Effect of Di(2-ethyl hexyl phthalate)/Epoxidized Soybean Oil and Calcium Stearate/Zinc Stearate Ratios on the Tensile Properties of Plasticized PVC Formulations. A Study for Calcium Stearate Rich Formulations

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Summary: 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 (phr/phr) were considered: (a) 0.6/0.4, (b) 0.8/0.2 or, (c) 1.0/0.0; all formulations were prepared with a total content of stearate(s) 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. The changes of tensile properties produced by the degradation process were measured in ribbons obtained by extrusion.

Keywords: calcium stearate; degradation; mechanical properties; plasticized PVC; zinc stearate

Introduction

Unless it is stabilized, PVC is degraded during processing. Such thermal degradation is the result of a process called "zipper dehydrochlorination", which generates polyene sequences in polymer chains that may produce an undesirable color in the material.[1] In addition, since polyenes are highly reactive, they may react to form crosslinked polymer chains,[1–3] as well as low molecular weight molecules.[1–4] As a consequence of such secondary reactions, the mechanical behavior and the color of the formulations[1] 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] Strong basic carboxylates (e.g. K, Ca or Ba) that have a weak or no Lewis acidity are mostly HCl scavengers (secondary stabilizers)[1] and, Zn and Cd carboxylates, which have a stronger Lewis acidity, are able to scavenge HCl and react with labile chlorine atoms.[1] An undesirable effect of the stabilizing action of zinc stearate ($ZnSt_2$) is the production of $ZnCl_2$, which can promote the sudden dehydrochlorination of PVC chains.[1,6–8] However, it has been claimed that such sudden process occurs only after the $ZnCl_2$ concentration reaches a certain level[7–8]; in such process, $ZnCl_2$ is consumed.[6] $ZnCl_2$ is able to accelerate the rate of crosslinking and, since crosslinked molecules can be cleaved in a subsequent reaction, the chain scission reactions are indirectly accelerated.[9] Conversely, $CaCl_2$ does not promote sudden dehydrochlorination.[6] Besides, it has been experimentally demonstrated that, formulations prepared with mixtures of Zn and Ca carboxylates show a synergistic stabilizing action.[8,10–19]

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In fact, it has been reported that calcium carboxylates act as ester-exchangers with $ZnCl_2$.[8,10–12] Besides, Thomas[12] suggested that $ZnCl_2$ formation is prevented, when enough calcium stearate ($CaSt_2$) is present in the system. It has also been reported that mixtures of $CaSt_2$ and $ZnSt_2$ are able to form a complex through heating.[10,13–16] However, there is controversial evidence regarding the efficiency of the formed complex to react with allylic chlorine atoms in PVC chains.[10,13–16] Nevertheless, Benavides et al.[15–16] showed that, in some cases, the preheating of stearates can improve the thermal stability of a given formulation. Epoxidized compounds are recognized as HCl scavengers.[1,17–18] 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).[18] 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] In two previous papers,[19,20] two series of materials (the first one used preheated stearates[19] and the second one used non-preheated stearates[20]) were characterized, measuring the HCl evolved by pellets heated at 170 °C and the color evolution of ribbons heated at 175 °C, as well as the stress-strain behavior of the materials without post-processing. To extend the characterization of the materials considered in such studies, in this paper some of these formulations were processed again to obtain ribbons, by using the same preparation procedure described in these studies.[19,20] The newly processed samples were heated at 120 °C or 150 °C, and characterized by measuring the changes on the tensile properties produced by the degradation process.

Experimental Part

PVC resin from Policyd S.A. de C.V (Vinycel G-30; K-Fikenstcher value of 70) was used to prepare the compounds. Di (2-ethyl hexyl phthalate) (DEHP; purity of 99.5%) was purchased from Síntesis Orgánicas S.A. de C.V. ESO was acquired from Resinas y Materiales S.A. de C.V (Pantopox; oxirane number 6.95% oxygen). Finally, calcium stearate (CaO essay 9.0–10.5%) and zinc stearate (ZnO essay 12.5–14%) were purchased from Jalmek.

