

Effect of DEHP/ESO and Ca/Zn ratios on MWD, polyene formation and mechanical properties of plasticized pvc formulations. A study for calcium stearate rich formulations

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1. ABSTRACT.

Two series of plasticized PVC formulations were prepared, containing one of the following di 2-ethyl hexyl phthalate/epoxidized soybean oil ratios (phr/phr): (a) 35/3, (b) 55/3, (c) 45/0 or, (d) 45/6. For each ratio, the following calcium stearate/zinc stearate ratios were considered: (a) 0.6/0.4 or, 0.8/0.2; all formulations were prepared with a total content of stearates of 1.0 phr. The difference between the series was the preheating of stearates (150°C, 90 min) carried out before the dry-blend preparation. Thermal stability characterization was carried out in ribbons obtained by extrusion, determining the changes on: (a) the MWD, (b) the concentrations of polyenes (UV-Visible spectroscopy) and, (c) the mechanical properties.

2. INTRODUCTION.

Unless it is stabilized, the PVC is degraded during processing. Such thermal degradation is the result of a process called “zipper dehydrochlorination”, which generates polyene sequences in polymer chains, which may produce an undesirable color in the material [1]. In addition, since polyenes are highly reactive, they may react to form crosslinked polymer chains [2-4], as well as low molecular weight molecules [1-4]. As a consequence of such secondary reactions, the mechanical behavior and color of formulations [4] may be importantly modified. It is generally accepted that stabilizers may react with labile chlorine atoms in PVC chains (preventing further dehydrochlorination) and/or react with the HCl generated by the degradation process (which accelerates the thermal degradation of PVC) [1,5]. An undesirable effect of the stabilizing action of zinc stearate (ZnSt_2) is the ZnCl_2 production, which can promote a sudden dehydrochlorination of PVC [1, 6]. However, it has been claimed that such sudden dehydrochlorination occurs only after the ZnCl_2 concentration reach a certain level [7], and that ZnCl_2 is consumed in such processes [6]. Conversely, CaCl_2 does not promote sudden dehydrochlorination [6]. It has been experimentally demonstrated that, formulations prepared with mixtures of Zn and Ca carboxylates show a synergistic stabilizing action [14-27]. In fact, it has been reported that calcium carboxylates act as ester-exchangers with ZnCl_2 [8,9]. Besides, Thomas [9] suggested that, when enough calcium

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stearate (CaSt_2) is present in the system, ZnCl_2 formation is prevented. It has also been reported that mixtures of CaSt_2 and ZnSt_2 are able to form a complex through heating [10,11]. However, there are controversial evidences regarding to the efficiency of the formed complex to react with allylic chlorine atoms in PVC chains. Epoxidized compounds are recognized as HCl scavengers [1, 12, 13]. However, it has also been proposed that epoxidized soybean oil (ESO) participates in other stabilization reactions, where it reacts simultaneously with HCl and zinc stearate (“free” or complexed) [13]. Besides, in the catalytic presence of ZnCl_2 , epoxidized compounds react with such chloride to produce a chemical compound that is able to remove allylic chlorine atoms in PVC chains through an etherification reaction [1]. Finally, Benavides et al. [14] showed that, in some cases, the preheating of stearates can produce an improvement on the formulation thermal stability. In two previous papers [15, 16], certain characterization for this work materials was included; specifically, the HCl evolving and the color evolution were measured. At those circumstances, the measurements related to the changes that the degradation process produce on the mechanical properties, MWD, and concentration of polyenes are here reported. The mechanistic proposals in this work included, have been supported considering, in an integral way, all the experimental results.

