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A STUDY FOR A CLASS OF FLAME RETARDANT SYSTEMS BASED ON THERMAL, OPTICAL AND MECHANICAL ANALYSIS

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This study depicts the research on novel formulations for Polyvinylchloride (PVC) compounds used for wire and cable industry. Neat PVC is the most important halogen-containing polymer. It has high chloride content (about 56 %); and hence, it is an incombustible material. Yet, flexible PVC composites, due to the plasticizer content, have reduced resistance to fire, and therefore flame-retardant agents must be used. A way of achieving enhanced flame-retardant activity is to add flame retardants, such as, chlorinated paraffin, aluminum hydroxide, antimony trioxide (Sb_2O_3), zinc borate, red phosphorus, etc. However, it was proved that antimony presents toxicity because of the impurities contained in the commercial products, 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 Ultracarb (a mixture of hydromagnesite and huntite - HMH), $CaCO_3$, and synergic agents, i.e. zinc borate were investigated as potential systems to replace the antimony in the commercial PVC compounds. The compounds were reinforced with the various types of fillers and other additives and the influence of these materials was investigated in terms of thermal behavior (TGA, DMA and DSC), materials roughness by DHM analysis - optical analysis (based on the physical aspect of each region of interest 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 optical analysis) and flame-retardant properties characterized by LOI analysis.

Keywords: replacing Sb_2O_3, zinc borate, LOI

1. Introduction

Polyvinylchloride (PVC) is a versatile thermoplastic material which has been intensively used in different[3] industries, with various purposes, such as wires and cables, building materials and commodity stuffs (children toys, food packing, medical tubing), due to its excellent mechanical strength, thermal stability, flame

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retardant properties and insulation characteristics [1-2]. Because of high content of chlorine, which interrupts the exothermic processes and suppresses combustion, PVC has high flame-retardant characteristics. The addition of large amounts of plasticizers into PVC matrix to obtain flexible PVC reduces the flame retardant properties [3]. The most used flame-retardant agent is antimony trioxide. Reactions of antimony trioxide and PVC have been studied and described in many papers and distinct antimony oxychlorides have been revealed. Some oxychlorides can volatilize into the flame, and it is believed that antimony is the principal contributor in the delay of the flame reactions by purging free radicals; and hence, the flame retardation mechanism of antimony trioxide occurs in the gas phase [4-7]. Despite this role, it was proved that antimony presents toxicity because of the impurities contained in the commercial products, such as arsenic. Arsenic causes acute and chronic adverse health effects, including cancer. Antimony trioxide by itself is potentially toxic and carcinogenic, and can lead to diseases of the skin, liver, cardiovascular and respiratory systems. Also, excessive amounts of antimony may cause acute cardiac diseases. The toxicity of this substance depends on its chemical form: the toxicity of organic antimony compounds is lower than that of inorganic. Moreover, the limited reserve of antimony element in the earth crust leads to increasing price of this substance [8-9]. Hence, new solutions are needed to substitute the antimony –based compounds.

In addition, during PVC degradation a large amount of HCl gas is emitted. The inorganic gas aggravates the irritating and choking effects of the smoke released during PVC combustion. Moreover, HCl is highly corrosive and an acid rain contributor. It leads to formation of toxic dioxins and furans during combustion. When these pollutants are released into the atmosphere, it becomes poisonous for the environment and human health [10-12].

These being said, the main goal of the study was to substitute or to partially replace the use of antimony trioxide in flame retardant flexible PVC systems. For that, various flame retardants such as alumina trihydrate (ATH), hydromagnesite and huntite (UltraCarb) and zinc borate were combined to obtain similar results with flexible PVC compounds containing antimony. The obtained compounds were thermally, structurally and optically analyzed. Nevertheless, LOI analyses were best suited to evaluate the flame-retardant properties of new PVC compounds.

2. Materials and methods

Some of the analyzed compounds were obtained industrially and others in the laboratory. The compounds were reinforced with different types of fillers and the influence of these additives was investigated. The main application of these materials is for wire and cable industry.

In this research, commercial raw materials were used: PVC Ongrovil S5070 from BorsodChem (K-value 70.4), diisononyl phthalate (DINP) as plasticizer (LG Chem), Ca-Zn salt as heat stabilizer (Baeropan MC 91446 KA/3, Baerlocher), calcium carbonate particles of 2 μm (noted VO2) as reinforcing agent (Omya Calcita), Martinal ATH OL-104 LEO (Huber), HMH (Ultracarb, LKAB Minerals), antimony trioxide (Sb_2O_3, SICA), as flame retardants, zinc borate (Borax) as synergic agent and stearic acid as lubricant (Stera Chemicals).

