aim of obtaining "green grains" free of Sb_2O_3 which is carcinogenic and flexible polyurethane foams based on polyols obtained from olive oil.

The following report presents the main data obtained from the two studies performed.

We mention that the numbering of the chapters, figures and tables corresponds to the thesis in extenso.

Keywords: environment, low smoke emissions, renewable resources, olive oil, flexible foams

2. Doctoral thesis scope and objectives

The thesis is mainly aimed at studying composite materials and is organized in two sections.

The first part deals with composites based on PVC thermoplastic resin. The key aspect was the synthesis of „green grains" based on PVC suitable for electric cables. To achieve this, the following specific objectives must be fulfilled:

1. The study on the influence of stearic acid and calcium stearate;
2. The influence of plasticizer nature and of processing mode;
3. A study on the effect of a class of flame retardant systems based on PVC.

The second part belongs to composite materials with thermoreactive matrix based on olive oil. The principal scope of this part consists of the synthesis of PU flexible foams based on renewable raw materials, replacing petroleum polyols.

The originality consists of using for the very first-time olive oil in the obtaining of PU flexible foams suitable for mattress production.

To meet this main scope, several secondary objectives must be accomplished, as follows:

1. The process study on epoxidized olive oil synthesis;
2. The process study on the synthesis of polyols starting from epoxidized olive oil;
3. Synthesis of PU flexible foams using petroleum polyols and olive oil-derived polyols;
4. The characterization of synthesized flexible foams with the end of establishing the optimal recipe.

3. Original contributions

Europe and our country are facing energy challenges: how can we provide alternative energy resources, how can we increase security of energy supply and how can we reduce greenhouse gas emissions.

Current trends in the market for low-smoke PVC granules are expanding rapidly, as new regulations regarding the performance of electrical cables on reaction to fire (Performance of electrical cables on reaction to fire SR EN 50575: 2015 / A1: 2016), cable manufacturers are increasingly rigorous, and PVC granule manufacturers must ensure a product as efficient as possible, in terms of fire resistance.

Thus, this doctoral thesis was carried out, which contributes to the protection of the environment by using "green granules" obtained from PVC, used in the manufacture of electrical cables. Therefore, the use of these granules allows the reduction of smoke and HCl emissions in case of fire, having a combustion resistance which doesn't allow the flame to spread, due to aluminum trihydrate (ATH), hydromagnesite and huntite mixture (HMH) and zinc borate. On the other hand, the synthesis of these new granules will replace antimony trioxide, which is carcinogenic.

Also, another important aspect in terms of environmental protection and the use of renewable resources is polyurethane foams. They are obtained from the reaction of a polyol obtained from oil resources and a diisocyanate. Due to the drastic decrease of oil resources, new polyols will be obtained from olive oil with subsequent applications in flexible polyurethane foams, contributing to environmental sustainability.

Following those previously described, in this doctoral thesis, structured in two parts, two different categories of materials will be presented: one part will be assigned to thermoplastic matrices, and the second one to thermoreactive matrices.

Both studies aim to protect the environment, by partially or totally replacing petroleum raw materials, which pose an increased risk to human health and environment.

For PVC-based composites, three studies were performed, constituting the specific objectives of the first part:

1. The influence of lubricant nature on the properties of PVC based composites.

The novelty of this study is the parallel study of the two types of lubricants, used for PVC composites, to determine the optimal formulation, in terms of lubricant used, but also in terms of the interaction of the lubricant with the reinforcement and flame retardant agent, respectively.

The originality of this study is also given using the mixture of huntite and hydromagnesite as a flame retardant in PVC based composites. Comparative studies have also been performed between calcium carbonate, commonly used in PVC composites for electrical cables, ATH and HMH.

2. The influence of the plasticizer nature and the processing method on the properties of PVC composites.

The originality of the study is represented by the comparative study of the plasticizers used in industrial scale and on the processing of composites by passing through the extruder the PVC mixtures twice, for a better homogenization.

3. The study of flame retardant systems upon PVC based composites characteristics. This study has shown that the use of a mixture of ATH with zinc borate can successfully replace the use of Sb_2O_3.

The degree of novelty is given by the new formulations and comparative studies on the antimony trioxide replacement.

In the second part of this doctoral thesis, flexible polyurethane foams are synthesized, polymeric composites in which the reinforcing agent is represented by the air. These studies were conducted because of industry and research focus on the chemical production of environmentally friendly materials, which replace petroleum-derived raw materials with renewable raw materials.

In the category of renewable raw materials, vegetable oils are the most widely natural source of precursors, used for the synthesis of polymers.

In this study, the polyols synthesized from olive oil, by chemical modification, were used to obtain flexible polyurethane foams, which can be used as memory foams in the upholstery, mattress, and other industries. The synthesis of flexible polyurethane foams comprises three steps:

1. Olive oil epoxidation;
2. Synthesis of polyols from epoxidized olive oil, by opening the epoxy cycle with acetic acid, ethanol and diethylamine;
3. Synthesis of polyurethane foams using commercial polyol and diisocyanate. The formulations contain 15, 25 and 35% polyol derived from olive oil, respectively.

The originality consists in obtaining flexible foams based on polyols obtained from renewable raw materials, respectively from olive oil.

Its use is a world premiere, and the properties of composites obtained from mixtures of polyol of petrochemical origin - polyol synthesized from renewable raw materials, is a clear proof of the need to replace fossil raw materials with raw materials of plant origin, recoverable.

Polymeric composites based on PVC

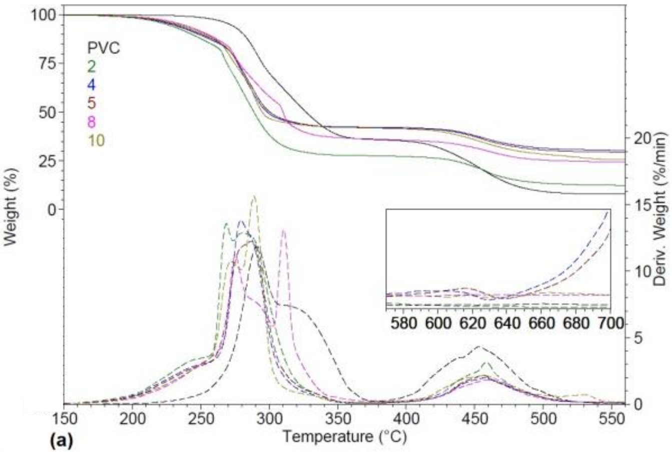
First part of the thesis has three studies upon PVC based composites:

1. Studies on two types of PVC composites, with different lubricants: stearic acid and calcium stearate, and minerals used as reinforcement agent or flame-retardant agent: calcium carbonate, aluminum trihydrate and hydromagnesite and huntite– (HMH);
2. Studies on PVC composites to determine the plasticizer and processing mode influence;
3. Studies on different flame retardant systems, such as ATH, HMH, calcium carbonate and synergic agents, zinc borate, used for stibium trioxide replacing.