To analyze the effect of the preheating of stearates on the thermal stability of compounds, two series of 12 compounds were characterized. The first series was formulated using non-preheated stearates (NPH formulations) and the other one was prepared with stearates preheated at 150 °C during 90 min (PH formulations). To study the composition effect, 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 $CaSt_2$/$ZnSt_2$ ratio (phr/ phr) of 1.0/0.0, 0.8/0.2, or, 0.6/0.4 was used; in all formulations the total content of stearates was 1.0 phr. The samples to be post-processed were prepared as follows[19,20]: (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 in the above extruder to obtain samples with ribbon geometry. To degrade the samples, they were heated at 120 ± 5 °C (12 or 24 h) or, 150 ± 5 °C (2 or 4 h). The post-processing thermal stability was followed determining the changes on the stress-strain behavior of degraded samples; measurements were carried out in a Universal Testing Machine from United (SFM10), considering the following test conditions: room temperature, type II specimens and, cross-head speed of 50 mm/min.

Results

The stress-strain curves showed a monotonic increase of stress with deformation;

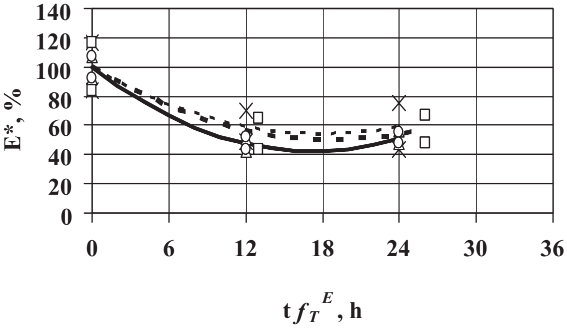
therefore, its behavior was represented by its Young modulus (E), ultimate stress (σ) and deformation at break (ε). To evaluate the modifications on the tensile properties that were produced by the heating, the following normalized properties were defined: a) normalized modulus ($E^*(t) = 100\ E(t)/E(0)$), b) normalized ultimate stress ($\sigma^*(t) = 100\ \sigma(t)/\sigma(0)$) and, normalized deformation at break ($\varepsilon^*(t) = 100\ \varepsilon(t)/\varepsilon(0)$); the degradation time is indicated in parentheses. The use of such normalized variables allowed separating the plasticizing effects of the DEHP and the ESO from their stabilizing effects. For each set formulation-degradation temperature-time (i.e. Formulation A-150 °C-2 h), four samples were characterized, therefore, a set of 16 values was calculated for each normalized property; each set was represented by the extreme values of the error range, defined as its average value ± its standard deviation. Finally, to evaluate the effect of the degradation temperature in the normalized properties, shifting thermal factors (f_T^j, where j is one of the following: E, σ or, ε) were defined, which represent how many times the degradation process was faster at a temperature T, compared to the process carried out at 120°C (note that $f_{120}^j \equiv 1$); such factors were obtained by a curve fitting procedure, where the difference between the trend curves corresponding to a given tensile parameter (E^*, σ^* or, ε^*) and formulation were minimized.

DEHP Effect on NPH Formulations

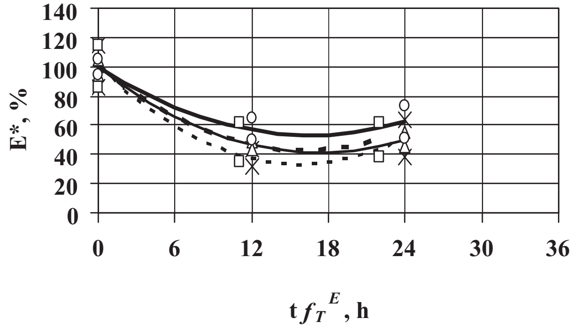
The respective evolutions of E^* as a function of "scale time" (tf_T^E), were fitted by the quadratic functions showed in Figure 1. This figure shows that, in general terms, all formulations behave in a similar way, showing an important decrease of the E^* value in the initial part of the process (approximately one half of the initial value), followed by a slight recovery of the E^* value in the second part of the heating process. Additionally, it is possible to observe that the differences in the evolution of E^* produced by the different DEHP content cannot be quantitatively evaluated (due to the involved experimental error); however, it is clear that they are not significant. Finally, the accelerating effect of the temperature on the degradation process was estimated considering the different values of f_{150}^E presented in Figure 1, which in all cases were close to 6 ($5 < f_{150}^E < 6.5$).

