پایداری دمایی طولانی مدت توسط polyols (طبیعی) در فلزات سنگین بدون روی (Vinyl chloride)

چکیده :

راندمان ثبات گرمایی بلند مدت افزودنی های Polyol در پی وی سی های فلزات سنگین بدون روی مورد بررسی قرار گرفته است.

در تحقیقات نشان داده شده است که پلی اتیلن ها مانند Xylitol و Sorbitol به طور قابل توجهی میزان دی هیدرو کلریده شدن را کاهش می دهند و ارزش های قرمز Congo را بهبود می بخشند.آزمایش های صورت گرفته بر روی PVC مخلوط و پردازش نشده در تخریب حرارتی ۲۰۰ درجه سانتیگراد نشان داده است که به خصوص در PVC های زمینی پردازش نشده Sorbitol تا حد زیادی به مونو و دی آنهیدرودراتیوز ۱ و ۴ تبدیل می شوند.

ظاهرا HCl آزاد شده در طول تخریب حرارتی به عنوان کاتالیزورعمل می کند.

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Long-term heat stabilisation by (natural) polyols in heavy metal- and zinc-free poly(vinyl chloride)

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Abstract

The long-term heat stabilisation efficiency of (natural) polyol additives in heavy metal- and zinc-free poly(vinyl chloride) (PVC) has been investigated. It is shown that polyols, such as sorbitol and xylitol, markedly reduce the dehydrochlorination rate and improve Congo Red values. Extraction experiments on unprocessed and ground-processed PVC-sorbitol (1.0 phr) mixtures after thermal degradation at 200 C revealed that especially in the ground-processed PVC-sorbitol system, sorbitol is partly converted into its mono- and dianhydro-derivatives 1,4-sorbitan and isosorbide, respectively. Apparently, the HCl released during thermal degradation acts as the catalyst. Similar intramolecular cyclodehydration reactions also occur with the natural polyols, erythritol and xylitol, under these conditions. Scrutiny of the measured dehydrochlorination rates and the Congo Red values for ground-processed heavy metal- and zinc-free PVCepolyol mixtures show that in particular polyols containing primary hydroxyl groups exert long-term heat stabilisation and that they act as efficient HCl scavengers.

Keywords: PVC; Additives; Thermal degradation; Stabilisers; Renewable resources; Sorbitol; 1,4-Sorbitan; Isosorbide; Intramolecular cyclodehydration

1. Introduction

In 2000, ca. 5.8 ! 10^6 ton of poly(vinyl chloride) (PVC) was used in Europe [1]. Notwithstanding due to its intrinsic thermal instability, the application of heat stabilisers (additives) is a prerequisite for PVC processing, i.e. under processing conditions HCl will be released from the PVC, which ultimately acts as an auto-catalyst leading to severe discolouration and degradation of the polymer. Of the annual European stabiliser consumption (approximately 1.8 ! 10^5 ton) ca. 70% still consists of lead salts and soaps [2]. Since there is a societal concern with respect to the application of heavy metals, the European PVC industry has made a commitment to phase out the use of lead stabilisers by 2015 [2]. Although alternative stabiliser systems based on tin, calcium/zinc and calcium/organics are already available, they still require further improvement in order to achieve a comparable price/performance. In this context the application of efficient and cost effective long-term co-stabilisers is of interest. For example, the natural polyol, sorbitol, may offer a ‘green’, environmentally benign solution. Sorbitol is an abundant, food-grade and cost-effective polyol that can be readily handled and

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processed. In fact, sorbitol is already applied as an additive for long-term heat stabilisation in heavy metal-stabilised PVC [3,4]. Besides natural polyols synthetic polyols, viz. pentaerythritol, dipentaerythritol and tri-methylolpropane (TMP), are also used [5]. However, they suffer from drawbacks like high costs and unsuit-able melting points for processing.