For the first study on lubricants natura, the FTIR analysis present characteristic bands for PVC, DINP, lubricants and reinforcement agents.

Thermogravimetric curve of net PVC, determined in N_2 is presented in **Figure 4.2.3.2.**, where is compared with composites curves.

Thermal degradation of PVC takes place in two stages as follows: in the first stage (260-380 °C), release of hydrochloric acid, followed by the formation of polyene structures, and in the second stage (380- 550 °C) cyclization of the polyene structures with the formation of aromatic compounds. Thermal decomposition in the second step is represented by degradation of PVC backbone and, therefore, lower molecular weight compounds (and smoke) are produced [66-69].

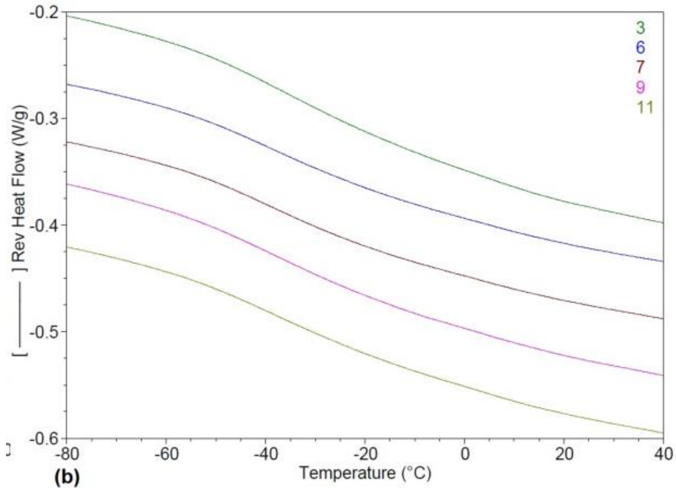


a)

Figura 4.2.3.2. *Thermogravimetric analysis for PVC based composites with and without filler: a) PVC composites based on stearic acid as lubricant and b) PVC composites based on calcium stearate* ***[65]***

Using DSC, the fluctuations in the glass transition temperature, Tg, of obtained composites were evaluated. The need for studying this behavior of PVC composites refers to the fact that decomposition temperature of neat PVC (above 160 °C) is lower than the melting temperature (260 °C). As a result, it is necessary to lower the Tg to prevent degradation of the polymer before processing, but also to establish a maximum temperature of processing and application of the composites [73-76].

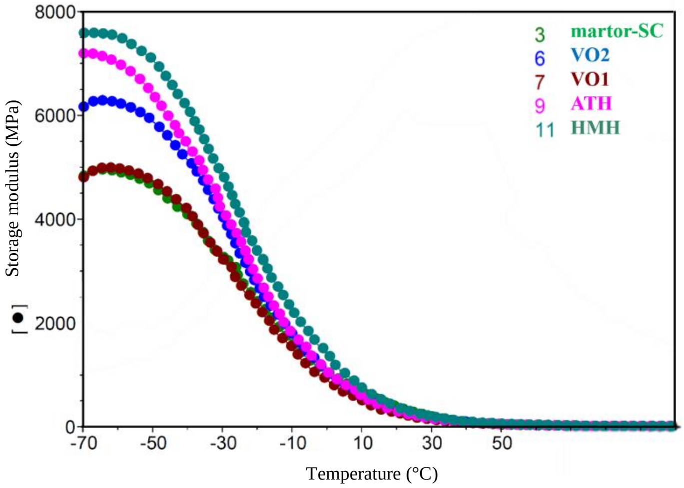
In the DSC diagrams, **Figure 4.2.3.3. a** and **b**, the shift of the baseline following the glass transition for each PVC sample can be observed. The variations in the Tg depend upon the type of filler but also upon the type of used lubricant.



b)

Figure 4.2.3.3. *Differential scanning calorimetry for PVC based composites with and without filler: a) PVC composites based on stearic acid as lubricant and b) PVC composites based on calcium stearate* ***[65]***

The effect of filler loading on the dynamic mechanical properties of PVC composites was studied. DMA was complementary on determining the storage modulus and loss modulus. When the storage modulus (E’) increases with the filler loading usually indicates that mobility of the polymer chain is decreased in the presence of the reinforcing/flame-retardant agents. In this study, **Figure 4.2.3.4. a** and **b**. it was observed that filler incorporation into the PVC matrix may decrease the mechanical damping of PVC [79, 80].



b)

Figure 4.2.3.4. *Dynamic mechanical analysis for PVC based composites with and without filler: a) PVC composites based on stearic acid as lubricant and b) PVC composites based on calcium stearate* ***[65]***

To evaluate the quality of flexible PVC composites in industrial application, one of the most important properties is tensile strength. It can be observed from **Figure 4.2.3.6. a, b, c** and **d** that elongation at break and tensile strength of test samples decreased with the filler loading for each type of PVC composite. This decrease in mechanical properties is attributed to restriction of polymer chain movements [81, 82]. For control sample 2 and 3 with no filler, the highest mechanical properties values are obtained. Calcium stearate ensures more uniform mechanical properties due to better compatibility with calcium carbonate.

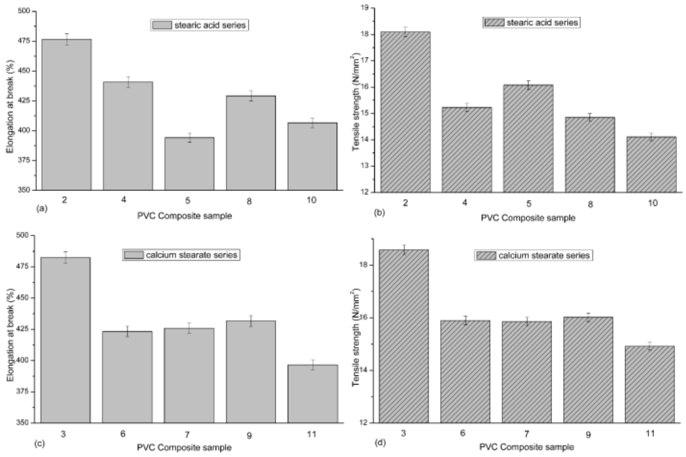


Figure 4.2.3.6. *Mechanical properties for the two PVC series of composites: a) Elongation at break for the stearic acid-based composites; b) Tensile strength for the stearic acid-based composites; c) Elongation at break for the calcium stearate-based composites; d) Tensile strength for the calcium stearate-based composites* ***[65]***

The LOI values of tested PVC composites are shown in **Figure 4.2.3.7. a** and **b**.

For control samples 2 and 3 with no filler in the composition the LOI value is around 21, so the sample can ignite in air easily. As expected, when adding filler in the composition, the LOI value increase.