The time evolution of the ultimate properties of formulations 35/3 and 55/3 were fitted by a straight line, therefore, in Table 1 the values of $d\sigma^*/dt$ and $d\varepsilon^*/dt$ are presented. For formulations considered in this section, the difference between the extreme points of the error range for σ^* (L_σ^*) was 20%, on average. Therefore, modifications on $\sigma^* < 20\%$ were not considered significant; that is equivalent to changes on $d\sigma^*/dt < 0.8$ at 120 °C or, changes on $d\sigma^*/dt < 5.0$ at 150 °C. Therefore, it is possible to affirm that, within the experimental conditions considered, the DEHP content has an effect that cannot be quantitatively measured, however, it is clear that, from the aqualitative point of view, the effect is small.

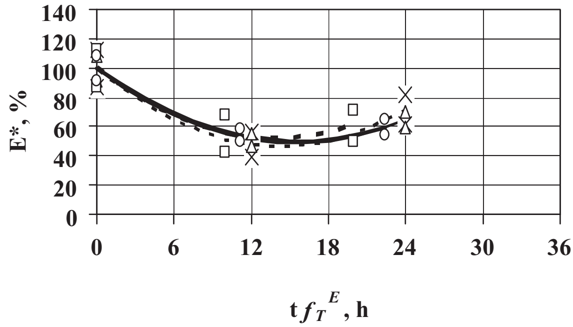
Analyzing the evolution of ε^* on the formulations without $ZnSt_2$ ($X_{CaSt2} = 1.0$), it is clear that the DEHP content does not have an effect on $d\varepsilon^*/dt$; in fact, the modifications produced by the degradation processes in the values of ε^* fall within the experimental error ($L_\varepsilon^* \sim 20\%$). On the other hand, formulations containing $ZnSt_2$ show a behavior depending on the X_{CaSt2}; in the formulation prepared with an $X_{CaSt2} = 0.8$, the $d\varepsilon^*/dt$ decreases as the DEHP content increases, while the formulation prepared with $X_{CaSt2} = 0.6$ presents an opposite trend. An integral analysis of such behavior indicates the existence of reactions that produce opposite effects (for example: chain scission and branching reactions), which are modified differently by the temperature increment, when X_{CaSt2} is varied. Regarding the temperature effect, it is clear that the increment of the degradation temperature increases the rate of ε^* modification. Nevertheless, since the variations produced by the degradation process were not significant in most samples, the correspondent



X_{CaSt2}=1.0 f_{150}^E(35/3): 6.5; f_{150}^E(55/3): 6.0



X_{CaSt2}=0.8 f_{150}^E(35/3)=5.5; f_{150}^E(55/3)=6.0



X_{CaSt2}=0.6 f_{150}^E(35/3)=5.0; f_{150}^E(55/3)=5.6

Figure 1.

Extreme values of error range and trend curves for E* vs t f_T (the f_{150} values are shown in the figure), corresponding to non-preheated formulations prepared with the following DEHP/ESO ratios (phr/phr): 35/3 (120 °C: ×; - - - 150 °C: □; ▬ ▬) and, 55/3 (120 °C: △; —— 150 °C:○; ▬) and different X_{CaSt2}.

shifting thermal factor was not evaluated for formulations considered in this section.

To qualitatively understand the observed trends, it must be considered that the modifications on the mechanical behavior of the different materials produced by the heating process are a complex function of the following factors:

a) A decrement in the DEHP and ESO content in the sample, as a consequence of the evolving of such components

Table 1.
Mechanical parameters required to analyze the DEHP effect in non-preheated formulations.