Here, we wish to report the results of a systematic investigation on the long-term heat stabilisation of (natural) polyol additives in a heavy metal- and zinc-free PVC formulation with varying compositions. The long-term heat stability is assessed using well-established methods [6e18], such as the measurement of dehydro-chlorination (DHC) rates and the determination of Congo Red (CR) values. To gain more detailed insight in the chemical behaviour and fate of the polyol additive after dispersion within a PVC matrix and prolonged thermal treatment at 200 C [19e32], the polyol and its possible reaction products were extracted from the heat-treated unprocessed or ground-processed PVCepolyol mixtures. The product composition of the extracts was established using quantitative ^{13}C NMR spectroscopy.

2. Experimental

2.1. PVC-sample preparation

All experiments were performed with a standardised pre-mix, a so-called ‘‘naked’’ pipe-formulation, which was kindly supplied by Allstab Chemicals (Table 1).

Polyols were added to the pre-mix and mixed manually. For the sample referred to as unprocessed PVCesorbitol mixture the amount of sorbitol added was 1.0 part per 100 parts of resin (1.0 phr).

Ground-processed PVC samples were obtained by processing the pre-mix/polyol mixture (120 g) on a two-roll mill (Schwabenthan Berlin, roll width 22.5 cm, circumference 35 cm, rotation speed front/back: 19/23) at 196 C for 2 min, giving a rigid PVC sheet. These sheets were manually cut into small pieces (2 cm^2), and subsequently ground (Retsch ultra-centrifugal grinder, ZM 100) under cryogenic conditions, using a 3 mm sieve. Approximately 66% of the particles had a particle size smaller than 1.5 mm; they are referred to as ground-processed PVCepolyol mixtures.

Table 1

Composition of the rigid heavy metal- and zinc-free PVC ‘‘naked’’ pipe formulation

Pre-mix: rigid PVC formulation	Parts per hundred resin (phr)
S-PVC (Marvylan S6806, ex-LVM)	100.00
$CaCO_3$ (Omyalite 95T)	2.00
Paraffin wax (drop point 106e112 C)	0.16
Synthetic paraffin (m.p. 73 C)	0.46
LDPE wax (drop point 103e110 C)	0.10

The ground-processed PVCepolyol mixtures either contain various amounts of sorbitol (0.25, 0.50, 1.0 and 1.5 phr, respectively) or, instead of sorbitol, other polyols, such as xylitol, erythritol, 1,4-sorbitan, iso-sorbide, 1,4-galactitan and trimethylolpropane (TMP), respectively) in an amount of 1.0 phr.

2.2. Measurement of the DHC rate

Unprocessed- (10.0 g) or ground-processed PVC samples (5.0 g) were heated at 200 C in a DHC set-up that consisted of a reactor (glass reactor, height 160 mm, and diameter 52 mm) covered with a removable lid containing an N_2 gas inlet (flow rate 20 ml/min using a Brookfield Sho Rate flow meter) and a curved tube for gas exhaust. Before entering the reactor the N_2 gas was first passed through a conc. NaOH solution to remove CO_2 and subsequently through a conc. H_2SO_4 solution to remove remaining traces of water. The reactor was immersed in a silicone oil bath (10 l) with a temperature accuracy !1 C. The exhaust gas from the reactor was collected and transferred to the bottom of a titration cell via a small glass tube containing a porous glass diffuser in order to evenly distribute the gas as small bubbles in the titration cell. The titration cell fitted with an Ag/AgCl pH-electrode (Metrohm) was filled with an aqueous NaOH solution (pH 10). A pH of 10 was chosen to ensure rapid extraction of gaseous HCl from the N_2 gas stream into the magnetically stirred solution in the titration cell. The pH in the titration cell was maintained at pH 10 by automatic titration with a NaOH solution (Titrisol 0.1 M, Merck) using a 718 STAT TITRINO apparatus (Metrohm). Hence, the amount of consumed NaOH is directly related to the amount of released HCl from the sample. Data points were sampled and stored in a PC every 30 s and include time, pH and the amount of NaOH added to the titration cell.