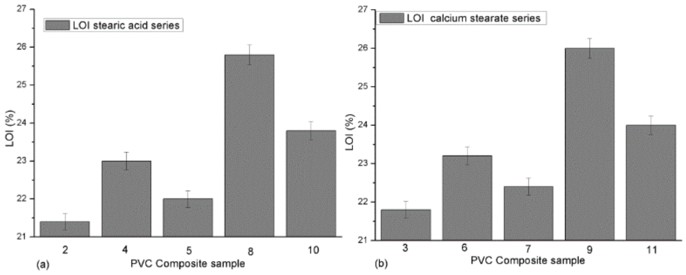


Figure 4.2.3.7. *LOI values for the two PVC series of composites a) stearic acid-based composites, and b) calcium stearate-based composites* ***[65]***

Contact angle (CA) is the most important parameter used to quantify the wettability of solid surfaces. In this respect, the need to preserve or enhance the hydrophobicity of the composite materials, which are used in out-door applications, refers to stability in moist environment and preservation of flame-retardant properties on long term [92].

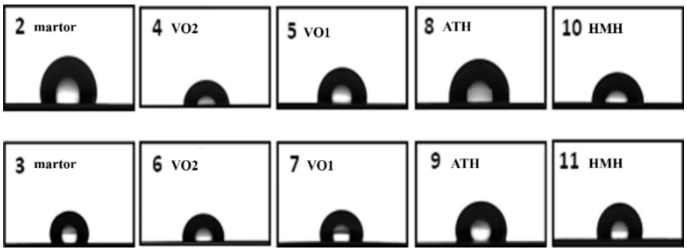
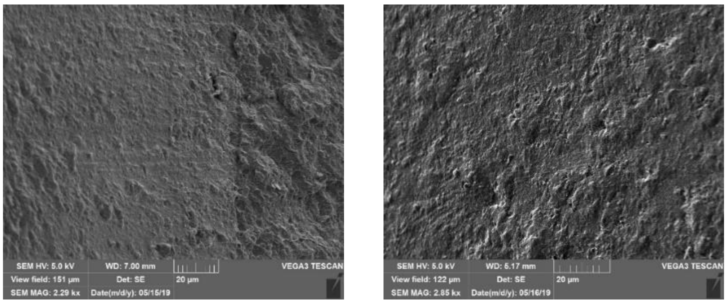


Figure 4.2.3.9. *Contact angle for PVC series a) with stearic acid, b) with calcium stearate* ***[65]***

The final step to establish an optimum formulation for flame-retardant flexible polyvinylchloride composites was scanning electronic microscopy of PVC composites. As it can be seen in **Figure 4.2.3.10.**, calcium stearate used as lubricant led to more homogenous composites and the presence of macropores was reduced, compared to the series of samples with stearic acid. The composites with $CaCO_3$ of 1 μm (samples 5 and 7) presented macropores and agglomerations.

The samples with HMH (sample 10 with stearic acid and sample 11 with calcium stearate) were rather homogenous, presenting some zones with smooth surfaces. Nevertheless, the samples with ATH (sample 8 with stearic acid and sample 9 with calcium stearate) presented a more discrete surface arrangement with a better dispersion of solids and more homogenously dispersed macropores, particularly for sample 9.



11-HMH with calcium stearate 10-HMH with stearic acid

Figure 4.2.3.10. *SEM analysis for the two PVC series of composites a) stearic acid-based composites, and b) calcium stearate-based composites* ***[65]***

By conducting this study, the first objective of the first part of the thesis was achieved, **the influence of stearic acid and calcium stearate, used as lubricants, on the properties of composites**, demonstrating that calcium stearate is compatible with the raw materials used to obtain PVC composites.

As for the flame retardant the most effective proved to be ATH, demonstrated by DSC and LOI analysis.

The subject of the second study refers to the influence of the plasticizer nature and the processing mode upon the characteristics of PVC composites. Thus, in this study two types of industrial plasticizers were used to study their influence on the final properties of composites. The lubricant used was stearic acid, the most common and cheapest additive used in industry for cable manufacturing.

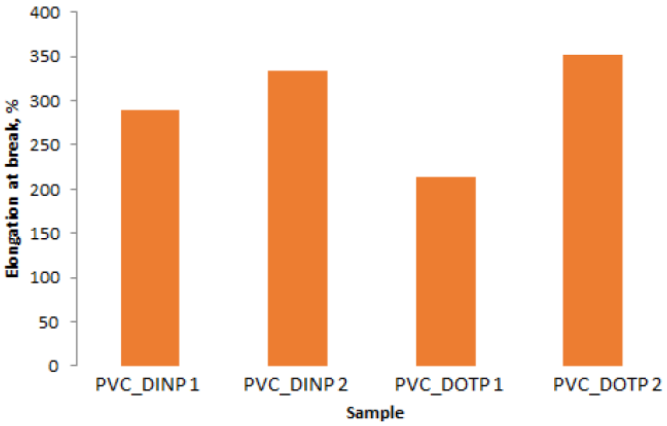
FTIR analysis are similar with the anterior study because no chemical bonds are created between the components.

From the two series of PVC composites, it was noticed that series 2 (composition two times passed through the extruder) presented higher decomposition temperatures, indicating a better homogeneity of the material; this is highly desired to prevent decomposition of PVC before processing. Hence, TGA analysis, underlined that PVC composites with DINP presented similar thermal stability to those with DOTP, as lubricant, but a much better thermal behavior compared to either neat PVC or the first series of samples passed only once through the extruder.

Table 4.3.3.1. *TGA results for PVC composites* ***[103]***

Sample	40-150 °C	150 – 380 °C		380 – 540 °C		540 – 640 °C		Start		Residue AT 700 °C	
	Mass	Mass	Tmax$_1$	Mass	Tmax$_2$	Mass	Tmax$_3$	Temp	Mass	(N$_2$)	(Aer)
	%	%	°C	%	°C	%	°C	°C	%	%	%
NET PVC	0.01	64.19	291	27.85	453.2	0.42	-	274.2	99.99	7.29	0.001
PVC_DINP 1	0.15	51.49	286.4	16.70	458	1.81	620.4	253.7	98.98	28.63	19.48
PVC_DINP 2	0.16	46.73	275.7	16.89	459.1	2.38	597.9	262.8	98.95	32.78	19.76
PVC_DOTP 1	0.08	61.31	284.6	14.43	456.8	1.02	622.1	261.4	99.06	21.22	13.54
PVC_DOTP 2	0.08	49.18	274.3	11.38	453.3	1.56	556.9	261.8	99.10	33.86	26.77

It can be observed from **Figure 4.3.3.4. a** and **b** that elongation at break and tensile strength of test samples increased when the samples were passed two times on the extruder. For PVC composites with DINP the increase of tensile strength and elongation at break is approximately 14 %, but for those with DOTP the increase for these properties was about 65 %. Samples with DINP did not attained remarkable mechanical properties compared to neat PVC. Therefore, it can be concluded that DOTP is more efficient when the composites are passed twice through the extruder. The improvement of mechanical characteristics can also be partially attributed to the increase of PVC mobility after passing twice on the extruder [106].



b) elongation at break

Figure 4.3.3.4. *Mechanical properties for the two PVC series of composites* ***[103]***

The plasticizer plays an important role, as well, in the flame-retardancy of the PVC samples. Usually, plasticized composites are more flammable than rigid composite, due to the plasticizer. The highest and lowest LOI were attained for PVC_DINP 2 and PVC_DOTP 1, respectively. Comparing the two series of composites, with DINP or DOTP, it can be observed that the highest value for oxygen index is achieved when the samples are extruded two times. Hence, the sample with DINP (second pass) presented a LOI of 26 % and the one with DOTP (second pass) a LOI of 24.5 %.