DEHP/*ESO*	T_{deg}: 120 °C		T_{deg}: 150 °C	
	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h
		$X_{CaSt2} = 1.0$		
35/3	−0.7	0.1	−2.3	3.6
55/3	−1.1	0.1	−5.1	4.0
		$X_{CaSt2} = 0.8$		
35/3	−0.5	1.4	−1.8	9.0
55/3	−0.8	0.6	−3.6	1.0
		$X_{CaSt2} = 0.6$		
35/3	−0.7	−0.7	−6.8	−5.1
55/3	−1.1	0.0	−1.8	10.2

during the heating process[21]; evidently, this favors that the degraded sample shows higher values of modulus and ultimate strength, as well as lower values of deformation at break.[22]

b) Modification of molecular weight distribution, which is produced by the chain scission reactions[3,5,11] (which produce a decrement in E and σ, and an increment of ε[23]) and the chain branching reactions (which produce the opposite effect[23]) occurring simultaneously during the heating process.

c) Decrease of the magnitude of intermolecular interactions, due to a decrement in the global polarity of the system, which occurred as a consequence of the elimination of many C-Cl polar bonds; this produces a softening of the material.[24]

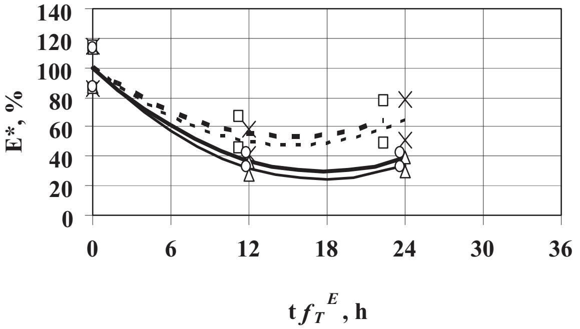
d) Modification of the rigidity of the polymeric chains, as a consequence of the formation in some chain sections of conjugated double bonds, and the decrement in the steric hindrances produced by the elimination of chlorine atoms.[25]

Considering the above factors, it is clear that a more in depth explanation of the observed trends requires additional experimental data, which will be presented in a future study.[26] Nevertheless, it is clear that the trends reported can be used to design an industrial type PVC plasticized formulation useful in an application where the mechanical performance is critical.

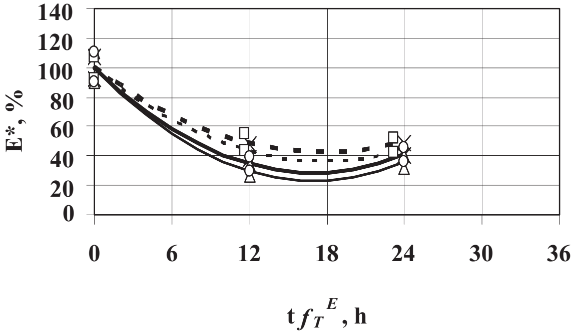
ESO Effect on NPH Formulations

The changes of E^* were also fitted by means of the quadratic functions (Figure 2). Such figure shows that, in general terms, all formulations show a drastic decrement of the E^* value during the initial part of the heating process (values lower than one half of its initial value were obtained), followed by a slight recovery in the second part of the process. In general, the formulations containing ESO showed a larger decay on E^* than formulations prepared without such component; this effect decreased as the relative content of $ZnSt_2$ increased. Regarding the temperature effect, it can be mentioned that the values of f_{150}^{E} indicated in Figure 2 are close to 6 ($4.9 < f_{150}^{E} < 7.4$), especially those corresponding to formulations with a high $CaSt_2$ content ($X_{CaSt2} = 1.0$ or, 0.8).

