The Influence of Plasticizer Nature and of Processing Mode Upon the Characteristics of Flexible Poly(vinyl chloride) Composites

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The topic of this paper refers to the influence of the plasticizer and the processing mode upon the characteristics of the poly(vinyl chloride) (PVC) composites. Thereby, in this study two types of industrial plasticizers were used to highlight their influence upon the properties of final composites. The employed lubricant was stearic acid, the most common and cheapest additive used in the industry for cables manufacturing. For economic reasons, calcium carbonate of 2 µm size was used as reinforcing agent. Further on, two sets of samples were prepared, targeting the influence of the processing mode upon the properties of final composites. Beside the structure (by FT-infrared), thermal behavior (thermal analyses and differential scanning calorimetry) and mechanical properties (dynamic mechanical analyses, tensile strength and elongation at break) of PVC composites, the limiting oxygen index (LOI) and the overall morphology of the samples were also investigated.

Keywords: plasticizer influence, LOI, processing methods

PVC is intensively used nowadays, due to its low cost, fire resistance, chemically resistance to acids, salts, bases, fats, and alcohols, making it resistant to the corrosive effects of sewage (which is why it is extensively utilized in manufacturing sewer piping systems), electrical protecting properties, good insulation properties, good tensile strength, ability to use it in rigid, semi flexible or flexible state and because it can be colored in a wide range of colors [1-5]. In industry, the most important issues are the quality of the product and the price [6]. It can be said that both are on the same line. Therefore, in this paper a commercial formulation of flexible PVC composite was modified to obtain a more cost-efficient product with improved properties.

To accomplish these objectives, diisononyl phthalate (DINP) and dioctyl terephthalate (DOTP) were used as plasticizers. These two plasticizers are intensively used in the industry, because they are cheap and also because they deliver the required properties for the PVC composites according to their final application. DOTP is a non-phthalate plasticizer, being the diester of terephthalic acid and of branched-chain 2-ethylhexanol. DINP is usually a mixture of chemical compounds consisting of various isononyl esters of phthalic acid [7-8]. Polyvinyl chloride (PVC) is rigid at normal temperature due to intermolecular forces between molecules and short distances between them. When the polymer is heated to a high temperature, the energy of the molecular motions exceeds the energy of the intermolecular forces, and this broadens the molecular distances resulting in PVC softening. Addition of plasticizer prevents the PVC molecules from coming closer to each other. The molecules of the polymer are isolated even at normal temperature and its softening is preserved. This process is called plasticizing [9]. Diisononyl phthalate is categorized as a commodity phthalate ester plasticizer and maintains good performance of composites at low temperature. Dioctyl terephthalate is preferred for volatility resistance, which prevents the health and toxicity issues [10].

Lubricants play a fundamental role in the way in which polyvinyl chloride melts and flows during compounding [11]. Lubricants can be internal, external or combined. External lubricants are used to reduce the friction between the polymer melt and metal surfaces during processing, and internal lubricants are used to reduce frictional forces within the polymer matrix and to lower the effective viscosity. Mixed lubricants have both uses. The employed lubricant in this study was stearic acid, which is a mixed lubricant [12-14].

The calcium carbonate reinforcing material is cheap and also provides good fire-resistance properties to PVC composites. When the compounds are exposed to a flame, $CaCl_2$ is produced and captures the hydrochloric acid emitted during decomposition of the PVC matrix [15-16]. \

In a previous study of the same group the influence of the lubricant upon the properties of PVC composites was investigated [17]. As a result, considering the present literature, this paper provides forward a comparative study on the influence of plasticizers and of the processing mode. Therefore, the study was performed on two variation levels, which implied analyzing two series of PVC composites (with DINP and DOTP) for structure, thermal stability, homogeneity

and fire-resistance. The samples were prepared using different processing modes, i.e. by passing once or by passing twice through the extruder. The literature of PVC composite materials is abundant with new fillers or nanofillers and new plasticizers, but they lead to very high production costs. Therefore, this study also provides an alternative to the eccentric recipes for PVC composites by improving the existing commercial formulations, at lower costs.