An estimate of the time needed to heat the glass reactor and its contents to 200 C was obtained by applying the Fourier method; a time of ca. 2000 s was found (cf. Appendix), which corresponds to the in-duction period and the onset of the (near) linear part of the DHC rate curve.

2.3. Congo Red measurements

Congo Red (CR) values were determined by transferring ground-processed PVC samples (6.0 g) to a closed test tube, which was heated to 200 C until a strip of CR paper placed at the top of the tube changes colour from blue to red [14]. The time required for the colour change to occur is referred to as the stability time (t_s).

2.4. Extraction procedure

After heat treatment at 200 C for a certain period of time (either in the DHC set-up or in a Werner Mathis oven) the unprocessed as well as ground-processed PVCepolyol mixtures were extracted in order to isolate the polyol and their possible reaction products. The following procedure was used. PVC samples (5.0 g) were suspended in a mixture of cyclohexanone (150 ml) and water (80 ml). The suspension was intensively stirred for 48 h at room temperature. The resulting viscous emulsion that contains highly swollen PVC granules was poured on to a sieve and repeatedly washed with cyclohexanone/water (v/v 2:1). The emulsion was sub-sequently broken by centrifugation (Centaur 2 at 3000 rpm). The water phase was transferred to a sepa-ratory funnel and extensively washed with diethyl ether (2 ! 100 ml). Next, the water layer was separated and concentrated under reduced pressure using a rotary evaporator at 60 C. The product composition of the remaining solid residue was established using quantita-tive ^{13}C NMR spectroscopy (Bruker DPX-300 NMR spectrometer operating at 75.5 MHz and 27 C; solvents $CDCl_3$ and/or DMSO-d_6).

3. Results and discussion

3.1. General

Although polyols already find application as addi-tives in heavy metal-stabilised PVC compounds [3,4], information about the long-term heat stabilising mechanism of polyols in heavy metal- and zinc-free PVC compounds is limited. Hitherto, two possible mecha-nisms have been suggested, e.g. (1) the polyol inhibits degradation by substitution of labile chlorines in the PVC polymer backbone or (2) the polyol acts as an HCl scavenger and therefore suppresses autocatalytic degradation. Since it has been reported that sorbitol does not react with 4-chloro-2-hexene (a PVC model compound) even in the presence of zinc chloride [18,33], a stabilising mechanism by substitution of labile chlorines in the PVC chain is highly unlikely. This is substantiated by the observation that sorbitol exerts a positive effect on the long-term heat stability; it appears to act as an HCl scavenger. Removal of the released HCl from the PVC matrix by sorbitol can be achieved either via co-ordination/complexation of HCl by the polyol as found with zinc containing PVC formulations [34] or by a reaction between the polyol and HCl, e.g. substitution of hydroxy groups by chloride ions. It is unlikely, however, that HCl complexation by metals as previously found with zinc-containing PVC formulations [34] will play a major role, since we apply a heavy metal- and zinc-free PVC premix. Thus, in order to assess which of the two mechanisms contribute in the case of a heavy metal- and zinc-free PVC formulation the effect of various types of (natural) polyols, viz. sorbitol, xylitol, erythritol, 1,4-sorbitan, isosorbide, 1,4-galactitan and trimethylolpropane (TMP), respectively, on the long-term heat stability of PVC has been investigated in both unprocessed and ground-processed PVCepolyol mixtures.

3.2. Unprocessed PVCesorbitol mixture

Firstly, we have studied the effect of sorbitol on the dehydrochlorination (DHC) rate of an unprocessed PVCesorbitol (1.0 phr) mixture during thermal degradation at 200 C. As shown by the DHC rate curves in Fig. 1, neither the induction period (ca. 1000 s) nor the DHC rate change when 1.0 phr sorbitol is only manually mixed with the PVC compound (see Section 2.1). This is a significant observation. Note that it has been reported that both the induction period and the DHC rate change when additives capable to react with labile chlorines in the PVC backbone are used. For example, a change of the induction period in combination with a decrease of the DHC rate has been found for 1,3,4-oxadiazole additives, which react with labile chlorines [7] (see also reference [18]). Hence, the lack of any effect for our unprocessed PVCesorbitol (1.0 phr) mixture hints that sorbitol may indeed act as an HCl scavenger. This will be substantiated by the results obtained for ground-processed PVCesorbitol mixtures (Section 3.3, vide infra).