The test specimens were prepared in two different ways, as follows:

1. For the samples prepared in the laboratory, PVC was melted and mixed with the plasticizer, the heat stabilizer, lubricant and reinforcing agent/flame retardant. Afterwards, the specimens were blended into a two-roll mill at 160 °C for 20 min, followed by compression at 170 °C to form sheets with dimension 150×150×1 mm^3.
2. For the composites obtained industrially, the samples were processed according to the internal procedures of an industrial manufacturer (the company name is confidential). Thereby, the raw materials were introduced one by one and blended into a masticator. First, the PVC and heat stabilizer were loaded, then the plasticizer and reinforcing or flame-retardant agents, and finally zinc borate and stearic acid were introduced by conveyor belt. The materials were mixed and melted at 110 °C until a homogenous paste was obtained. After that the paste was discharged into a vat and cooled till 50 °C. The cooled material was feed into the extruder funnel. The material was melted at 160 °C under pressure and then granulated. The grains obtained were pressed at 170 °C to form sheets with dimension 150×150×1 mm^3. The composition of the samples is presented in Table 1. The materials were reported to PVC (phr = parts per hundred resin, reported to base polymer = PVC).

The compounds with a large amount of plasticizer were made industrially for a better mixing. All the samples contain 5 phr stabilizer and 0.5 phr stearic acid. DINP used as plasticizer gives flexibility to the compound and improve viscosity and processability [13]. This type of phthalate plasticizer is not chemically bound to PVC.

Table 1

Compositions of flexible PVC compounds

Sample	PVC	DINP	$CaCO_3$	ULTRACARB	ATH	Sb_2O_3	Zinc borate
1	100	60	38	-	30	1.5	1
2	100	60	38	-	30	-	1
3	100	60	50	-	40	-	1
4	100	50	-	50	-	-	-
5	100	50	-	75	-	5	5
6	100	50	-	50	30	-	5
7	100	50	40	-	40	-	5

In order to correlate the structure of compounded PVC with their final properties the samples were investigated by FTIR. The thermal behavior and mechanical properties of the PVC compounds was analyzed by TGA, DSC and DMA, respectively. Materials roughness was given by DHM analysis, and the flammability was characterized by LOI analysis. The methods are described below.

Infrared spectroscopy analysis (FTIR)

Molecular structure of PVC based composites was analyzed using an infrared spectrometer type JASCO FT/IR 6300 Specac Golden Gate (KRS5 lens) ATR with diamond in transmission mode. The measured range was 400-4000 cm^{-1} (30 scans at 4 cm-1 resolution).

Thermogravimetric analysis (TGA)

The thermogravimetric analysis was performed on a thermogravimetric analyzer (Q5000IR, TA Instruments) at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere or air. Samples of approximately 8 - 14 mg were analyzed in the 40-700 °C temperature range.

Differential scanning calorimetric analysis (DSC)

Differential scanning calorimetry (DSC) experiments were carried out using DSC Q2000 from TA Instruments, working in temperature-modulated mode (MTDSC) with dynamic purge gas (helium 99.99% with flow rate 25 ml min^{-1}, modulated scan). Approximately, 25 - 30 mg samples were weighted and heated from -110 to 155 °C with a heating rate of 20 °C min^{-1}.

Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) experiments were carried out using DMA Q800 from TA Instruments, module DMA Multi-Frequency–Strain, in the tension mode, obtaining thermal behaviors of the PVC based composites, through the temperature ramp method. The sample size was 13.5 × (6.4-7) × (0.77-0.79) mm and the heating rate was 5 °C min^{-1} from – 75 to 105 °C.

As a result of the experiments, the temperature dependences of the storage modulus (E′), loss modulus (E″) and the mechanical loss factor ($tg\ \delta = E'/E''$) of the investigated PVC composites were extracted [14-16].

Limited oxygen index (LOI)

The limited oxygen index (LOI) index was tested using a Stanton Redcroft FTA Flammability Unit instrument. The test specimens were 120×60 (L×W) mm in dimension.

Digital holographic microscopy (DHM)

The digital holographic technique has already demonstrated its capability in investigations for different types of samples targeting areas as material sciences [17], biology [18], and medicine [19].