Experimental part
Materials and method
For this research the following materials were used:

- PVC Ongrovil S5070 from Borsod Chem (K-value 70.4); Diisononyl phthalate (DINP) as plasticizer (LG Chem); Dioctyl terephthalate (DOTP) as plasticizer (Chem Flexx); Ca-Zn salt as heat stabilizer (Baeropan MC 91446 KA/3, Baerlocher); Calcium carbonate particles of 2 μm ($CaCO_3$) as reinforcing agent (Omya Calcita); Stearic acid (Stera Chemicals) as lubricant.

The test specimens were prepared by melting and mixing PVC with the heat stabilizer, reinforcing agent, plasticizer and lubricant. First of all, the heat stabilizer was mixed with PVC to prevent degradation before processing, afterwards the rest of materials were added in the following order: plasticizer, lubricant and reinforcing agent (formulations given in Table 1). The ingredients were blended in a masticator and heated at 110 °C. After 1 hour, the obtained mass was cooled-down at 50 °C. The next procedure consisted of passing the material through an extruder. The one series of PVC with plasticizer was passed once through the extruder and another series was passed twice. Afterwards, the grains resulted from extrusion were blended into a two-roll mill at 160 °C for 20 min. The temperature of roll milling depends on the final use of end product. For cable isolation, as final application of the employed PVC composites, the temperature is 160 °C. The roll milling smoothed the product by rolling followed by compression at 170 °C to form sheets with dimension $150 \times 150 \times 1$ mm^3.

Table 1
FORMULATIONS OF PVC BASED COMPOSITES

Sample code*	Plasticizer	Processing mode
PVC_DINP 1	DINP	1 extruder pass
PVC_DOTP 1	DOTP	1 extruder pass
PVC_DINP 2	DINP	2 extruder passes
PVC_DOTP 2	DOTP	2 extruder passes

*All the samples have the following formulation: PVC 100 phr, plasticizer 50 phr,
reinforcing agent 80 phr, lubricant 0.4 phr and heat stabilizer 4 phr

Infrared spectroscopy analysis (FTIR)
Molecular structure of the PVC composites was analyzed using an infrared spectrometer type JASCO FT/IR 6300 Specac Golden Gate ATR with diamond in transmission mode. The measured range was 400-4000 cm^{-1}, 16 scans.
Thermogravimetric analysis (TGA)
The thermogravimetric analysis was performed using 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. The thermal behaviour of the PVC composites was obtained through the temperature ramp method. The sample size was $13.5 \times (6.4\text{-}7) \times (0.77\text{-}0.79)$ mm and the heating rate was 5 °C min^{-1} from – 75 to 105 °C.
Tensile strength and elongation at break
The tensile strength and elongation at break of the samples were performed on a computer-controlled electronic tensile testing machine (Instron 3382) with a constant speed of 100 mm min^{-1} at room temperature.
Limited oxygen index (LOI)
The limited oxygen index (LOI) index was tested using a Stanton Redcroft FTA Flammability Unit instrument. The test specimens were $120 \times 60 \times 2$ (L×W×T) mm in dimension.

Scanning electronic microscopy (SEM)

Scanning electronic microscopy (SEM) was used to study the morphology and homogeneity of the PVC samples. Vega-3 (Tescan, Brno, Czech Republic) apparatus in high vacuum mode with working distances in the range of 4–8 mm and an acceleration voltage of 5 kV was used. Before examination, the samples were coated with a thin layer of gold with a gold coater (Quorum Q 150 RS; Quorum Technologies, Lewes, UK).

Results and discussion

FTIR analysis

Plasticizers provide compound flexibility, which improves viscosity and processability [18]. These types of phthalate plasticizers behave like solvents but they are not chemically bounded to PVC [19].