Extraction of the unprocessed PVCesorbitol (1.0 phr) mixture (powder) after thermal degradation at 200 C for 2.5 h in the DHC set up, followed by quantitative ^{13}C NMR analysis of the extract revealed that besides sorbitol (86%) its monoanhydro-derivative 1,4-sorbitan (14%) is also present. This suggests that sorbitol is partly converted to 1,4-sorbitan presumably via an acid-catalysed (HCl) intramolecular cyclodehy-dration reaction (see also Fig. 4, vide infra) [19e28].

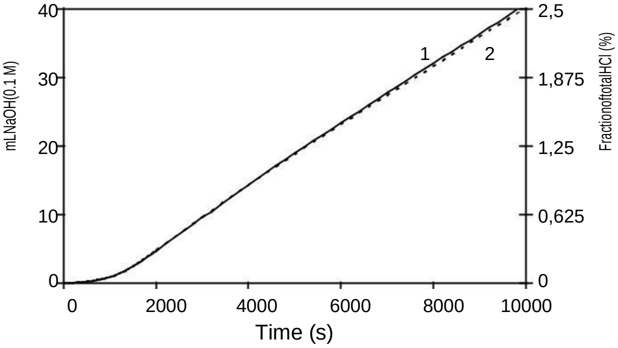

Fig. 1. DHC rates of unprocessed PVC compound in the presence (1; 1.0 phr) or absence (2) of sorbitol at 200 C.

3.3. Ground-processed PVCesorbitol mixtures

Next, the effect of homogeneously dispersed sorbitol in the PVC matrix was studied. This was achieved by processing PVCesorbitol mixtures that contain increas-ing amounts of sorbitol (0, 0.25, 0.50, 1.0 and 1.5 phr, respectively), on a two-roll mill at 196 C. The obtained rigid PVC sheets were subsequently ground under cryogenic conditions to particles of size % 3 mm, i.e. the ground-processed PVCesorbitol mixtures. These samples were subjected to thermal degradation at 200 C in the DHC set up (see Fig. 2).

The data show that for the blank (0 phr sorbitol) dehydrochlorination starts at ca. 1000 s. This induction period is in reasonable agreement with a qualitative estimate of the time required to heat the glass reactor and its contents to 200 C as determined by the Fourier method (cf. Appendix). After the initial 1000 s the DHC rate for the blank remains nearly constant for the next 5000 s, after which degradation becomes autocatalytic. Although upon addition of increasing amounts of sorbitol the induction period (ca. 1000 s) does not change significantly, a substantial decrease of the DHC rate between 1000 s and 5000 s is found. Concomitantly, the onset of autocatalytic degradation is delayed; the change being proportional to the amount of sorbitol added. For example, addition of 1.5 phr sorbitol results in a shift of the onset of autocatalytic degradation from 5000 s (blank) to 10 000 s. These observations give credence that in the applied ground-processed heavy metal- and zinc-free PVC formulation sorbitol indeed acts as a HCl scavenger.