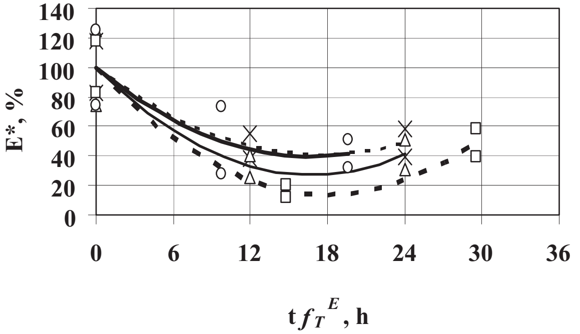
For the formulations analyzed in this section, the average value of $L_{\sigma}{}^*$ was 15%; this value was used as a reference to assign a statistically distinguishable difference. Thus, by a comparative analysis of the values of $d\sigma^*/dt$ shown in Table 2, it is possible to affirm that the presence of ESO in the formulations does not produce distinguishable differences in the changes produced on σ^* by the degradation process. In fact, with the exception of the formulations prepared with $X_{CaSt2} = 0.6$ that showed a moderate change of σ^*, the rest of formulations presented changes that, in general terms, fell within the experimental error. Since the σ^* values were slightly modified by the heating process, it was not



X_{CaSt2}=1.0 f_{150}^{E}(45/0): 5.6; f_{150}^{E}(45/6): 5.9



X_{CaSt2}=0.8 f_{150}^{E}(45/0)=5.8; f_{150}^{E}(45/6)=6.0



X_{CaSt2}=0.6 f_{150}^{E}(45/0)=7.4; f_{150}^{E}(45/6)=4.9

Figure 2.

Extreme values of error range and trend curves for E^* vs t f_T (the f_{150} values are shown in the figure), corresponding to non-preheated formulations prepared with the following DEHP/ESO ratios (phr/phr): 45/0 (120 °C: ×; - - - 150 °C: □; ▬ ▬) and, 45/6 (120 °C: △; —— 150 °C:○; ▬) and different X_{CaSt2}.

possible to adequately estimate the correspondent f_{150}^{σ} factor.

On the other hand, in most of the samples, the heating process produced a significant increase of the value of the deformation at break. In the formulations containing $ZnSt_2$, the $d\varepsilon^*/dt$ value was not modified by the ESO presence in the system. However, in the

Table 2.
Mechanical parameters required to analyze the ESO effect in non-preheated formulations.

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

formulations lacking such stearate, the presence of ESO produced a drastic increment in the $d\varepsilon^*/dt$ value, which was in agreement with the larger modulus decay shown by such formulations. Both effects can be partially explained as a consequence of the increment on the relative importance of the chain scission reactions, promoted by the presence of ESO. In this case, although the experimental error partially masked the modifications produced by the heating process on ε^*, the f_{150}^{ε} factors were roughly estimated close to 5.

DEHP Effect on PH Formulations

As in the equivalent NPH formulations, in the systems considered in this section (Figure 3), the heating process produced an initial decay on their modulus (to a value slightly lower than one half of their respective initial values), followed by a slight recovery as the degradation process continued. Figure 3 also shows that the DEHP content does not produce important changes on the evolution of E^* with the "scale time". Besides, in general terms, the differences among equivalent formulations prepared with different X_{CaSt2} are not statistically significant. Regarding the degradation temperature effect, the f_{150}^{E} factors for formulations 55/3 were very close to 6, and they were practically independent of the relative content of $CaSt_2$; similar circumstances occurred to the equivalent NPH formulations. However, for formulations 35/3, the shifting thermal factor presented a slight inverse dependence on the $CaSt_2$ content, showing values between 5.7 and 8.1. The equivalent NPH formulations showed the opposite trend, with extreme values of 5.0 and 6.5. Regarding the effect of the preheating of stearates, it is possible to notice that, in general terms, such preheating produced a slight improvement in thermal stability evaluated by the changes in E^*.

To analyze the ultimate properties, the data shown in Table 3 and the following experimental errors: $L_\sigma = 15\%$ and $L_\varepsilon = 23\%$ are required. This table shows that, the DEHP content does not produce important differences on the values of $d\sigma^*/dt$. Besides, it can also be observed that only slight changes on σ^* are produced by the degradation process, therefore, the corresponding f_{150}^{σ} factors are not proposed. In the formulations considered here, the preheating of stearates does not produce significant changes on the $d\sigma^*/dt$ values.