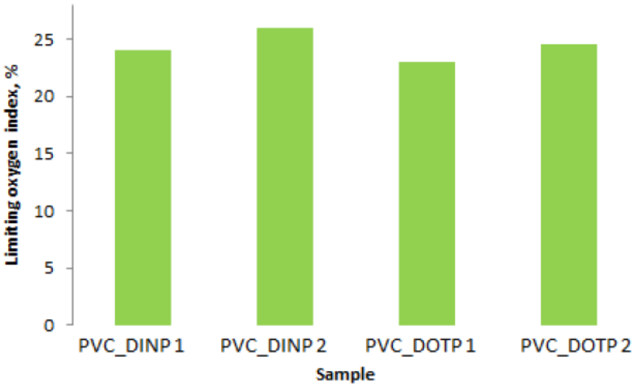
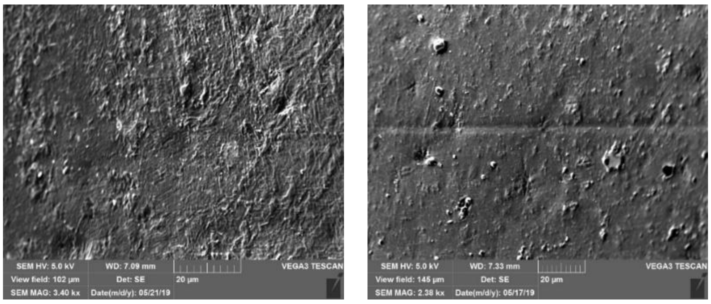


Figure 4.3.3.5. *LOI values for PVC composites* ***[103]***

The final study regarding the PVC samples is the morphology of the composites. As it can be seen from the micrographs in **Figure 4.3.3.6**, the samples passed twice through the extruder are more homogenous. The plasticizer exhibited an influence on the surface morphology, as well. Samples with DOTP presented a smoother surface compared with DINP samples. This means the compatibility of DOTP with the other raw materials was better assured.



PVC_DOTP 1 PVC_DOTP 2

Figure 4.3.3.6. *SEM analysis for PVC composites*

Therefore, it can be stated that the optimum formulation of PVC composites for this application should be based on DOTP as plasticizer. Plus, the material should be passed through the extruder two times, for better homogenization, as the overall characteristics of the composites have proven to be highly dependent upon the homogenization degree.

The second objective was accomplished, **the study of the influence of plasticizer nature and processing mode upon PVC composites**, proving the advantage of DOTP using as plasticizer in PVC composites and twice passes through the extruder, which lead to better homogenization.

The third study is based on the analysis of the influence of flame retardant systems upon PVC composites properties. Stibium trioxide is extensively used as flame retardant agent in PVC formulations despite his toxicity, due to the impurities such as arsenic.

As a result, the main goal of the study was to substitute or to partially replace the use of antimony trioxide. In this respect, flame retardants systems, i.e., aluminum hydroxide (ATH) or HMH (a mixture of hydromagnesite and huntite), $CaCO_3$, and synergic agents, i.e., zinc borate were investigated as potential systems to replace the antimony in the commercial PVC compounds.

LOI results of flexible PVC composites are shown in **Figure 4.4.3.9.** As expected, the highest LOI value is achieved by sample 5, which contains Sb_2O_3 and zinc borate. Sample 1 show also good synergistic flame retardancy because of antimony trioxide and zinc borate combination. The LOI value for this composite is 27%. Samples 2 and 3 with zinc borate presented good LOI values (25, respectively 24,4%), due to the incorporation of ATH. This type of flame-retardant agent acts as a heat sink by dehydration. Composite 7 with calcium carbonate, ATH, Ultracarb and zinc borate presented close LOI value to that of ATH alone-based composites, around 25,2%. It is also noteworthy, that Ultracarb alone-based PVC formulations led to a slightly higher LOI value of 26%. When only ATH and zinc borate are combined into the PVC formulations the LOI value increases significantly, up to 29,4 %. These results show that the mixture of ATH and zinc borate promotes the char formation of PVC and implicitly leads to a decrease of the hazardous gases, such as benzene and toluene, released during PVC combustion.

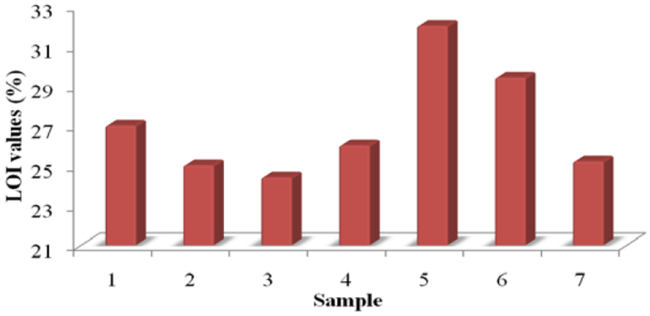
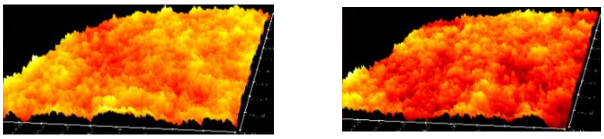


Figure 4.4.3.9. *LOI values for PVC based composites* ***[115]***

From digital holographic microscopy DHM, depicted in **Figure 4.4.3.10**, the three-dimensional images were used to evaluate the roughness for the representative samples 2-7. Based on the physical aspect of each ROI and on the roughness parameters, it was observed that the type of filler loading in the composites does not have an influence on the roughness of samples; but it depended more on the amount of filler. These results agreed well with the DMA measurements.

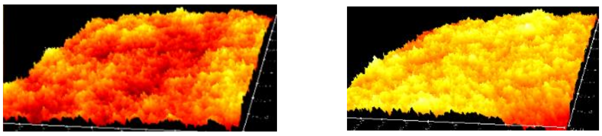


2

$CaCO_3$(38)-ATH(30)- zinc borate (1)

3

$CaCO_3$(50)-ATH(40)- zinc borate (1)



4

HMH(50)

5

HMH(75)-Sb_2O_3(5)- zinc borate (5)

Figure 4.4.3.10. *Three dimensional images of PVC based composites (samples 2,3,4,5,6 and 7), different regions of interest used to compute the roughness parameters* ***[115]***

The optimal formulation that leads to satisfactory properties, with stibium trioxide replaced, is sample 6.