Figure 1 presents the plasticizers IR spectra, which are very much similar due to similarities of the structure. Figure 2 shows the characteristic bands of PVC, plasticizer, lubricant and CaCO$_3$. The presence of PVC is given by de C-Cl bond appearing around 600 cm^{-1}. The band at around 1720 cm^{-1} is attributed to the C=O vibrations belonging to the ester plasticizer. The decrease of the band intensity at 1720 cm^{-1} suggests the plasticizer migration. It can be observed that the compound with DINP had a higher decrease of intensity compared to DOTP-based composites. This means that DINP migrate faster from the compound than DOTP [20].
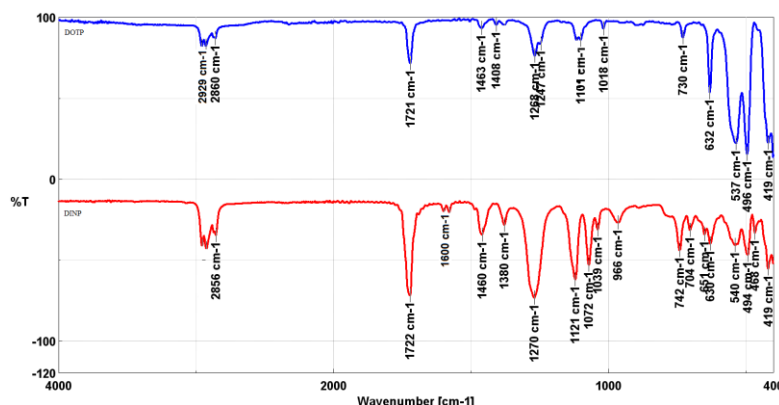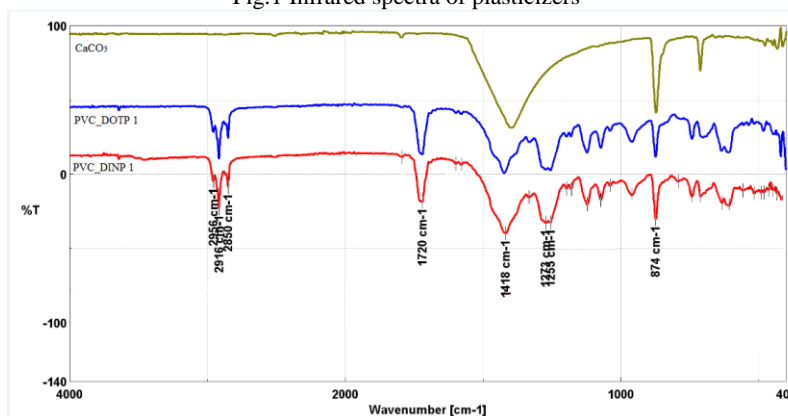

Fig.1 Infrared spectra of plasticizers

Fig. 2 FTIR spectra of CaCO$_3$ and 2 PVC composites

For carbocatenary long chain (CH and CH$_2$ bonds) of the plasticizer and of the lubricants are overlapping with those of PVC chain at 2850 and 2916 cm^{-1}. At 1270-1273 cm^{-1} the vibrations of C-O groups belonging to the lubricant (aliphatic carboxyl) and phthalate plasticizer (aromatic carboxyl) appear [21]. The reinforcing agent displays specific bands around 874 cm^{-1} attributed to Ca-O vibrations, and the bands from 1418 cm^{-1} corresponding to C-O group from the carbonate structure [22]. The series of PVC composites passed 2 times through the extruder, presented the same bands as the series passed 1 time through the extruder.

Thermogravimetric analysis (TGA)

TGA analysis (Table 2) showed that the total mass loss of neat PVC, in the first stage (150 - 380 °C) is about 64 wt.%. In the 40 - 150 °C temperature range no significant mass losses are observed (approximately 0.01 wt.%). The thermal degradation of PVC takes place in two steps, as follows: in the first step (150 - 380 °C), hydrochloric acid is emitted and polyene structures are formed, and in the second step (380- 540 °C) the cyclization of the polyene structures takes place with the formation of aromatic compounds. In the second stage the mass losses are about 27 %. The second stage represents the thermal decomposition of PVC backbone and, therefore, lower molecular weight compounds and smoke are produced [23-25].