Digital holographic microscopy is a method based on an interferometric setup: the Mach-Zehnder interferometer with a reference arm and object arm (the arm where the sample is inserted). Two additional microscopic objectives are added in both arms: in the object arm to magnify the object details and in the reference arm to obtain the same wave front curvature. The setup is designed and built in the off-axis configuration (between the reference and object arm is a small angle) in transmission, for transparent samples. The procedure contains few main steps: 1. experimental recording of the hologram on the CCD, 2. numerical reconstruction of the three-dimensional image of the object based on the scalar diffraction theory in near field, Fresnel approximation, 3. selection of representative areas (10 regions of interest ROI for each sample) to apply the roughness tool from the main menu bar of the Koala^R commercial software. The roughness parameters of the surface texture are automatically computed and displayed based on the phase information (the phase shift introduced by the sample in the optical path).

3. Results and discussions

FTIR analysis

The transmission mode was applied to obtain the spectra for PVC composites. Figure 1 and 2 shows the characteristic bands of PVC, plasticizer, lubricant and heat stabilizer. In the both spectra the presence of CH and CH_2 bands from the PVC backbone are present at 2850-2849 and 2915-2916 cm^{-1}. The presence of PVC is also given by de C-Cl bond appearing at 602-605-606 cm^{-1}. Bands from 1720-1727, 1721-1730 cm^{-1}, corresponding to C=O vibrations is attributed to the lubricant (aliphatic carboxyl) and phthalate plasticizer (aromatic carboxyl). Carbocatenary long chain (CH and CH_2 bonds) of the plasticizer and of the lubricant are overlapping with those of PVC at 2850-2849 and 2915-2916 cm^{-1}. At 1268-1273 and 1475 cm^{-1} the vibrations of C-O groups belong to the lubricant (aliphatic carboxyl) and phthalate plasticizer (aromatic carboxyl) [20]. Figure 1 and 2 also depicts the spectra of PVC based composite with filler (i.e. flame-retardant agents). From it, the presence of additional new bands corresponding to each incorporated filler is observed. Composites with calcium carbonate presents specific bands around 874 cm^{-1} attributed to Ca-O vibrations and bands from 1418-1424 cm^{-1} correspond to C-O group from carbonate structure [21].

The presence of ATH in the PVC composites is demonstrated by the band corresponding to hydroxyl group at 3618-3647 cm^{-1} [22]. Further on, for the PVC composites with HMH inorganic filler the bands observed at 3513 cm^{-1} belong to -OH group from hydromagnesite [23]. The low wavenumber region 400-800 cm^{-1} depicts the lattice vibrations of Sb_2O_3. Specific bands were observed at 446, 479, 517, 556, 703, 712 cm^{-1} and correspond to symmetric and antisymmetric Sb-O-Sb vibrations [18]. The presence of zinc borate additive is demonstrated by small peaks at 960-961-962 and 1334 cm $^{-1}$[22].

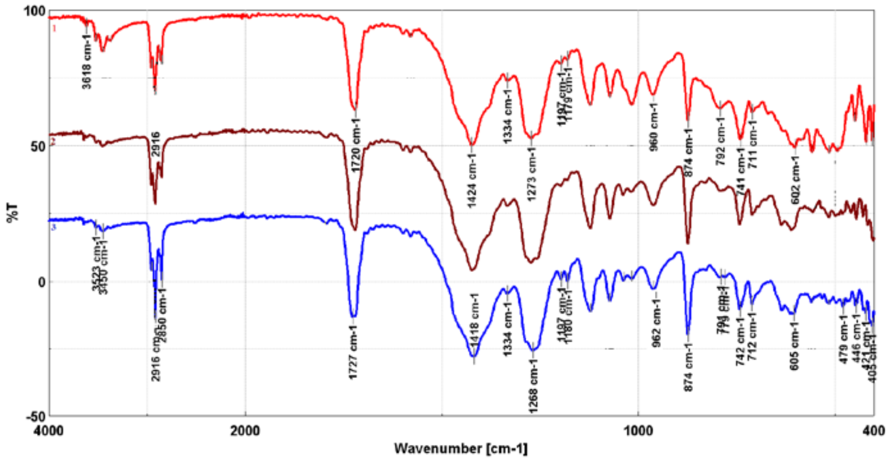


Fig. 1. FTIR analysis of PVC composites (samples 1, 2, 3)