Next, a ground-processed PVCesorbitol (1.0 phr) mixture was thermally degraded in a Werner Mathis oven (200 C) from which samples were taken after 1, 1.5, 2.0, 2.5 and 3 h, respectively. Each sample was extracted and the product composition of the extract was determined using quantitative ^{13}C NMR spectroscopy. The results unequivocally show that with increasing time sorbitol is progressively converted into its anhydro-derivatives 1,4-sorbitan and finally isosorbide, respec-tively. As shown by the results in Fig. 3, after 2.5 h, a significant part of the sorbitol is converted into 1,4-sorbitan (25%) and isosorbide (15%). A comparison of the results with those found after extraction of an unprocessed PVCesorbitol (1.0 phr) mixture that was also thermally degraded for 2.5 h at 200 C (vide supra) reveals that roll-mill processing enhances the conversion of sorbitol into its intramolecular cyclodehydration products (ground-processed 40% vs. unprocessed 14%). In combination with the significant reduction of DHC rate this points to a relationship between intramolecular cyclodehydration and the propensity of the added polyol to exert long-term heat stabilisation via HCl scavenging.

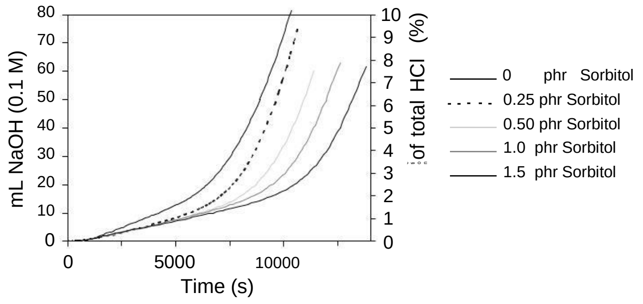

Fig. 2. DHC rates of ground-processed PVC sheets containing various amounts (in phr) of sorbitol at 200 C.

3.4. The effect of different polyols on DHC rates and CR values

To gain insight in the effect of intramolecular cyclodehydration of (natural) polyols on their long-term heat stabilising efficacy, different types of polyols (sorbitol, xylitol, erythritol, 1,4-sorbitan, isosorbide, 1,4-galactitan and trimethylolpropane (TMP), respec-tively) were applied as additives (see Section 2.1). Since the polyols are highly diluted (ca. 1%) in the ground-processed PVCepolyol mixtures, we disregard the occurrence of intermolecular dehydration reactions. The applied polyol additives differ in composition (number and type of hydroxyl groups), as well as their propensity to give stable intramolecular cyclodehydra-tion products via 1,4- and 1,5-elimination reactions (Fig. 4). Note that the occurrence of intramolecular cyclodehydration in the case of erythritol, xylitol, and sorbitol, giving 1,4-erythritan, 1,4-xylitan, and 1,4-sorbitan and isosorbide (1,4-sorbitan itself may undergo intramolecular cyclodehydration), respectively, at ele-vated temperatures is documented (Fig. 4) [23e28]. In contrast, 1,4-galactitan does not cyclodehydrate in solution [29]. Note that other possible cyclodehydration reactions, such as 1,2- and 1,3-elimination, will give

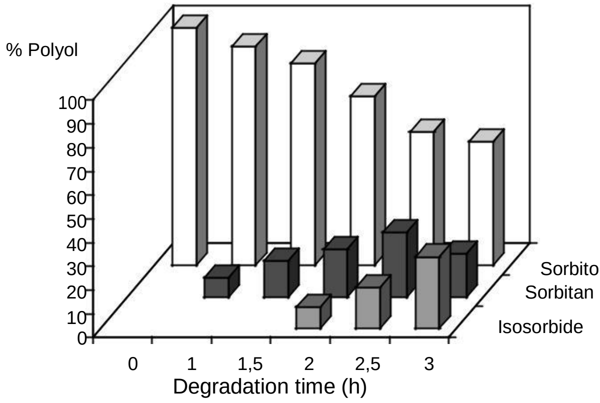

Fig. 3. Extraction results of ground-processed PVC-sorbitol (1.0 phr) mixtures after thermal degradation at 200 C vs. time.