For the PVC composites however, an improvement regarding the weight losses in both stages can be observed. After addition of plasticizer, lubricant, stabilizer and reinforcing agent, the mass loss in the first step is about 47-51 wt.% for DINP-based composites and 49-61 wt.% for DOTP-based composites. This mass loss is due to plasticizer desorption [26]. In this temperature range (i.e. 150 – 380 °C), decomposition of the stearic acid lubricant (and of Ca-Zn stabilizer, which is also a metal carboxylate) also begins. In the second step, the composites lose approximately 20 wt. % from the total mass and $CaCO_3$ starts to decompose slowly. Hence, it can be confirmed that this stabilizer is good for this temperatures range as the composites were much more stable at higher temperatures. $CaCO_3$ also minimizes the emissions of hydrochloric acid during the PVC composites degradation by adsorbing hydrochloric acid released during PVC decomposition, leading to the formation of $CaCl_2$. $CaCO_3$ with 2 µm particle sizes can absorb higher amounts of hydrochloric acid [17]. Therefore, it can be stated that calcium carbonate acts as a heat stabilizer by trapping hydrochloric acid.

Table 2
THERMOGRAVIMETRIC ANALYSIS FOR RAW MATERIALS USED IN PVC COMPOSITES

Sample	40 - 150°C	150 - 380°C		380 - 540°C		540 - 640°C		Onset Point		Residue at 700°C	
	Wt. loss	Wt. loss	Tmax 1	Wt. loss	Tmax 2	Wt. loss	Tmax 3	Temp	Weight	(N₂)	(Air)
	%	%	°C	%	°C	%	°C	°C	%	%	%
Neat PVC	0.01	64.19	291.0	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	458.0	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**

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.

Differential scanning calorimetric analysis (DSC)

To evaluate the glass transition temperature (T_g) of the composites, DSC was used. The T_g is very important for the composites in general, to establish the processing temperature without degrading the polymer. The decomposition temperature of neat PVC (around 160 °C) is lower than the melting temperature (260 °C). Therefore, it is mandatory to decrease the T_g in order to prevent degradation before processing [27-28].

In Table 3, the T_g for each PVC composite can be observed. Neat PVC, without additives, has a T_g of approximately 85 ℃. According to Table 3, the lowest T_g values were obtained for the samples that passed two times through the extruder machine. This is due to a better homogenization of the materials, gained when the raw materials were extruded twice. PVC compositions with DINP presented a decrease of T_g with about 3 ℃, compared to those with DOTP. This may be due to a more hydrophilic character of DINP, as suggested by the TGA as well (higher water weight loss).

Table 3
DSC RESULTS FOR PVC BASED COMPOSITES

1st Heating Total heat Flow	PVC - Glass Transition			
	Onset (°C)	T_g (°C)	End (°C)	ΔC_p [J/(g·°C)]
PVC_DINP 1	-56.1	-28.9	-2.4	0.252
PVC_DINP 2	**-58.0**	**-36.4**	**-2.8**	**0.275**
PVC_DOTP 1	-53.7	-25.6	6.0	0.309
PVC_DOTP 2	**-56.6**	**-33.4**	**-2.3**	**0.256**

Dynamic mechanical analysis (DMA)

One of the most important characteristics for processing the polymeric materials is viscoelasticity.

This parameter may be evaluated using a dynamic mechanical analysis instrument, to measure the storage modulus, loss modulus and damping properties.

An important index for measuring the stiffness and elasticity of polymeric materials is the storage modulus. Figure 3 shows the storage modulus of PVC composites in DMA temperature scans. It can be seen that composites presented

higher storage modulus than neat PVC through the whole temperature scan range. Slight difference can be observed between the samples due to different plasticizers. Composites with DINP showed a higher storage modulus than those with DOTP.