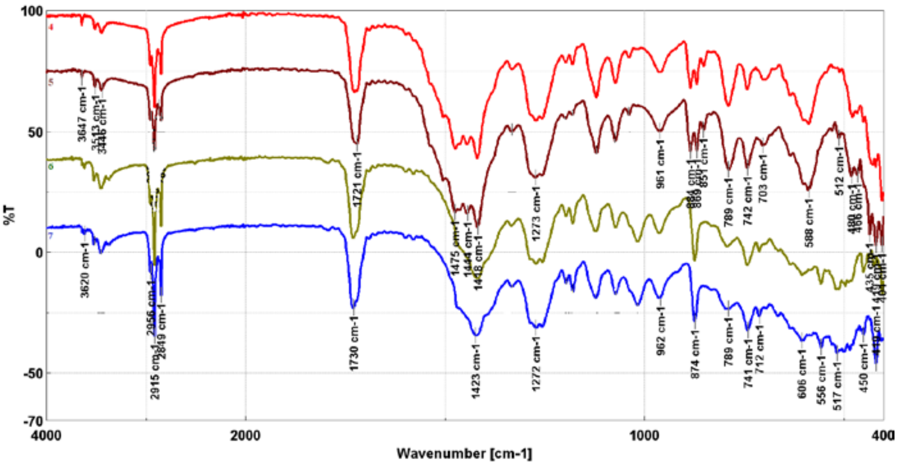


Fig. 2. FTIR analysis for PVC composites (samples 4, 5, 6, 7)

Thermogravimetric analysis (TGA)

The thermal decomposition of flexible PVC composites is divided into two stages as shown in Fig. 3 and 4. Dehydrochlorination of the polymer chain and plasticizer degradation takes place in the first stage. The second stage mainly involves cyclization of conjugated polyene sequences, formed in the first stage after HCl elimination, to form aromatic compounds. Neat PVC had a weight loss of 64 %. It can be observed from Table 2 that the weight loss decreases significantly, compared to neat PVC, when flame-retardant agents are added. The smallest weight loss in the first stage of PVC degradation is achieved for samples 5, 6 and 7, which contained zinc borate. Sample 5, with 46,7 % weight loss contained also antimony trioxide. Samples 4, 5 and 6 with Ultracarb, presented a higher weight loss in the second stage (380 – 540 °C), due to the decomposition of hydromagnesite and huntite.

It is well known that antimony trioxide renders excellent flame-retardancy to PVC, because of the synergistic flame retardant between Sb_2O_3 and PVC. Sb_2O_3 is inert in the early stage of fire situations because it sublimes at 1550 °C. The reactions between Sb_2O_3 and PVC lead to oxychlorides ($SbCl_3$ has the boiling point at 223 °C and SbOCl a boiling point at 170 °C). Some oxychlorides can volatilize into the flame. It is believed that antimony oxychlorides are the main contributors in the inhibition of the flame reactions, acting as free radicals scavenging flame poisons. Hence, the flame retardant mechanism of Sb_2O_3 remains in the gas phase [6,24]. Zinc borate is another flame retardant, prepared as an insoluble double salt from water-soluble zinc and boron compounds. Compounds having varying amounts of zinc, boron, and water of hydration are available. Boron functions as a flame-retardant in both the condensed and vapor phases. Under flaming conditions, boron and halogens form the corresponding trihalide. Zinc borate reacts with HCl released from PVC and form $ZnCl_2$, which is an effective Lewis acid that promote early cross-linking and minimize the decomposition of the polymer into volatile flammable gases.