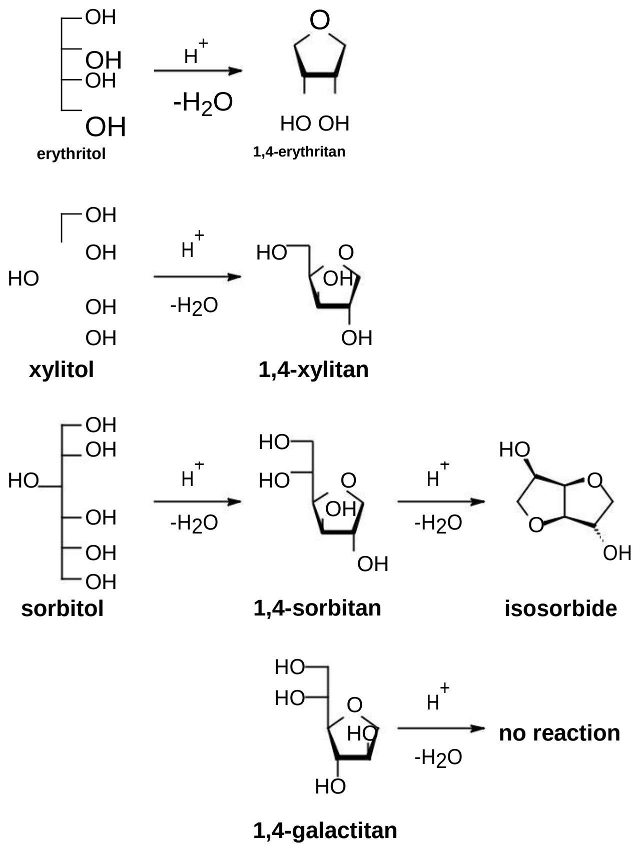

Fig. 4. Natural polyols and their accessible intramolecular cyclodehydration products.

reactive epoxides and oxetanes (e.g. trimethylolpropane (TMP)), respectively, which are expected to readily react with the released HCl giving ring-opened products containing covalently bound chlorine [30] (Table 2).

The DHC rates and CR values of ground-processed PVC samples containing different types of polyols (1.0 phr) are presented in Figs. 5 and 6, respectively. The results show that the number, type (primary vs. secondary) and the configuration of the hydroxyl groups are important factors for the long-term heat stabilising effect of the polyols.

Isosorbide, the dianhydro-derivative of sorbitol, which only contains secondary hydroxyl groups, exerts little effect on both the DHC rate and the CR value when compared to the blank. In contrast, trimethylol-propane (TMP) and 1,4-galactitan, show a significant effect on the long-term heat stability. This suggests that primary hydroxyl groups play an important role for imparting long-term heat stability. According to the measured DHC rates and CR values, both sorbitol and xylitol have the most pronounced effect. It has been established that the intramolecular cyclodehydration of sorbitol to 1,4-sorbitan is ca. 17! faster than that of xylitol to 1,4-xylitan [31] and that of sorbitol to 1,4-sorbitan is ca. 15! faster than that of 1,4-sorbitan to isosorbide [27]. Thus, despite the difference in reactivity of sorbitol and xylitol, only moderate differences are found with respect to their effect on long-term heat stability. The comparable performance of 1,4-sorbitan and 1,4-galactitan indicates that cyclodehydration does not play a major role in the stabilising mechanism (Fig. 5). The only apparent anomaly is erythritol, which according to the DHC rate data is the best performing polyol, while according to its CR value erythritol only exerts a moderate effect. One should take into account, however, that the DHC rate and CR methods are different procedures (see Section 2). Notwithstanding, they generally provide a qualitatively similar efficacy order for HCl acid scavenging properties of additives with reasonable reproducibility. Therefore, our long-term thermal stability results in combination with the known reactivity for polyols to undergo intramolecular cyclodehydration leads to the following conclusions: (1) intramolecular cyclodehydration does not contribute to the stabilisation mechanism itself, but represents a competitive reaction that affects the long-term heat stabilis-ing efficacy of the polyol (compare the behaviour of sorbitol, 1,4-sorbitan and isosorbide; see Figs. 4e6).