An analysis of the data shown Table 3 allowed to affirm that, the increase in the DEHP content produced an increment in the $d\varepsilon^*/dt$ value. Since only slight modifications of ε^* were produced by the heating process on 35/3 formulations, the f_{150}^{ε} factors were not estimated. Nevertheless, the higher modifications produced on 55/3 formulations allowed to roughly estimate that the f_{150}^{ε} factor increased as the X_{CaSt2} decreased ($4 < f_{150}^{\varepsilon} < 7$). In formulations 55/

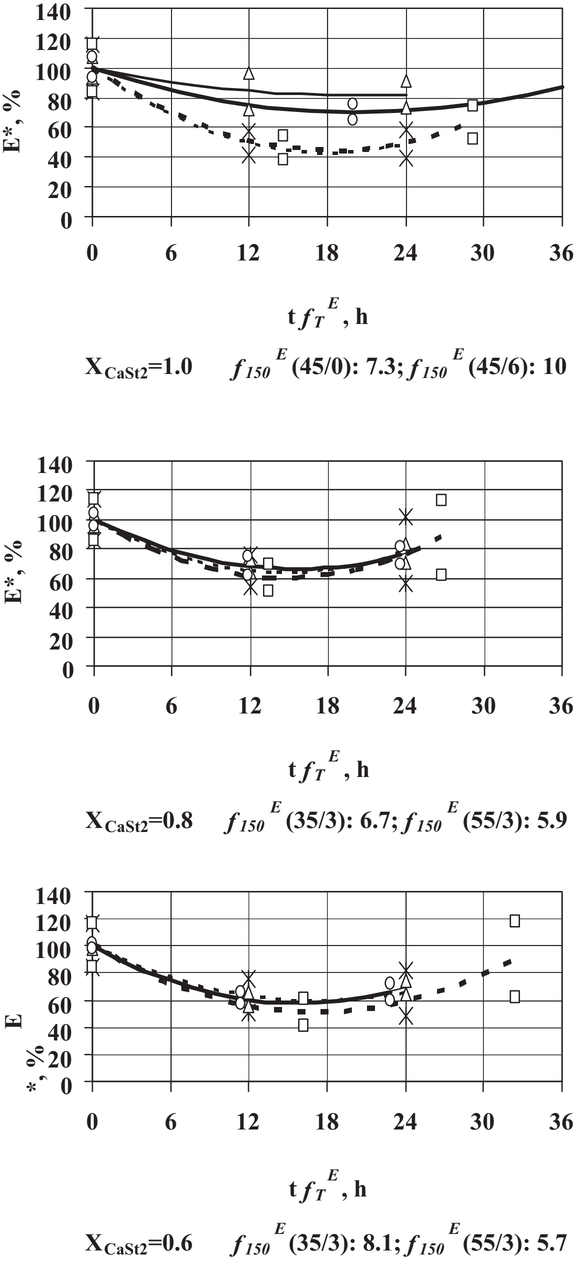


Figure 3.

Extreme values of error range and trend curves for E* vs t f_T (the f_{150} values are shown in the figure), corresponding to preheated formulations prepared with the following DEHP/ESO ratios (phr/phr): 35/3 (120 °C: ×; - - - 150 °C: □; ▬ ▬) and, 55/3 (120 °C: △; —— 150 °C:○; ▬) and different X_{CaSt2}.

3, the preheating of stearates produced less stable formulations, that is, formulations where the rate of change of ε^* was faster. However, the 35/3 formulations showed a behavior that was dependent on X_{CaSt2} (for $X_{CaSt2} = 1.0$, there were no important changes and, for $X_{CaSt2} = 0.8$ or 0.6, the preheating enhanced the stability).

Table 3.
Mechanical parameters required to analyze the DEHP effect in preheated formulations.