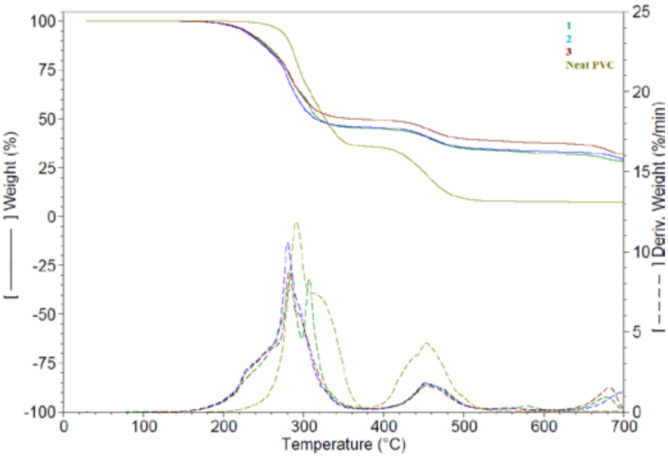


Fig. 3. TGA curves for samples 1, 2, 3 and neat PVC

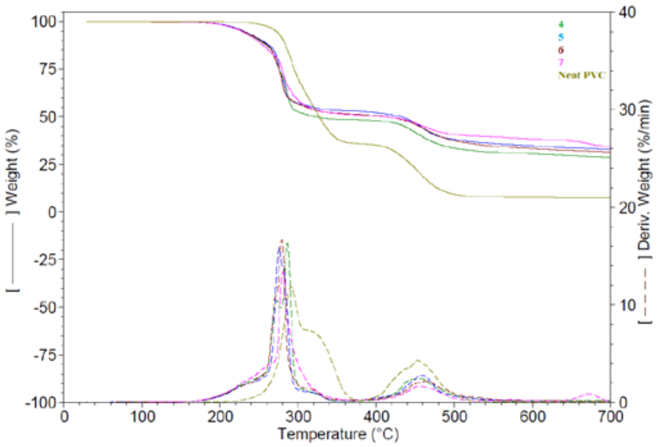


Fig. 4. TGA curves for samples 4, 5, 6, 7 and neat PVC

These trihalides are also volatile; they vaporize into the flame and release halogen which then functions as a flame inhibitor. When exposed to a flame, the boron and hydroxyl groups from ATH form a glassy ester that coats the substrate and reduces the PVC degradation [25]. Regarding, the residues of the samples with ATH and $CaCO_3$ at 700 °C, for measurements performed in air indicated that that samples 3 and 7, with 90 phr reinforcing and 80 phr flame-retardant agent, respectively, were more efficient for suppressing the smoke emitted during combustion, due to the char amount.

Table 2 **Weight losses for PVC based composites**

Sample	40 - 150° C	150 - 380°C		380 - 540°C		540 - 640°C		640 - 700°C		Residue at 700°C
	Wt. loss	Wt. loss	Tmax$_1$	Wt. loss	Tmax$_2$	Wt. loss	Tmax$_3$	Wt. loss	Tmax$_4$	(Air)
	%	%	°C	%	°C	%	°C	%	°C	%
1	0.07	54.82	284.4 / 307.0	11.26	457.9	2.09	578.9	3.20	677.7	22.28
2	0.06	54.18	280.0	11.40	452.2	1.40	561.0	3.65	696.3	22.22
3	0.03	50.22	282.1	10.93	451.3	1.70	557.3	5.09	681.5	26.62
4	0.15	51.49	272.8 / 286.4	16.70	458.0	1.81	620.4	1.22	-	19.48
5	0.16	46.73	275.7	16.89	459.1	2.38	597.9	1.07	707.6	19.76
6	0.16	48.69	279.2	16.16	462.8	2.59	614.6	0.85		20.97
7	0.08	49.05	280.4	11.15	454.6	2.22	575.2	3.08	673.8	27.65
Neat PVC	0.01	64.19	291.0	27.85	453.2	0.42	-	0.27	661.1	0.001

Differential scanning calorimetric analysis (DSC)

Using differential scanning calorimetry, the fluctuations in the glass transition temperature, T_g, of PVC composites were evaluated. To prevent decomposition of the polymer before processing it is necessary to lower the T_g and to establish a maximum temperature for processing and use of the final composites.

In the DSC diagrams (Fig.5 and 6) the variation of the glass transition for each PVC sample can be observed. The T_g depends upon the type of filler but also upon the quantity of filler used. Neat PVC, without additives, shows a T_g of 85 ºC. According to Fig.5, the smallest T_g is obtained for the sample with calcium carbonate and ATH, (sample 2, T_g = -46,6 ºC). PVC composites with Ultracarb and mixture of Ultracarb and ATH (Fig.6) have slight higher T_g values (sample 4 -36,4 °C, sample 5 -28,9 °C and sample 6 -35,3 °C). The shift in glass transition for samples 4, 5 and 6 can be a cause of using a large amount of flame retardant agent (antimony trioxide or zinc borate). It can also be mentioned that the recorded heat capacity that accompanies glass transition presented lower values for all the samples, with small variations between composites.