Thereby, following the obtained results, it can be concluded that the third objective was achieved: **the analysis of the influence of flame retardant systems, that replace stibium trioxide, upon PVC composites properties.**

Synthesis of composites based on polyurethane matrix

The purpose of this study was to synthesize polyols from renewable resources, that replace conventional fossil-based polyols in polyurethane foams (PUF) in a multistep approach based on green chemistry, to bring both improved properties and sustainability.

a conventional and fossil-based polyol was partially replaced by up to 35% of each synthesized biobased polyol, alone or mixed. The structural, morphological, mechanical, and thermal properties of the PFUFs obtained from the mixture of the biobased polyols were superior to the ones obtained using a sole biobased polyol. Surprisingly, these biobased foams present higher properties than the conventional and fully fossil based PUF.

Reference foam (R.F.) contains 100 % commercial polyol (ARCOL P1374).

It was considered that olive oil is a triglyceride with three chains of oleic acid, predominantly oleic acid 83 %. Double bonds from oil were converted in epoxides (EOO-epoxidized olive oil). Then, the epoxy cycle was opened with ethanol (EtOH), EOO_EtOH, acetic acid (AA), EOO_AA or dimethylamine (DEA), EOO_DEA to synthetize the polyols. The polyol properties were determined by ^{1}H NMR, FTIR, SEC, rheology, hydroxyl index.

Figure 5.2.1.4. *FPUF (flexible polyurethane foam) from multistep process* ***[185]***

Three different series of foams was obtained. All the series was obtained in two steps. The foams were let to rise freely in a PP cup. The foams were cured at room temperature at least 24h before analysis. First series (Series A) is represented by EOO_EtOH polyols, the second one is represented by EOO_AA and the third series contains 1:1 EOO_EtOH and EOO_AA.

Cellular structure of foams, mechanical, thermal, and structural properties was investigated.

- ***Synthesis of OO-based polyols***

Several studies have shown that the presence of double bonds in the fatty acid chains of vegetable oil speed up oxidative degradation [186-189]. The epoxidation reaction of OO was performed with peroxoacetic acid and formed *'in situ'*. According to other previous studies with relevant results, the molar ratio for OO epoxidation was 1: 0.5: 1.5, corresponding to double bonds from OO: acetic acid: hydrogen peroxide, to avoid side reaction such as epoxide ring-opening and dimerization [190-192]. The epoxidation reaction is based on two steps:

(i) peroxoacetic acid formation, from acetic acid and hydrogen peroxide in acid-catalyze,

(ii) epoxides formation *via* peroxoacetic acid attack of OO double bonds, without any catalyst.

Epoxidation of OO double bonds was shown by the substantial decrease of vinyl protons at 5.34 ppm and the appearance of the epoxide signal at 2.91 ppm (5') (**Figure 5.2.3.2. a** and **b**). By reporting the integral of epoxide to vinyl, 85% yield of epoxidation was obtained.

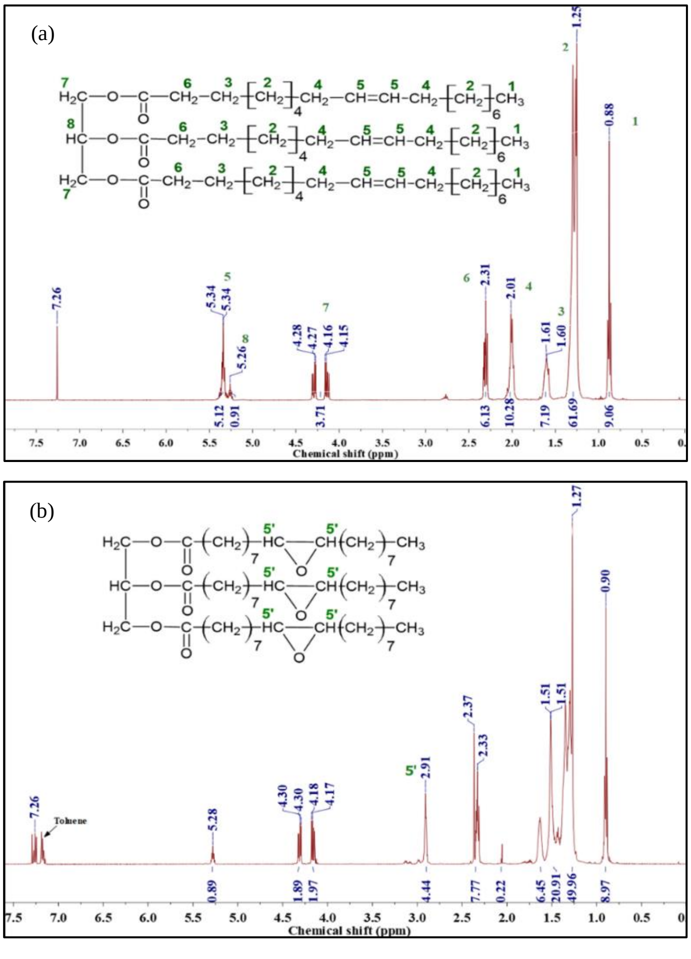


Figure 5.2.3.2. *^{1}H NMR Spectra for a) OO and b)EOO*

The second step was ring opening of epoxidized olive oil (EOO) with AA, EtOH and DEA. The NMR result showed a selectivity of 98 % EOO_EtOH, 72 % for EOO_AA and 50 % for EOO_DEA.

The hydroxyl index (I_{OH}), the molar masses (M_w and M_n) and the viscosity of OO-based polyols (in **Table 2**) are key parameters that impact the foaming process of and, consequently, the properties of the FPUFs. **Table 5.2.3.1.** shows that viscosities increased with the molar masses, confirming the success of the epoxidation reaction. The difference in I_{OH} between the theoretical value (calculated for 100% selectivity) and the experimental I_{OH} determined by analysis, confirmed the difference in selectivity as calculated from ^{1}H NMR analysis. The side reactions that occur especially after the ring-opening refer to oligomerization and, thus, could explain the difference in I_{OH} between the two bio-based polyols. The EOO_AA was synthesized in more acidic conditions, which favored the oligomerization of the epoxide. This hypothesis was confirmed by the molar mass values measured by SEC, presented in Table 5.**2.3.1.**

Table 5.2.3.1. *Physical properties of OO, EOO and OO-based polyols*

Polyol	I_{OH}th	I_{OH}exp	Viscosity la 25 °C, mPa·s	M_n	M_w	M_w th	PDI
OO	-	-	70	878	902	884	1,028
EOO	-	-	170	973	994	932	1,021
EOO_AA	112	99,43	2489	1190	1236	1112	1,039
EOO_EtOH	120	134,25	375	1033	1055	1070	1,022
EOO_DEA	153	86	2500	1067	1096	1099	1,027
ARCOL P1374	-	27	1170	10129	10270	-	1,014

FTIR spectra of the OO, EOO, EOO_AA and EOO_EtOH **(Figure 5.2.3.5)**, compared to ARCOL, confirmed the completion of the epoxidation and the ring opening reactions. OO and thereof presented several common bands, characteristic to triglycerides.