The second pass through the extruder is important and it can be observed by the difference in the storage modulus. According to Figure 3 the second series of PVC composites (PVC_DOTP 2 and PVC_DINP 2) registered an increase of the storage modulus and a decrease of the loss modulus. These results confirmed once again that passing the material twice through the extruder leads to more homogenous and compact composites. Tan delta (Figure 4) however, did not present significant differences between composites. The range of this parameter was between 0.39 and 0.4.

Concluding, the plasticizer incorporation increased the storage and loss modulus, compared with neat PVC, which explained the higher heat dissipation in the PVC composites compared with neat PVC, confirming that the new formulations of PVC are flexible.
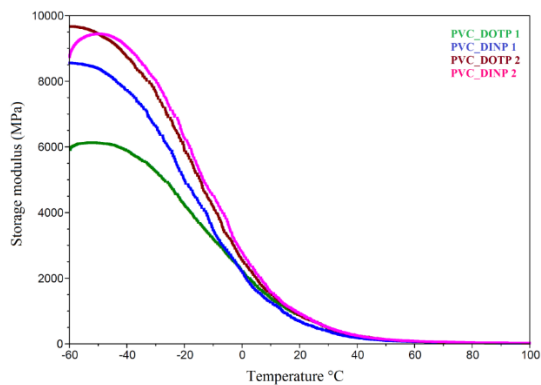

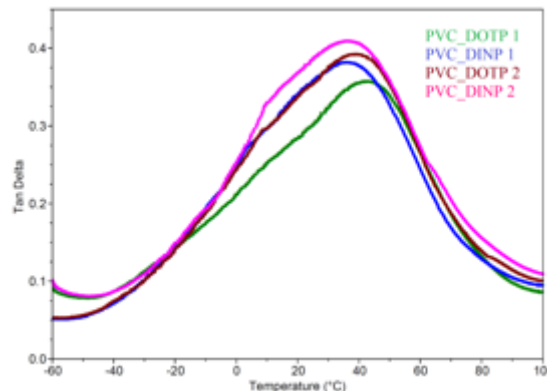Fig. 3 Storage modulus of PVC composites

Fig. 4 Tan delta for PVC based composites

Tensile strength and elongation at break

In practical applications, for evaluating the quality of flexible PVC composites, the most important properties are the mechanical properties such as: tensile strength and elongation at break. It can be observed from Figure 5 a and b that elongation at break and tensile strength of test samples increased when the samples were passed two times on the extruder. From the Figure 5, it can be stated that the mechanical properties made the difference between the two plasticizers. 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 [29].

a)   b)
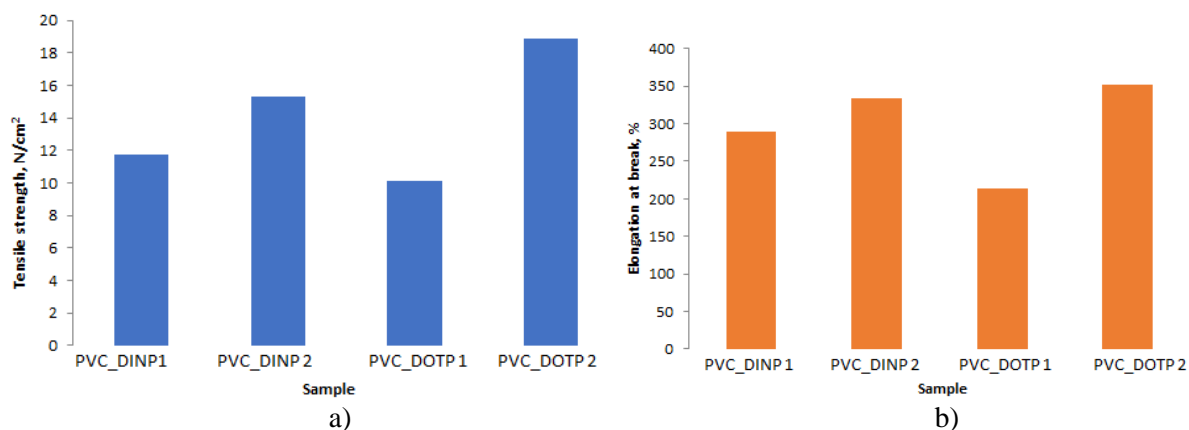
Fig. 5 Mechanical properties for the two PVC series of composites a) tensile strength, b) elongation at break