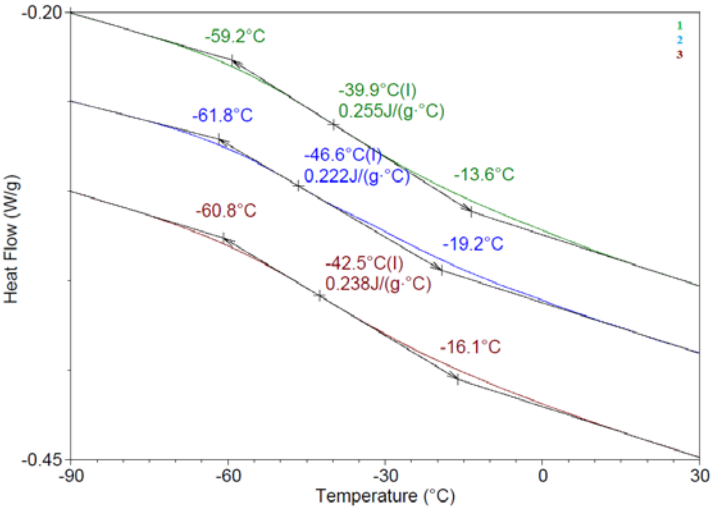


Fig. 5. DSC analysis for samples 1, 2, 3

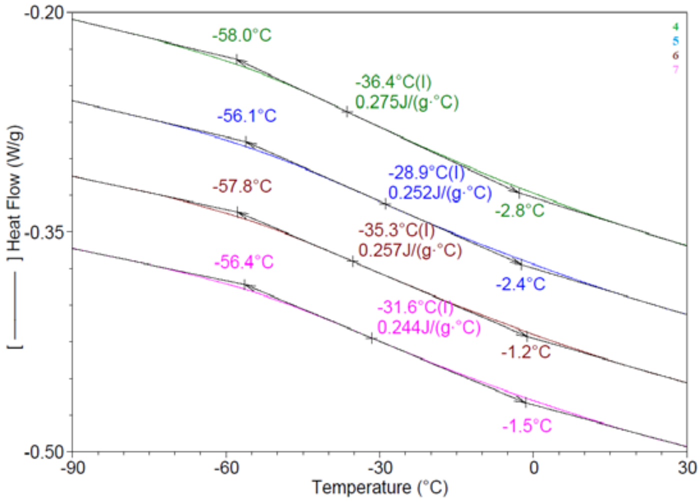


Fig. 6. DSC analysis for samples 4, 5, 6, 7

Dynamic mechanical analysis (DMA)

Further on, the dynamic mechanical properties of PVC composites were studied. DMA was complementary on determining the storage modulus, the loss modulus and the dynamic loss factor at maximum value. The increase of storage modulus with filler loading usually indicates that the mobility of the polymer chain is decreased in the presence of the filler and thereby the T_g is shifted to higher temperatures. It was observed that the incorporation of the filler into the PVC matrix may decrease or increase the mechanical damping of the polymer (Fig. 7 and 8**)**.

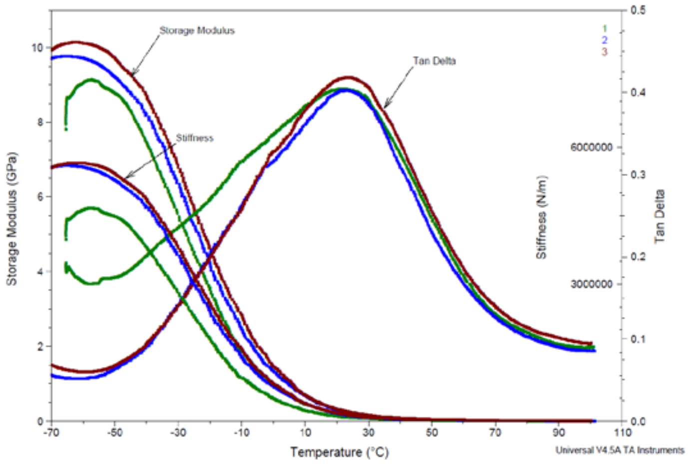


Fig. 7. DMA of PVC based composites (samples 1, 2, 3)

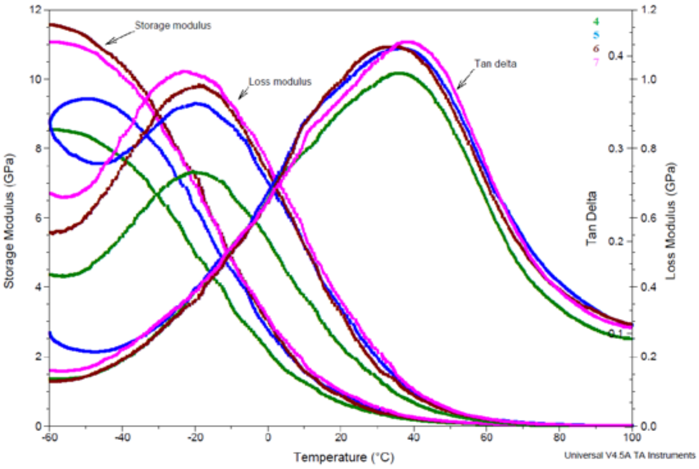


Fig. 8. DMA of PVC based composites (samples 4, 5, 6, 7)

Fig. 7 proves that type of filler does not have a major influence upon the samples stiffness, but a larger amount of filler increases the stiffness. It was also observed that the storage modulus of all composites is greater than that of PVC. Hence, filler incorporation increases the storage modulus for all samples. The increased peak intensity of the loss modulus indicated higher heat dissipation in the PVC composites, compared to neat PVC, demonstrating that the new formulations of PVC are flexible. The height and position of the loss modulus and loss factor for the composite samples varied with the type and the filler quantity. From Fig. 8, it can be observed that the values for the storage modulus decreased, while the loss modulus values gradually increased with the increase of temperature.