(2) The presence of primary hydroxyl groups is a prerequisite to exert long-term heat stability in our heavy metal- and zinc-free PVC systems. The polyols that enhance long-term heat stability act as HCl scavengers.

(3) The presence of additional neighbouring (secondary) b-hydroxy groups next to the primary hydroxy groups enhances the propensity of polyols, which further improves long-term heat stability in heavy metal- and

Table 2
Properties of the (natural) polyol additives tested in the rigid heavy metal- and zinc-free PVC ''naked'' pipe PVC formulation (see Table 1 and Fig. 4)

Polyols	Primary OH	Secondary OH	Stable intramolecular cyclodehydration product	M_W	mmol/phr
Trimethylolpropane (TMP)	3	e	No	120	10.0
Erythritol	2	2	Yes; 1,4-erythritan	122	9.8
Xylitol	2	3	Yes; 1,4-xylitan	152	7.9
Sorbitol	2	4	Yes; 1,4-sorbitan	182	6.6
1,4-Sorbitan	1	3	Yes; isosorbide	164	7.3
1,4-Galactitan	1	3	No	164	7.3
Isosorbide	0	2	No	146	8.2

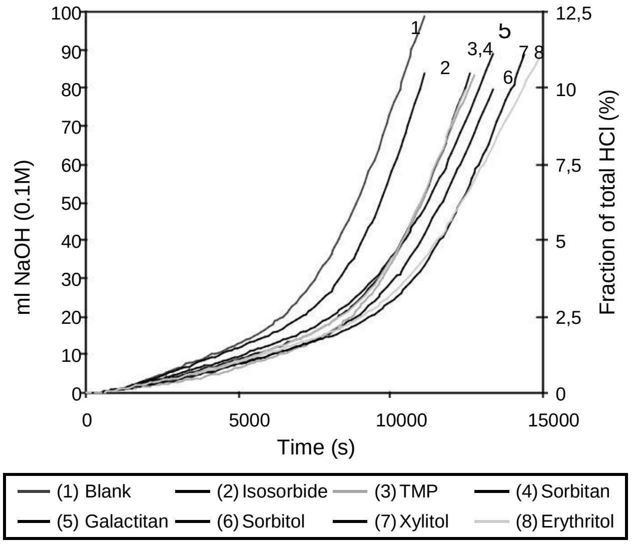

Fig. 5. DHC rates of ground-processed PVC–polyol (1.0 phr) mixtures at 200 °C.

zinc-free PVC systems (compare the behaviour of trimethylolpropane (TMP), 1,4-sorbitan and 1,4-galactitan; see Figs. 4–6).

In line with our results van Tran and Guyot [35] have found a correlation between the number of hydroxyl groups in polyol additives for heavy metal containing PVC and their effect on long-term heat stabilisation. Likewise, Elliott and Hills [36] observed in heavy metal containing PVC that alcohols with only secondary or tertiary hydroxyl groups all represent poor stabilisers. Thus, we conclude that the most viable mechanism is covalent interaction between the released HCl and the primary hydroxyl moieties of the polyols, e.g. pre-sumably via acid-catalysed substitution of primary hydroxyl group by chloride. Although this possibility has been suggested previously [35,37,38], experimental evidence was hitherto unavailable.

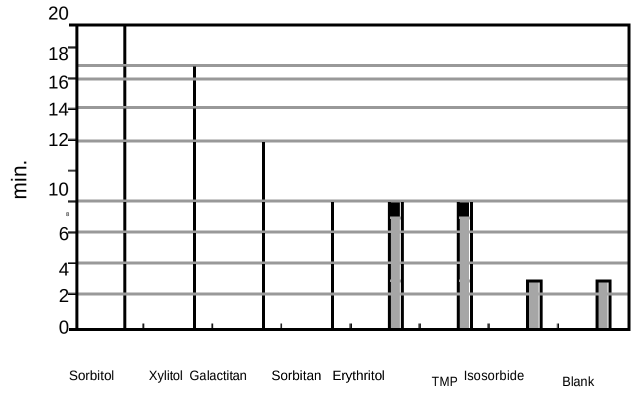

Fig. 6. Congo Red (CR) values of ground-processed PVC–polyol (1.0 phr) mixtures (cf. also Fig. 5).