DEHP/ESO	T_{deg}: 120 °C		T_{deg}: 150 °C	
	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h
		$X_{CaSt2} = 1.0$		
35/3	−0.3	0.9	−3.6	2.8
55/3	−0.4	1.9	−5.2	7.4
		$X_{CaSt2} = 0.8$		
35/3	−0.2	0.5	−3.3	3.4
55/3	−0.5	1.4	−3.1	8.0
		$X_{CaSt2} = 0.6$		
35/3	−0.9	−0.2	−3.0	2.2
55/3	−0.9	1.0	−5.5	6.9

ESO Effect on PH Formulations

The values of E^* and the quadratic trend curves corresponding to PH formulations 45/0 and 45/6 are shown in Figure 4. In this figure it can be clearly appreciated that the most stable formulations contained ESO; the highest stability enhancement was produced in formulations prepared with an $X_{CaSt2} = 0.8$, which showed a modulus increment from the beginning of the isothermal heating. To analyze the X_{CaSt2} effect, it is possible to appreciate that the equivalent formulations prepared with an $X_{CaSt2} = 1.0$ or 0.6 showed a similar behavior among them. In addition, among all formulations considered in this section, the formulation lacking in ESO prepared with an $X_{CaSt2} = 0.8$ showed the worst modulus stability, while the equivalent 45/6 formulation showed the best stability. Concerning the degradation temperature effect, it is possible to affirm that formulations containing $ZnSt_2$ showed values of f^E_{150} slightly smaller ($6.5 < f^E_{150} \leq 7.3$) than the ones showed by formulations lacking such component ($f^E_{150} \geq 7.3$). Besides, in Figure 4 it is possible to observe that the preheating of stearates produced a notable enhancement in the thermal stability (evaluated considering modulus data) of the formulations containing ESO. However, in formulations lacking ESO, the preheating did not produce important changes in the thermal stability.

The analysis of the trends regarding the ultimate properties can be carried out considering the results shown in Table 4 and the following experimental error values: L_σ: 14% y L_ε: 21%. This table shows that the presence of ESO in the system does not have a significant effect on the rate of change of σ^*. Since all formulations are highly stable, the f^σ_{150} factor cannot be adequately estimated. In formulations with a high content of $CaSt_2$ ($X_{CaSt2} = 1.0$ or, 0.8), the preheating of stearates does not have an important effect on the $d\sigma^*/dt$ values. However, in both formulations prepared with an $X_{CaSt2} = 0.6$, the preheating produces a slight improvement in the thermal stability.

From the rate of change on ε^* shown in Table 4, it is possible to affirm that its behavior is notably dependent on the X_{CaSt2} in the system. Thus, on the formulations lacking $ZnSt_2$, the isothermal heating process produced non-significant increments in the ε^* values and, therefore, the ESO content effect on their thermal stabilities was negligible. In the case of formulations prepared with an $X_{CaSt2} = 0.8$, the ESO content had a slight stabilizing effect; in 45/6 formulation the increments on ε^* produced by the degradation process were negligible, whereas in the 45/0 formulation such increments were statistically significant. Finally, in the case of formulations with a lower relative content of $CaSt_2$ ($X_{CaSt2} = 0.6$), the degradation process produced important changes on the ε^* values; however, these changes were independent of the ESO content. Concerning the preheating of stearates, in the formula-