Limited oxygen index (LOI)

The limiting oxygen index (LOI) is a procedure for evaluation the flammability of materials. LOI is defined as the minimum concentration of oxygen in an oxygen-nitrogen mixture, required to sustain burning of a vertically mounted specimen. Thus, the more required oxygen (higher LOI), the stronger the flame retardancy effect. Consequently, high LOI values indicate better flame retardancy and small LOI values are representative for flammable materials. LOI results of flexible PVC composites are shown in Fig. 9.

As expected, the highest LOI value is achieved by sample 5, which contains 5 phr Sb_2O_3 and 5 phr zinc borate. Sample 1 show also good synergistic flame retardancy as a result of antimony trioxide and zinc borate combination. The LOI value for this composite is 27%. Samples 2 and 3 with 1 phr zinc borate presented good LOI values (25, respectively 24,4%), due to the incorporation of ATH.

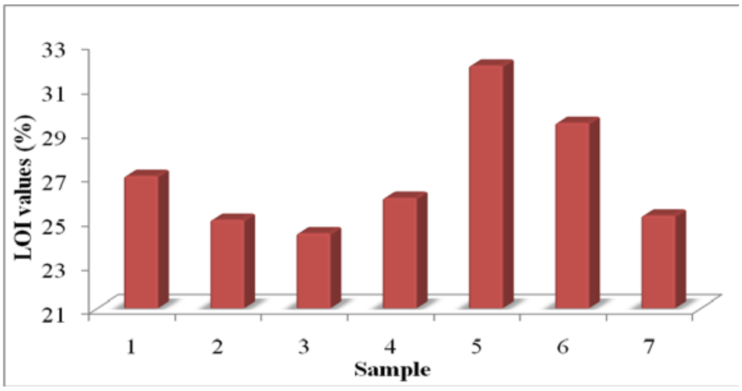


Fig. 9. LOI values for PVC based composites

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 slight 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 [26-27]. More importantly, the smoke density of these latter composites is much lower than that of antimony trioxide-based composites. Therefore, using the proposed formulations for flexible PVC, the LOI values attesting high flame-retardant properties can be achieved. Concluding, antimony trioxide can be successfully replaced with zinc borate and ATH or Ultracarb, and also with mixtures of ATH and calcium carbonate, or ATH and Ultracarb.

Digital holographic microscopy (DHM)

From digital holographic microscopy DHM, depicted in Fig. 10, the three-dimensional images were used to evaluate the roughness for the representative samples 2-7. Roughness parameters referred to: 1. waviness, defined as the irregularities whose spacing is greater than the roughness sampling length, 2. bearing ratio which could be found from a profile trace by drawing lines parallel to the datum and measuring the fraction of the line which lies within the profile. In Fig. 11 an example of one region of interest and its computed roughness parameters are displayed on the software interface. 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.