4. Conclusions

A systematic investigation of the effects of natural polyols on the long-term heat stability of a heavy metal- and zinc-free rigid PVC formulation has provided new insights. Firstly, according to DHC-rate measurements and the assessment of CR values sorbitol does not react with labile chlorines on the PVC polymer backbone. Instead the polyol exerts long-term heat stabilisation by HCl scavenging, viz. suppressing/delaying autocatalytic degradation, after homogeneous dispersion of the polyol in the PVC matrix.

The application of (natural) polyols of varying composition as additives and their effect on the long-term heat stability of the corresponding ground-pro-cessed PVC–polyol mixtures after prolonged thermal degradation at 200 °C shows that polyol stabilising efficacy depends on their composition (number and type of hydroxyl groups present). The presence of primary hydroxyl groups is a prerequisite to impart long-term heat stability, which can be further reinforced by the presence of β-hydroxy groups. Despite the occurrence of competitive intramolecular cyclodehydration reactions, natural polyols like sorbitol and xylitol are effective HCl scavengers. Hence, it appears that these (natural) polyol additives in heavy metal- and zinc-free PVC scavenge HCl by substitution of primary hydroxyl groups by chloride ions. The identification of the intermediates that contain covalently bound chlorine is currently under investigations.

Finally, the important aspect of the extent of discolouration, i.e. in particular the effect of (natural) polyol additives on the initial colour of heavy metal- and zinc-free PVC, will be addressed in a subsequent manuscript.

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Appendix. Estimate of the time involved in raising the temperature of the PVC batch

An estimate of the time required to raise the temperature of the PVC in the DHC set up to the temperature of the oil bath was obtained by the following procedure. The bulk volume of ground PVC (5.00 g) was measured; a volume of 7.1 ml was found, which results in a bulk density of 704 kg/m^3. From the density of PVC (1390 kg/m^3) the porosity of ground

PVC is determined to be 49%. The radius of the spherical vessel of the DHC set up is 2.9 cm. Fourier's number (F_0), i.e. a measure of the heat conducted through a body relative to the heat stored, is calculated using Eq. (1):

$$F_0 Z \frac{\frac{l}{c_p!r}!t}{L^2}$$ ð1Þ

with l Z 0.165 J/s m K (the thermal conductivity of PVC), c_p Z 2 ! 10^3 J/kg K (the heat capacity of PVC), L Z 0.029 m (the characteristic length (radius) of the sphere) and r Z 704 kg/m^3 (bulk density of ground PVC). This leads to the following F_0 value:

$$F_0 Z1:39!10^{74}!t$$ ð2Þ

A difference in mean temperature from the temper-ature of the oil bath according to Eq. (3)

$$\frac{T_1 7 CT D}{T_1 7 T_0} Z10^{72}$$ 3 ðþ

in which T_1 is the temperature of the oil bath (200 C), T_0 the initial temperature of the PVC powder (20 C) and CTD the mean temperature of the PVC powder. From the Heisler charts [39] a Fourier number of 0.9 is deduced using a difference in mean temperature of 10^{72} C (Eq. (3)) and an estimated Biot number (Bi) equal to 10.

From Eq. (2) it follows that

$$1:39!10^{74}!tZ0:9$$

and

$$tZ6459 \text{ s}$$

Thus, the time to heat the entire sphere is ca. 6500 s. Note, however, that only part of the sphere has to be heated. The layer of ground PVC is at most only 0.8 cm thick. Therefore, the estimated time to heat this layer is (0.8 cm/2.9 cm) ! 6500 s Z 1800 s, e.g. the time to heat the grounded PVC layer is ca. 2000 s.

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