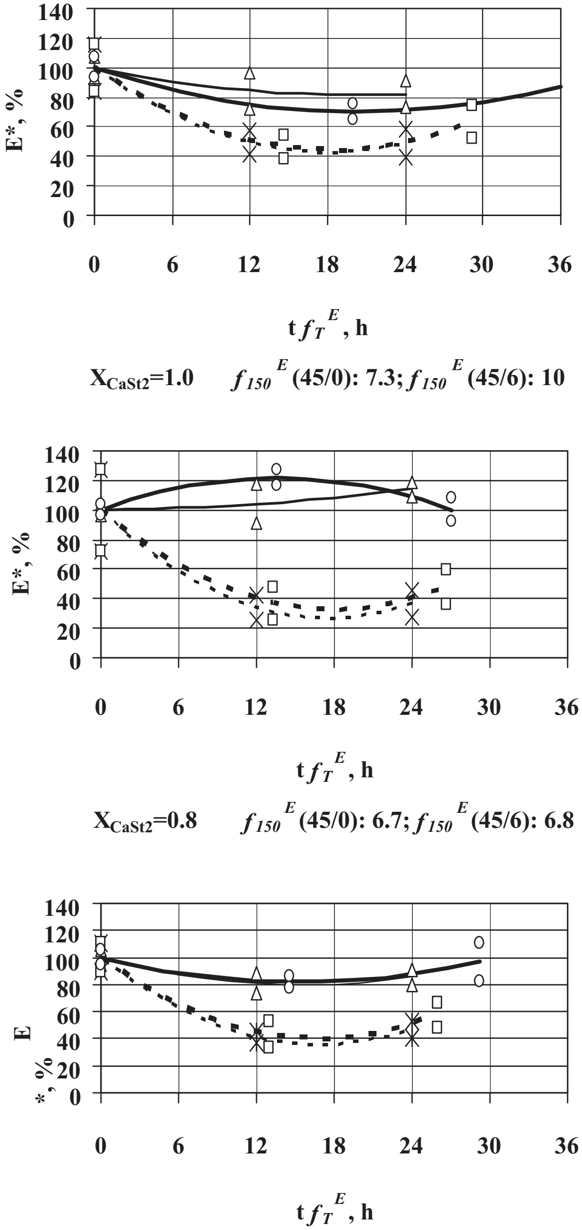


Figure 4.

Extreme values of error range and trend curves for E^* vs t f_T (the f_{150} values are shown in the figure), corresponding to preheated formulations prepared with the following DEHP/ESO ratios (phr/phr): 45/0 (120 °C: ×; - - - 150 °C: □; ▬ ▬) and, 45/6 (120 °C: △; —— 150 °C:○; ▬) and different X_{CaSt2}.

tions with high $CaSt_2$ content ($X_{CaSt2} = 1.0$ or, 0.8) and lacking ESO, the preheating did not produce significant changes on the values of $d\varepsilon^*/dt$; however, in the formulations containing ESO, the preheating produced an enhancement in their thermal stabilities. In addition, both formulations prepared with an $X_{CaSt2} = 0.6$ decreased

Table 4.
Mechanical parameters required to analyze the ESO effect in preheated formulations.

DEHP/*ESO*	T_{deg}: 120 °C		T_{deg}: 150 °C	
	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h	$d\sigma^*/dt$, %/h	$d\varepsilon^*/dt$, %/h
	$X_{CaSt2} = 1.0$			
45/0	−1.0	0.5	−4.9	1.5
45/6	−0.7	0.7	−4.4	1.5
	$X_{CaSt2} = 0.8$			
45/0	−0.7	1.7	−5.0	6.4
45/6	−0.7	0.0	−4.5	2.3
	$X_{CaSt2} = 0.6$			
45/0	−0.5	1.3	−0.6	10.1
45/6	−0.4	1.8	−2.6	9.1

their thermal stabilities as a consequence of the preheating.

Conclusions

The following statements arise from the results:

- The DEPH content produced important changes only in the evolution of ε^*; in NPH formulations the changes were dependent on the X_{CaSt2}, however, in all analyzed PH formulations, the increment in the DEHP content produced a decrement in the thermal stability of ε^*.
- For formulations 35/3 and 55/3, the preheating of stearates allowed to obtain a slight enhancement in the thermal stability evaluated by the changes in E^* and produced non-significant changes in the σ^* evolution. In addition, the changes produced by the preheating on ε^* were dependent on the DEHP content.
- In the NPH formulations, the ESO presence produced a slight decrement in the thermal stability evaluated by the changes in E^*; however, in PH formulations, the presence of such component was highly beneficial. Additionally, in general terms, the ESO content did not produce important changes in the evolution of the normalized ultimate properties.
- In formulations 45/0, the changes produced in tensile parameters by the preheating of stearates were dependent on the X_{CaSt2}. However, in formulations 45/6, preheating was highly beneficial for E^*, although, in general terms, it did not produced significant changes in the normalized ultimate properties.
- In most of the formulations, the shifting thermal factors for the normalized modulus were close to 6.

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