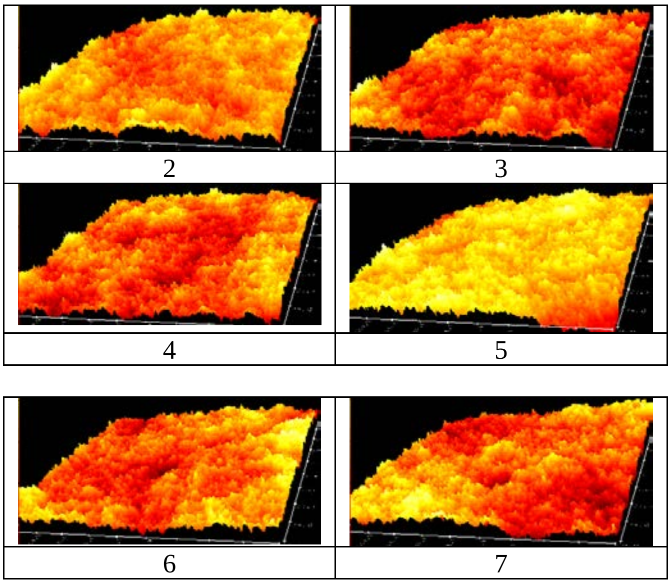
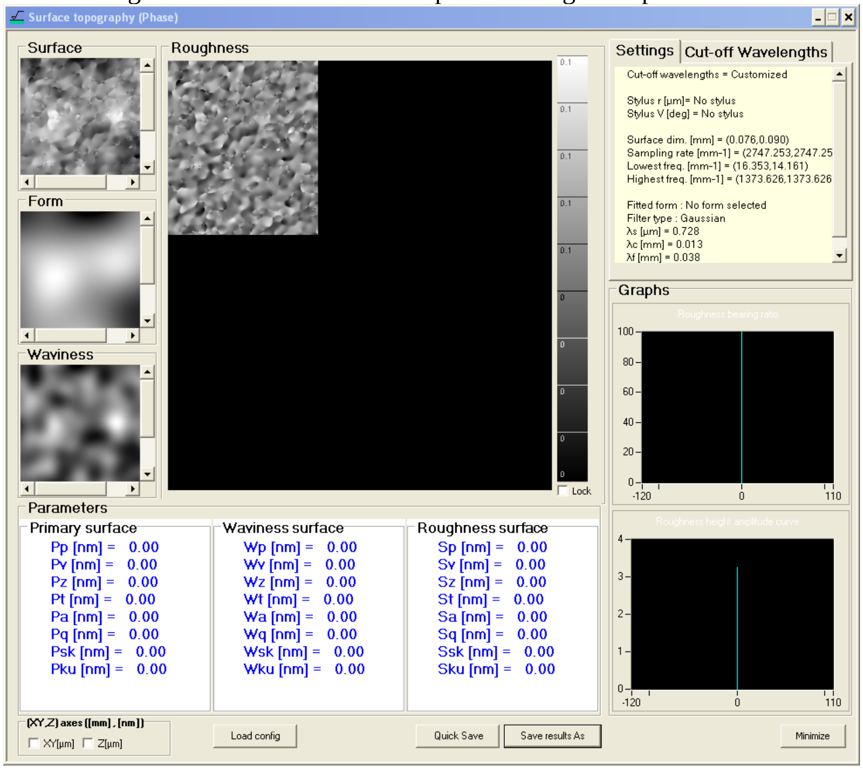


Fig. 10. Three dimensional images of PVC based composites (samples 2,3,4,5,6 and 7), different regions of interest used to compute the roughness parameters



Cut-off wavelengths = Customized

Stylus r [µm]= No stylus
Stylus V [deg] = No stylus

Surface dim. [mm] = (0.076,0.090)
Sampling rate [mm-1] = (2747.253,2747.25
Lowest freq. [mm-1] = (16.353,14.161)
Highest freq. [mm-1] = (1373.626,1373.626

Fitted form : No form selected
Filter type : Gaussian
λs [µm] = 0.728
λc [mm] = 0.013
λf [mm] = 0.038

Primary surface
Pp [nm] = 0.00
Pv [nm] = 0.00
Pz [nm] = 0.00
Pt [nm] = 0.00
Pa [nm] = 0.00
Pq [nm] = 0.00
Psk [nm] = 0.00
Pku [nm] = 0.00

Waviness surface
Wp [nm] = 0.00
Wv [nm] = 0.00
Wz [nm] = 0.00
Wt [nm] = 0.00
Wa [nm] = 0.00
Wq [nm] = 0.00
Wsk [nm] = 0.00
Wku [nm] = 0.00

Roughness surface
Sp [nm] = 0.00
Sv [nm] = 0.00
Sz [nm] = 0.00
St [nm] = 0.00
Sa [nm] = 0.00
Sq [nm] = 0.00
Ssk [nm] = 0.00
Sku [nm] = 0.00

Fig. 11. An example of a region of interest and the roughness parameters for sample 1

4. Conclusions

Sb_2O_3 can be replaced with zinc borate if a combination of flame-retardant agents or flame-retardant and reinforcing agent like calcium carbonate is used. LOI analyses indicated that a combination of ATH and zinc borate can lead to a similar flame-retardation effect to that of Sb_2O_3 alone, which is the commercial version used today for flexible flame-retardant PVC formulations.

Differential scanning calorimetry and dynamic mechanical analysis measurements proved that the plasticizer and fillers have a synergic effect upon the decrease of T_g values for the new PVC formulations. Thermogravimetric analysis showed that the rate of polymer decomposition was slowed down due to released water from the metal hydroxide, which diluted the flammable polymer residues and hence, the formed metal oxide residue acted as a thermal barrier to inhibit the decomposition of the underlying polymer. DMA and DHM analysis pointed out that only the amount of filler loading in the composites affected the roughness of samples.

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