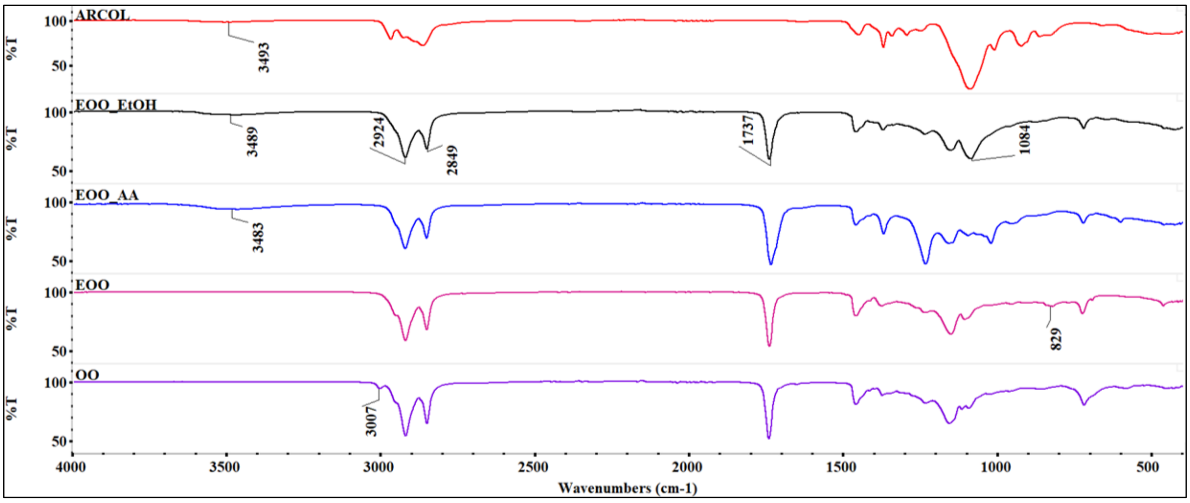
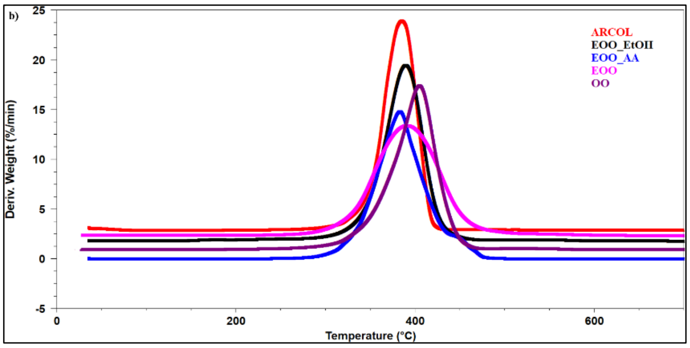


Figure 5.2.3.5. *FTIR Spectra for OO, EOO and OO-based polyols, compared to the reference polyol*

Thermal properties are presented in **Figure 5.2.3.6**. Herein, the epoxidation reaction shifted the onset degradation temperature from 322 (OO) to 332 °C (EOO).

The recorded onset degradation temperatures were 310 °C for the reference polyol, 304 and 336 °C for EOO_EtOH and EOO_AA, respectively. Degradation of polyols over 300 °C was associated with scission of ester and ether bonds followed by complete chai degradation. Both, the reference polyol and EOO_EtOH contain soft ether bonds, while EOO_AA is based on more rigid ester bonds. The oxidative cleavage of ether bonds occurred at lower temperature than the ester bonds [55], explaining the difference in thermal stability between both polyols. It was also observed that EOO_AA presented lower maximum weight loss, equivalent to the one registered for EOO (88 wt.%). The other polyols (EOO_EtOH and ARCOL) and OO registered around 91 - 93 wt.% maximum weight loss.



b)

Figure 5.2.3.6. *TGA (a) and DTG (b) curves for polyols, EOO and OO-based polyols, compared to the reference polyol*

The DSC thermograms of OO-based polyols significantly differed. We can also show the clear evolution from OO to the corresponding polyols. The primary crystallization and melting temperatures of the analyzed materials are given in **Table 5.2.3.2.** OO registered the lowest melting temperature, -47 °C and these values increased after each modification in the following order: EOO_AA<EOO_ETOH<EOO< ARCOL. With respects to the crystallization temperature, OO attained the highest value around -5 °C while the reference polyol the lowest (-68 °C) followed by EOO_AA, EOO_ETOH and EOO. Interestingly, EOO, EOO_AA and EOO_EtOH presented two crystallization temperatures (the second one between -18 and -10 °C), ascribed to different crystalline polymorphs, in which case may be due to the presence of oligomers in the composition

Table5.2.3.2. *Melting and crystallization temperatures of OO, EOO and OO-based polyols compared to the reference polyol*

Sample code	Melting temperature, °C	Crystallization temperature, T_{C1}, °C	Crystallization temperature, T_{C2}, °C
OO	-47	-6	-
EOO	-16	-7	-18
EOO_AA	-29	-41	-10
EOO_ETOH	-20	-10	-19
EOO_DEA	-16	-71	-14
ARCOL P 1374	-15	-68	-

- ***Synthesis of Flexible Polyurethane Foams (FPUFs)***

All FPUFs were prepared in a two-step method. Foams were prepared from two mix (A and B) and their mixing in a PP cup. Mix A consisted of the polyol's mixture where the fossil-based polyol was progressively substituted (by 15, 25 and 35 wt.%) by the biobased polyol(s) (alone or 50/50 wt/wt mixed). Then the catalysts, water, and surfactant were added, and the mix was homogenized using a mechanical stirrer at 2000 rpm, for 2 min. Mix B is only based on the diisocyanates, which were quickly added onto mix A. The mixture A+B was vigorously stirred at 2000 rpm for 5 s, after which the foam was let to rise freely. The foams were cured at room temperature for at least 24 h before analysis. The RF is based 100% fossil-based polyol and was used as a reference. Finally, 3 different series (Series A, B and C) have been performed with different formulations.

The isocyanate/hydroxyl molar ratio (NCO/OH) was set at 0.9 in all formulations. In this respect, all reactive hydroxyl groups from water (blowing agent,) or polyols, were considered to determine the added isocyanate. The surfactant, blowing and gelling catalyst were set at 0.15, 0.1 and 0.28 parts by weight (pbw), respectively, for all the foams.

