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Thermal stabilization and plasticization of poly(vinyl chloride) by ester thiols: Update and current status

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Abstract

Poly(vinyl chloride) (PVC) is one of the most important medical plastics. Recently, however, the safety of flexible PVC containing the common plasticizer, di(2-ethylhexyl) phthalate, has been called into question. Widely used heat stabilizers for PVC that incorporate toxic heavy metals also have fallen into disfavor. In order to address these problems, we have synthesized and tested, as potential replacements, several organic thiols that contain one or more carboxylate ester functions and thus are highly compatible with the polymer. When introduced into PVC at high loading levels (e.g., 30–35 parts by weight), the ester thiols are extremely effective as heat stabilizers and also useful as primary plasticizers. When used at a low loading level (e.g., 3 parts by weight), they still are excellent heat stabilizers for both plasticized and rigid PVC. Importantly, their high potency is achieved in the absence of any costabilizers that incorporate heavy metals. Their syntheses are simple and straightforward, and their odors are not offensive, because their volatilities are low. Described here are some typical results obtained with this new additive technology, which was licensed for commercialization in 2005.

Keywords: Poly(vinyl chloride); PVC; Thermal stabilizers; Plasticizers; Thiols

1. Introduction

Poly(vinyl chloride) (PVC), a very important plastic for medical applications [1], experiences thermal dehydrochlorination that can be prevented by various additives. The mechanisms for the thermal degradation of PVC and its prevention by commercial stabilizers have been discussed in detail in recent reviews [2,3]. Many of the most effective thermal stabilizers for this polymer contain toxic heavy metals, and the safety of certain PVC plasticizers, such as di(2-ethylhexyl) phthalate (DEHP), has become controversial. Thus, it has been highly desirable to replace these adjuvants with others that are at least as effective but are relatively innocuous from the standpoints of safety and health.

Here we present a brief update and status report on an approach to these problems that has proved to be so promising that it was licensed for commercial use in 2005. It involves the incorporation of thiol additives containing carboxylate ester groups. In the past, certain thiols have occasionally been suggested for use in PVC additive packages containing a primary thermal stabilizer that is metal-based. The literature suggests, however, that the beneficial effects of the thiols used thus far in such systems have not been especially large. Our fully organic ester thiols are highly efficacious and do not require admixture with metal-containing stabilizers in order to produce the results desired.

2. Results and discussion

2.1. Synthesis

In general, the ester thiols have relatively simple structures that can be accessed through tactical syntheses that are straightforward and short. The final step of these preparations is acid-promoted esterification. Some prototypical ester thiols are compounds **1–7**, where R = 2-ethylhexyl. The

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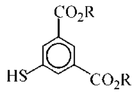

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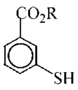

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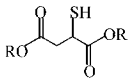

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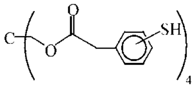

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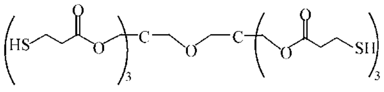

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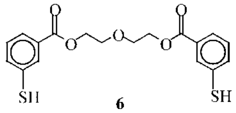

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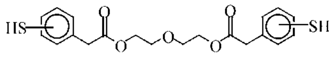

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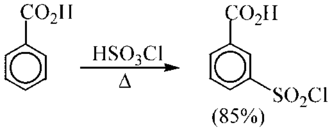
alcohols used to prepare these substances were acquired from commercial suppliers, as were the mercapto acids needed for the synthesis of thiols **3** [4] and **5**. The mercaptobenzoic acid precursor of thiols **2** and **6** was obtained conveniently via reactions (1) and (2) [5,6], while an analogous sequence yielded the mercaptophenylacetic acids that were converted into thiols **4** and **7** [7]. The mercaptoisophthalic acid whose esterification gave thiol **1** was made from the corresponding hydroxy acid by a route that incorporated a Newman–Kwart rearrangement of an intermediate thiocarbamate [4,6–11].



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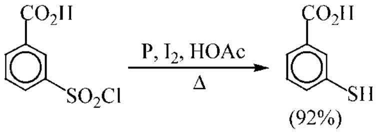

(2)

2.2. *Stabilization and plasticization*

Table 1 compares the behavior of formulations containing thiols **1** and **3** with that of control formulations (C-1 and C-2) in which the plasticizer DEHP and two commercial stabilizers were present. Note that both of these stabilizers are metal-based. The tabulated information shows that when **1** and **3** are introduced at the level of 30–35 phr, they not only are superlative heat stabilizers, but also are potentially useful as primary plasticizers [4,6–11]. Moreover, ester thiols can perform exceptionally well as stabilizers when they are used at a much lower level. This conclusion follows directly from the data in Table 2 for thiols **5**–**7** [6,7].

Information in the tables shows that stabilization by ester thiols may be improved by the introduction of epoxidized soybean oil. This material is thought to function, at least in part, as a scavenger for HCl [12], which acts as an autocatalyst for PVC thermolysis [2,3,12] in a way that is now understood mechanistically to a large extent [13]. Other acid scavengers also may enhance the thermal stability that ester thiols confer. Nevertheless, it is important to emphasize here that these stabilizers can give excellent results in the absence of any metals whatsoever.