Limited oxygen index (LOI)

The limiting oxygen index represents the percentage of oxygen present to support combustion of the plastic, therefore the higher the LOI the lower the flammability. Any material with LOI value of less than 21 will probably burn in an open-air situation. Values of LOI greater than 21 mean that the composites do not burn immediately in air [30-31].

To register the LOI values, the composite samples were trapped in a vertical glass column fed with a slow stream of oxygen/nitrogen mixture. The samples were ignited with a flame and burned downward. These results are shown in Figure 6. Calcium carbonate cannot be considered a flame-retardant agent, but it acts as a radical scavenger during the ignition and prevents the reaction between PVC molecules and oxygen [16]. The plasticiser 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 plasticiser.

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 %.
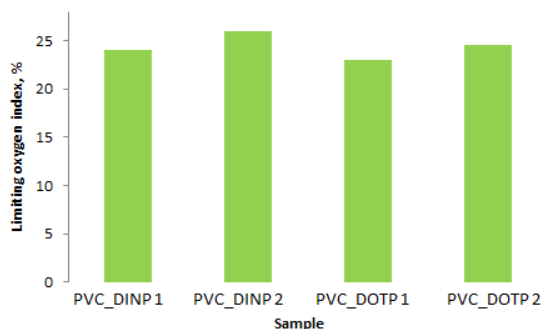

Fig. 6 LOI values for PVC composites

Scanning electronic microscopy (SEM)

The final study regarding the PVC samples is the morphology of the composites. As it can be seen from the micrographs in Figure 7, that the samples passed twice through the extruder are more homogenous.
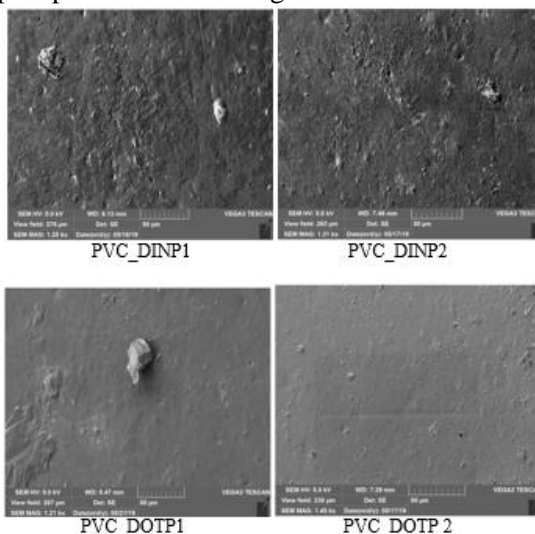

Fig. 7. SEM analysis for PVC composites

The raw materials are mixed better, and the particle agglomerations are avoided. Samples with one pass through the extruder presented macropores and agglomerations. The plasticiser 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.

Conclusions

PVC composites with potential applications in the industry for electrical wires and cables were prepared and characterized. Calcium carbonate with particle size of 2 μm as cheap version of flame-retardant filler was used as reinforcing agent. Further on, the influence of plasticizer was studied using two common commercial plasticizers used in the cable industry, i.e. DINP and DOTP. Both plasticizers have proven to decrease the T_g value of PVC and also to deliver adequate properties for the final products. The thermal, mechanical and flame-retardant properties of the PVC composites presented similar improvements when the material was passed twice through the extruder. Yet, a significant

increase was observed for the mechanical properties when DOTP was used. Therefore, it can be stated that the optimum formulation of PVC composites for this particular application should be based on DOTP as plasticizer. Plus, the material should definitely 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.

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