The FTIR spectra of the FPUFs with the highest content of OO-based polyols were compared with the reference polyol (**Figure 5.2.3.8)**. On FPUF, the stretching vibration of NCO located at 2269-2273 cm^{-1} almost disappeared. This indicated that isocyanate groups have reacted quantitatively with the hydroxyl groups of polyols to form urethane bonds.

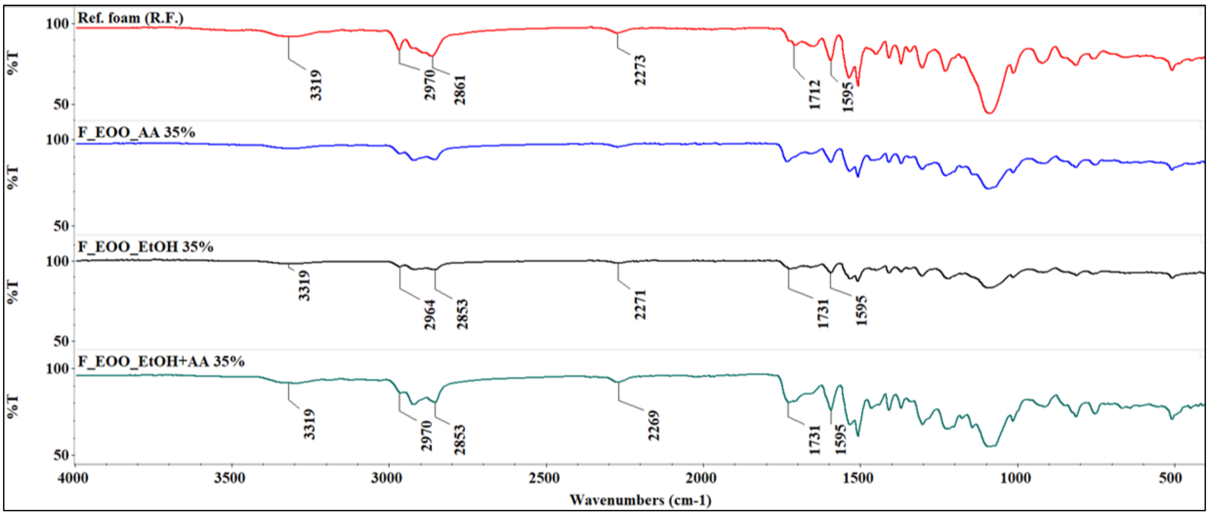


Figure 5.2.3.8. *FTIR spectra for FPUFs*

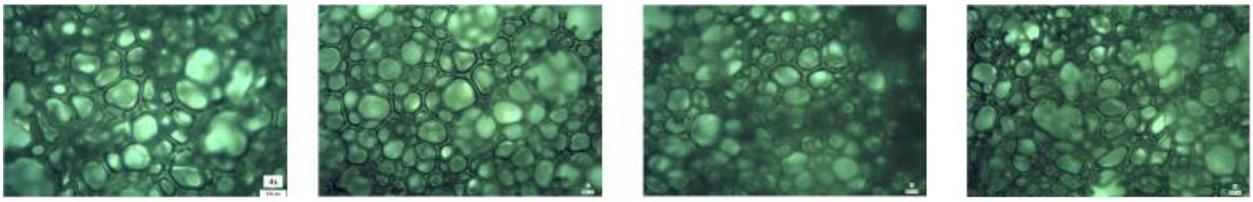
Density measurements, cell size and hysteresis loss are presented in **Table 5.2.3.7**.

Table 5.2.3.7. *Density, cell size and hysteresis loss from compression tests on FPUFs*

Series	Notation	ρ, kg/m^3	SD	SE	Cell size (µm)	SD	SE	Hysteresis loss, %
R. Foam	RF	51	±8	±4	124	±9	±2	52
A	F_EOO_AA 15%	48	±8	±4	109	±14	±3	55
	F_EOO_AA 25%	41	±3	±2	115	±20	±4	56
	F_EOO_AA 35%	54	±6	±4	119	±14	±3	60
B	F_EOO_ETOH 15%	53	±10	±5	100	±13	±4	55
	F_EOO_ETOH 25%	62	±15	±9	130	±20	±5	57
	F_EOO_ETOH 35%	74	±11	±5	140	±16	±3	58
C	F_EOO_ETOH+AA 15%	54	±7	±3	112	±11	±2	56
	F_EOO_ETOH+AA 25%	51	±2	±1	114	±12	±2	64
	F_EOO_ETOH+AA 35%	56	±2	±1	120	±18	±5	66

Density of the RF was 51 kg/m^3 while for of the FPUFs with OO-based polyols ranged from 41 to 74 kg/m^3. Furthermore, all the series of foams presented similar trends, meaning the densities increased with the amount of OO-based polyol. Similar observations were made by different authors, for instance in studies regarding soybean-based polyols [210, 211].

The optical micrographs of synthesized FPUF (**Figure 5.2.3.9**) revealed a clear open cell structure in perfect agreement with the focus of the study and the used blowing agent. The cells were irregular (polyhedral) in all foam series, consisting mainly of big cells with an average diameter of pores ranging from 100 to 124 μm and wide size distributions (see Table 5.2.3.7). Foams with higher blowing agent content (F_EOO_EtOH and F_EOO_EtOH+AA) revealed larger cell size that widen with the increasing amount of OO-based polyol. However, the series C with mixed OO-based polyols were more homogenous, with narrower distributions of cell size (112-119 μm), similar to the reference foam (around 124 μm). Series C presented more regular cell shapes and the recorded densities were in a close range (51-56 kg/m^3).

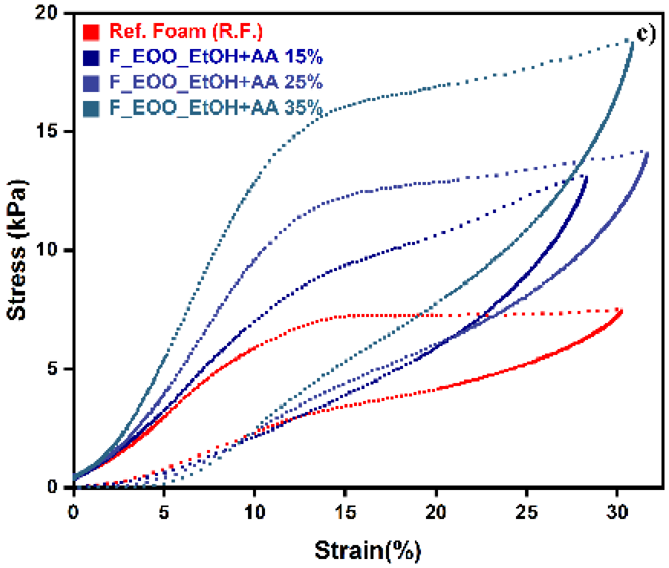


S. Ref. (S.R.) **F_EOO_EtOH+AA 15%** **F_EOO_EtOH+AA 25%** **F_EOO_EtOH+AA 35%**

Series 3: Reference foam, F_EOO_EtOH+AA 15%, F_EOO_EtOH+AA 25%, F_EOO_EtOH+AA35%

Figure 5.2.3.9. *Optical micrographs of FPUFs*

Lower hysteresis loss corresponded to a more rigid (macro)molecular structure, which required lower energy consumption while moving. High hysteresis loss indicated that the foam ability to absorb energy was higher. Compared to RF, foams with OO-based polyols presented higher hysteresis loss. Furthermore, it was observed that the stress increased with the amount of OO-based polyol. This phenomenon is due to the behavior of each polyol. The reference polyol, which is based on soft ether grafted chains, is replaced by stiffer polyols. It can be noted that the cell homogeneity of series C (F_EOO_EtOH+AA samples) has led to improved mechanical properties, with a hysteresis loss values between 56 and 66 %. These FPUFs exhibited similar physical properties than those of flexible foams found on the market, to fit to mattress or bedding applications.