3. EXPERIMENTAL.

To analyze the effect of the preheating of stearates on the thermal stability of compounds, they were characterized two series of 8 compounds. The first one was formulated using non-preheated stearates (NPH formulations) [16] and the other one was prepared with stearates preheated at 150°C during 90 min (PH formulations) [15]. In both series, formulations with the following DEHP/ESO ratios (phr/phr) were considered: (a) 35/3, (b) 55/3, (c) 45/0 and, (e) 45/6. For each one of the DEHP/ESO ratios, a $\text{CaSt}_2/\text{ZnSt}_2$ ratio (phr/ phr) of 0.8/0.2, or 0.6/0.4 was used; for all formulations the total content of stearates was 1.0 phr. The formulations were prepared as follows [15,16]: (a) manually premixing the required amount of stearates (previously preheated or not), (b) dry blending the components, (c) pelletizing the dry-blend using a twin-screw extruder (Leistritz 276L/32D) and, (d) extruding the pellets to obtain samples with ribbon geometry. The post-processing thermal stability under drastic conditions was followed determining the changes on: (a) the MWD (gel permeation chromatography), (b) the concentrations of polyenes (UV-Visible spectroscopy) and, (c) the mechanical properties (Universal Testing Machine).

4. RESULTS.

Analyzing the results showed in Figure 1, it is possible to appreciate that the addition of ZnSt_2 to the system promoted a slight increase on decay rate of the Young modulus during the degradation process ($X_{\text{CaSt}_2}=1.0$ vs. $X_{\text{CaSt}_2}=0.8$). Besides, it is possible to affirm that for the system with $X_{\text{CaSt}_2}=0.6$ the curves have similar trend, which magnitude is a function of the formulation composition and degradation temperature. For both DEHP/ESO ratio formulations, it can be seen that there is a slight improvement of the thermal stability as the relative amount of CaSt_2 increases when the degradation is carried out at 120°C . However, the stability is strongly affected by the formulation composition when the degradation is carried out at 150°C (for formulations 45/6 there is an improvement and for 45/0 there is deterioration). This complex behavior is a consequence of the balance between the mechanical effects produced by the chain-breaking and branching reactions.

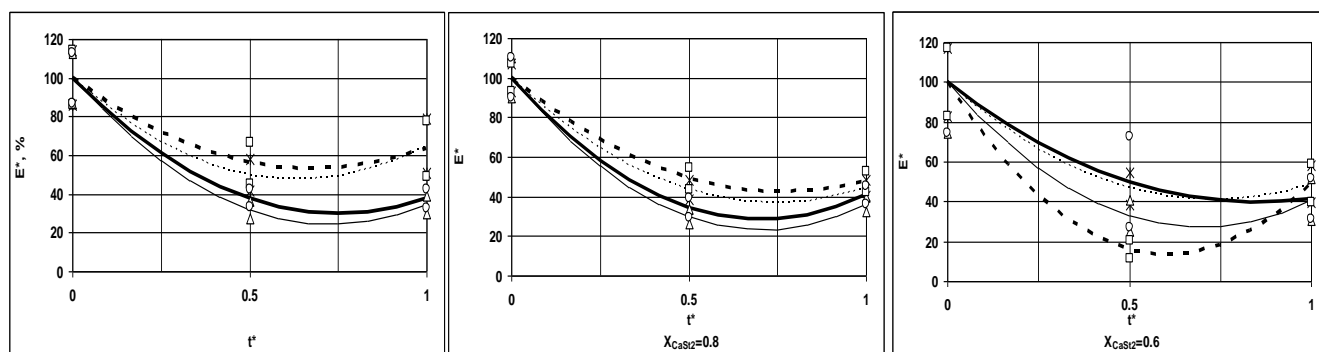


Figure 1. Experimental data (error range) and tendency curves for E^* ($=100 E/E_0$) vs t^* ($= t/t_{\max}$, for $T=120^\circ\text{C}$, $t_{\max}=24$ h, and for $T=150^\circ\text{C}$, $t_{\max}=4$ h), corresponding to the following non preheated formulations: a) 45/0 (120°C : \triangle ; 150°C : \square ; 120°C : —; 150°C : - - -) and, b) 45/6 (120°C : \triangle ; 150°C : \square ; 120°C : —; 150°C : - - -).