Table 1
Stabilization and plasticization of PVC by thiols **1** and **3**

	Formulation (phr)[a]					
	C–1	C–2	A	B	C	D
Ingredient[b]						
DEHP[c]	30.0	30.0				
1			35.0	30.0		
3					35.0	30.0
ESO[d]	5.0	5.0		5.0		5.0
Ba/Zn liquid[e]	3.0					
Dythal/Tribase[f]		4.0				
Test[g]						
Hardness (Shore C)[h]	85/74	86/75	94/85	94/86	80/72	80/73
Sp. gr.[i]	1.27	1.30	1.29	1.29	1.27	1.27
Tens. str.[j] (psi)	3398	3472	3467	3421	3588	3504
Elongation[k] (%)	332	305	281	328	311	342
Dyn. heat stab.[l] (min)	21	60	60	60	>60	>60
Init. yellow[m] (min)	15	10	10	10	15	15
Dec. time[n] (min)	45	>60	>60	>60	50	>60

[a] Parts by weight per hundred parts of PVC.
[b] All formulations also contained 0.1 phr of stearic acid.
[c] Di(2-ethylhexyl) phthalate.
[d] Epoxidized soybean oil.
[e] “General Purpose” commercial stabilizer.
[f] Blend of dibasic lead phthalate and tribasic lead sulfate.
[g] Deviations of replicate values usually were no greater than ca. ±5%.
[h] ASTM D 2240-86.
[i] Specific gravity, ASTM D 792-91.
[j] Tensile strength, ASTM D 638-91.
[k] ASTM D 638-91.
[l] Dynamic heat stability (205 °C, 100 rpm, #5 bowl), ASTM D 2538-95.
[m] Time required for initial yellowing, 210 °C, ASTM D 2115-92.
[n] Oven heat stability, 210 °C, ASTM D 2115-92.

At high temperatures, low levels of our ester thiols also are outstanding as color stabilizers for unplasticized PVC (W. H. Starnes Jr., S. Kim, to be published). Because of their rather high molecular weights, they tend to have low volatilities. For that reason, their odors are not offensive.

Table 2
Stabilization of plasticized PVC by thiols **5**, **6**, and **7**

	Formulation (phr)[a]					
	E	F	G	H	I	J
Ingredient[b]						
5	3.0	3.0				
6			3.0	3.0		
7					3.0	3.0
ESO[c]		5.0		5.0		5.0
Test[d]						
Dyn. heat stab.[e] (min)	41	>60	>60	>60	>60	>60
Init. yellow[f] (min)	10	15	10	10	10	10
Dec. time[g] (min)	40	>60	20	45	25	45

[a] Parts by weight per hundred parts of PVC.
[b] All formulations also contained 30.0 phr of di(2-ethylhexyl) phthalate and 0.1 phr of stearic acid.
[c] Epoxidized soybean oil.
[d] Values shown are from single runs.
[e] Dynamic heat stability (205 °C, 100 rpm, #5 bowl), ASTM D 2538-95.
[f] Time required for initial yellowing, 210 °C, ASTM D 2115-92.
[g] Oven heat stability, 210 °C, ASTM D 2115-92.

2.3. Mechanism of stabilization

A critical aspect of the stabilization by ester thiols is their degree of compatibility with the polymer. The compatibility is enhanced considerably by the ester group(s). Thiols with lower compatibilities are less effective as stabilizers, as is shown, for example, by the failure of 1-dodecanethiol to act as a color stabilizer for PVC at 170 °C [4,6–11].

Experiments with the polymer and model compounds [8–10,14] have indicated that the ester thiols increase stability by displacing halogen from the thermally labile structures in PVC (internal allylic and tertiary chloride segments [2,3,15]), as is shown in Eq. (3). Interestingly, in this

$$\mathrm{RCl} + \mathrm{R'SH} \rightarrow \mathrm{RSR'} + \mathrm{HCl} \qquad (3)$$

process, aryl ester thiol **2** is more reactive than completely aliphatic thiols, an unexpected observation that can perhaps be rationalized by a higher effective concentration of the nucleophile $\mathrm{R'S^-}$ in the case of **2** [14]. Electrophilic catalysis of C–Cl ionization by R′SH might also be a contributing factor. However, at present, its role seems likely to be less important, because the Brønsted acidities of all of the thiols used are very low [14].

Another possible mode of stabilization for which some evidence exists [14] is the addition of ester thiols to alkene double bonds. This reaction can occur by either a free-radical mechanism or an ion-pair pathway involving catalysis by HCl. It may remove color by shortening polyene chromophores, and if it causes the deactivation of allylic chloride structures (as in Eq. (4), for example), it will inhibit polyene growth.

$$-(\mathrm{CH{=}CH})_n\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}- \;+\; \mathrm{R'SH} \longrightarrow -\overset{\mathrm{SR'}}{\overset{|}{\mathrm{C}}}\mathrm{H}(\mathrm{CH{=}CH})_{n-1}\mathrm{CH_2}\overset{\mathrm{Cl}}{\overset{|}{\mathrm{C}}}\mathrm{H}- \qquad (4)$$

Because of the low dissociation energies of S–H bonds, thiols can easily deactivate radicals by hydrogen-atom transfer, as in Eq. (5). For that reason, ester thiols should tend to inhibit

$$\mathrm{R\cdot} + \mathrm{R'SH} \rightarrow \mathrm{RH} + \mathrm{R'S\cdot} \qquad (5)$$

autocatalysis during the thermal dehydrochlorination of PVC, since this catalysis is now known to occur via cation radicals that result from the interaction of HCl with conjugated polyene sequences [13]. Moreover, the neutral polyenyl radicals that are formed during PVC thermolysis [2,3] may also experience reaction (5). However, such radicals do not contribute directly to the degradation autocatalysis [13].

3. Experimental

Details of the synthesis of various ester thiols are disclosed in issued patents [4,6,7,11] or in patents that are pending [16]. Data for stabilization and plasticization by these additives also appear in patents [4,6,7,11,16] and in other references cited above [8–10].

Acknowledgements

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