Series 3: Reference foam, F_EOO_EtOH+AA 15%, F_EOO_EtOH+AA 25%, F_EOO_EtOH+AA35%

Figure 5.2.3.10. *Mechanical hysteresis behavior measured in a compression mode for all the FPUFs from Series A (a), series B (b) and series C (c)*

The thermal stability of FPUF was also evaluated. It is well known that the first stage in PU degradation corresponds to urethane bonds scission leading to the formation of primary or secondary amines and CO_2 [227-228]. Ester and ether bonds decomposition through chain scission takes place in the second stage of degradation while in the third stage occurs at higher temperatures (around 540 °C) when the polymer backbone was break down almost completely.

Series B and C with EOO_EtOH+ AA and F_EOO_EtOH presented improved properties compared to the F_EOO_AA-based system. For Series C, the first maximum degradation temperature was close to the one registered for RF and for the F_EOO_EtOH series, T_2 was the higher.

Glass transition temperature (T_g) of FPUF networks was determined by DSC analysis. The results showed that there were no significant changes in T_g for FPUFs compared to RF (**Table 5.2.3.8.**). However, distinct trends were observed in each series of foams. For instance, in Series A with EOO_AA the highest T_g was registered at 15% content of bio-polyol, in Series B with EOO_EtOH at 25% bio-polyol content and in Series C at 15% bio-polyol mixture. However, taking into account that SD in DSC is around 1°C, most T_g gaps are too low to be always significant.

Tab 5.2.3.8. Main *thermal properties of FPUF*

Sample	T_1, °C	T_2, °C	T_3, °C	Mass loss (second stage), %	T_g, °C
Ref. foam	302	389	488	71	58
F_EOO_AA 15%	298	395	478	65	60
F_EOO_AA 25%	296	400	475	66	59
F_EOO_AA 35%	294	404	474	65	60
F_EOO_EtOH 15%	297	394	485	71	56
F_EOO_EtOH 25%	298	402	478	71	61
F_EOO_EtOH 35%	298	405	480	70	56
F_EOO_EtOH+AA 15%	300	395	482	66	61
F_EOO_EtOH+AA 25%	300	401	476	61	60
F_EOO_EtOH+AA 35%	295	404	474	64	55

In conclusion, it seems that in the frame of environmentally friendly foams, the systems based on F_EOO_EtOH+AA present the optimal properties to fulfill requirements with various applications where semi-flexible foams can be used such as bedding application.

It can be concluded that the specific objectives were achieved, successfully establishing the foams F_EOO_EtOH+AA as the most optimal formulation in terms of properties obtained. Thereby, the four-specific objective of the second part of the thesis was accomplished:

1. **The process study on epoxidized olive oil synthesis;**
2. **The process study on the synthesis of polyols starting from epoxidized olive oil;**
3. **Synthesis of PU flexible foams using petroleum polyols and olive oil-derived polyols;**
4. **Foam characterization with the end of establishing the optimal recipe.**

General conclusions

Following the research carried out for the elaboration of the present doctoral thesis ***“Composite materials based on thermoplastic and thermoreactive resines with low environmental impact”,*** the following general conclusions can be formulated:

✓ Chapter 4 presents the results of research on obtaining PVC-based composites.

Subchapter 4.2 deals with the issue of obtaining flame retardant flexible composites. The most effective flame retardant is ATH, and calcium carbonate is beneficial for lowering the Tg value and optimizing mechanical properties (elasticity, elongation at break and tensile strength). Also, calcium stearate, used as a lubricant, is the optimal option, as it ensures better compatibility of raw materials (demonstrated by SEM analysis), increases hydrophobicity, and leads to homogeneous granules with superior physicochemical properties that recommend them for applications in the electrical cable industry.

Subchapter 4.3 is dedicated to the study of the plasticizer nature and the processing mode upon the characteristics of flexible PVC composites.

The homogeneity of the samples (demonstrated by SEM analysis) showed the importance of how to obtain PVC granules. The most homogeneous are the granules obtained by two passes through the extruder. As a result, the composites obtained with DOTP, as a plasticizer, and passed through the extruder twice have optimal properties with the potential applications for insulating electrical cables.

Subchapter 4.4 presents the data obtained for PVC-based composites, regarding the influence of flame retardant systems.

The study of flame retardant systems upon the characteristics of PVC-based composites has shown that the use of a mixture of ATH with zinc borate can successfully replace the use of Sb_2O_3 in the formulations for obtaining flame retardant granules. This leads to "green grains" free of Sb_2O_3 which is carcinogenic.

✓ In Chapter 5, the second part of the paper begins with a brief introduction presented in the literature. A classification of polyurethane foams is presented, and the main raw materials and materials used in their synthesis (polyols, catalysts, silicone surfactants, etc.) are reviewed.

Subchapter 5.2 deals with the issue of the synthesis of polyols from epoxidized olive oil. The synthesis of polyols requires three steps: the epoxidation of olive oil, the ring opening of the epoxy cycle to obtain polyols and the synthesis of polyurethane foams based on them.

Epoxidation of olive oil was performed by oxidizing it with a mixture of acetic acid with hydrogen peroxide in the presence of Amberlite IR 120 as a catalyst. The reaction took place in toluene medium. As the production of foams using only polyols from olive oil did not lead to adequate results, to highlight the influence of polyols on the characteristics of flexible polyurethane foams, mixtures with an industrial polyol were used. In these mixtures the percentage of polyol obtained from olive oil varied between 15 and 35%.

Paragraph 5.2.2 describes the raw materials and materials used for synthesis, their characteristics, and the way of working for the synthesis of epoxidized olive oil, polyols, and flexible foams.

The foams have characteristics similar to reference foam, which indicates the possibility of industrial use in the field of mattresses and upholstery. Thus, it can be concluded that F_EOO_EtOH + EOO_AA foams have optimal properties for use in the mattress and upholstery industry, due to the good results obtained from compression tests, densities suitable for this field, uniformity of cell size and higher degradation temperatures.

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