Table 1 shows the rate of change of the ultimate stress and the elongation at break for both DEHP/ESO ratios. In such table, it is possible to appreciate that the rate of change of ultimate stress of formulations prepared with a $X_{\text{CaSt}_2}=0.8$ is similar to the one presented by formulations which only contain CaSt_2 (slight modifications of the property). For formulations prepared with a $X_{\text{CaSt}_2}=0.6$ there is a larger decay rate compared with the other two formulations. However, for all formulations there is not an appreciable effect by the presence of ESO. Finally, when the rate of change on elongation at break is analyzed, it is possible to affirm that there is a notably effect (rate of change increases) by the ESO presence in the formulations prepared only with CaSt_2 , and

it seems that is reduced in formulations prepared with a $X_{CaSt_2}=0.6$ or 0.8. Moreover, it can be observed that most stable formulation is the one prepared with a $X_{CaSt_2}=0.6$.

Table 1. Mechanical parameters for non preheated formulations rich in $CaSt_2$

	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h
DEHP/ESO	$X_{CaSt2}=1.0$		$X_{CaSt2}=0.8$		$X_{CaSt2}=0.6$	
	$120^{\circ}C$					
45/0	-0.8	0.2	-0.3	1.9	-0.9	0.6
45/6	-0.7	2.7	-0.9	1.7	-1.0	1.0
	$150^{\circ}C$					
45/0	-3.5	5.3	-3.4	9.3	-7.2	3.0
45/6	-4.2	14.0	-1.9	8.0	-6.7	4.4

5. REFERENCES

- (1) Bacaloglu, R; Fisch, MH. *PVC stabilizers*. In: Zweifel H, ed. *Plastics Additives Handbook*. 5th ed. Munich: Hanser; **2001** ch. 3.
- (2) Tudos, F; Kelen, T; Nagy, TT; Turcsanyi, B. *Pure Appl Chem* **1974**, 38, 201.
- (3) Kelen T. *J Macromol Sci Chem* **1978**, A12, 349.
- (4) Lattimer, RP; Kroenke, WJ *J Appl Polym Sci* **1980**, 25, 101.
- (5) Hjertberg, T; Sörvik, EM. *J Appl Polym Sci* **1978**, 22, 2415.
- (6) Owen, ED; Msayib, KJ *J Appl Polym Sci Part A Polym Chem* **1989**, 27, 399.
- (7) Baltacioglu H; Balköse D. *J Appl Polym Sci* **1999**, 74, 2488.
- (8) Abbas, KB, Sorvik, E. *J Vinyl Addit Technol* **1980**, 2, 87.
- (9) Thomas, NL *Plast Rubber Compos Process Appl* **1993**, 19, 263.
- (10) Mckensey, MW; Willis, HA; Owen, RC; Michel, A. *Eur Polym J* **1983**, 19, 511.
- (11) Volka, K; Vymazal, Z; Stavek, J; Seidl, V. *Eur Polym J* **1982**, 18, 219.
- (12) Lerke, G; Lerke, I, Szymański, W. *J Appl Polym Sci* **1983**, 28, 519.
- (13) Grossman, RF. *J Vinyl Addit Technol* **1993**, 15, 25.
- (14) Benavides, R; Edge, M; Allen, NS; Shah, M *Polym Degrad Stab* **1997**, 57, 25.
- (15) González-Ortiz, LJ; Arellano, M; Jasso, CF; Mendizábal, E; Sánchez-Peña MJ. *Polym Degrad Stab* **2005**, 90, 154.
- (16) González-Ortiz, LJ; Arellano, M; Sánchez-Peña, MJ; Mendizábal, E; Jasso-Gastinel, CF. *Polym Degrad Stab* **2006**, 91, 2715

6. ACKNOWLEDGEMENTS

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