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The compatibility of (natural) polyols with heavy metal- and zinc-free poly(vinyl chloride): Their effect on rheology and implications for plate-out

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Abstract

This paper describes the rheological effects observed after addition of (natural) polyols to several different types of heavy metal-free PVC formulations. It is found that addition of natural polyols, such as sorbitol, leads to changes in the rheology of the system comparable to the addition of external lubricants. Hence as suggested previously, addition of (natural) polyols may lead to the occurrence of undesirable plate-out phenomena. The magnitude of the effect on the rheology depends on the number of hydroxyl groups in the polyol and its propensity to undergo intramolecular cyclodehydration reactions. It is established that the undesirable rheological effects, which coincide with plate-out phenomena, can be suppressed by the addition of various types of inorganic as well as organic substances, most of which are known PVC additives. This will allow for the use of (natural) polyols as efficient and benign co-stabilisers in next generation stabiliser systems.
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1. Introduction

Poly(vinyl chloride) (PVC) is a cost-effective and highly versatile polymer which is used in many construction applications, such as water, sewage and drainage pipes, and a variety of extruded profiles. However, due to the inherent poor thermal stability of PVC, high temperature processing and shaping operations, such as extrusion, are only possible with the aid of thermal stabilisers. These additives reduce colour formation and suppress HCl emissions, which would otherwise ultimately lead to fatal autocatalytic degradation of the material. Currently, the rigid PVC stabiliser systems dominant in Europe are still based on lead soaps and salts. However, the European PVC industry has committed itself to a complete phase-out of lead stabilisers by the year 2015. Short-term alternatives for the lead stabilisers can be found in the currently commercially available Ca/Zn, Ca-organic and tin-based stabiliser systems. Notwithstanding, all of these systems face issues with regard to either cost/performance or the use of ecologically disputed components [1]. Next generation stabiliser systems should therefore be based on effective, sustainable, undisputed, and environmentally benign components.

Recently we have reported on the use of natural polyols as (long-term) co-stabilisers in heavy metal-free PVC compounds [2]. Although polyols are already being used in lead- and zinc-stabilised PVC formulations, they are often thought to be the cause of poor early (initial) colour [3], and the formation of 'plate-out' or 'die build-up'. As we have shown previously, the use of natural polyols, such as sorbitol, does not necessarily lead to poor early colour [4]. In a heavy metal-free PVC formulation various types of natural polyols significantly improved both early colour as well as long-term

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stability. Subsequently, we have turned our attention to 'plate-out'. 'Plate-out' is observed during dynamic processing of PVC by extrusion or calendaring [5]. In the case of extrusion, the term 'die build-up' is frequently used, but probably a similar phenomenon occurs. By 'plate-out' is meant the formation of residual solid deposits on machine parts, such as extruder dies, calendar rolls or mill rolls, as the PVC resin is being processed. Such deposits will cause imperfections in the resin during processing, leading to considerable production losses, which will significantly affect product costs.

Plate-out is a very complex phenomenon that depends on the composition of the PVC compound, *e.g.* additives, such as stabilisers, pigments, fillers and lubricants, but also on the processing conditions, such as shear rate, temperature, etc. Despite its economic importance as a cost-contributing factor very little information has been published about the composition of plate-out deposits and the reasons for its occurrence [6–16]. Plate-out has always been strongly associated with the use of polyols, *e.g.* pentaerythritol, which are frequently used as secondary stabilisers [17]. However, (natural) polyols act as (cost-)efficient acid scavengers, which ideally could be a major component in future heavy metal-free stabiliser compositions [2]. Lubrication also has a significant effect on plate-out, depending on the types and amount of lubricants applied in PVC formulations [6,7,18]. During our investigations we have found that addition of polyols to lead- and zinc-free PVC compounds had a profound effect on the rheology, comparable to the addition of excess lubricants. Hence the subject of the present study was to investigate the effects of polyols on the rheology of lead- and zinc-free PVC compounds. We have also found that adverse rheological effects could be effectively suppressed by the use of various other PVC additives, *i.e.* especially inorganic substances, thus allowing for the use of (natural) polyols as efficient co-stabilisers in next generation stabiliser systems.

2. Experimental

2.1. Rheology

The rheology of the PVC compounds was measured with a Haake Rheocord 90 torque rheometer (plastograph) with a chamber volume of 69 ml. After charging a PVC compound, a torque curve was recorded at constant rotational speed and at constant temperature of the kneader chamber (175, 185 or 197 °C) [19].

An estimate of the optimum amount of compound added to the kneader in order to obtain the best torque curve was calculated from ASTM specifications [20]. In our case the sample size used for formulation 1 was approx. 63 g. Tests with sample sizes of 55 g up to 75 g were performed to confirm the calculated sample size. The results showed that 55 g of formulation 1 did not result in gelation of the sample, whereas 75 g resulted in too fast gelation. Optimal gelation behaviour was obtained with a loading of 63 g. Similarly, an optimal sample size of 67 g was obtained for formulation 2 (Table 1). The ASTM norm further specifies that a temperature/rotor

Table 1
Composition (in phr) of rigid PVC test formulations

Component	Pb-formulation	Formulation 1	Formulation 2
S-PVC (K68, Marvylan S6806)	100.0	100.0	100.0
$CaCO_3$ (Omyalite 95T)	8.0	2.00	8.0
Calcium stearate	0.3	–	0.6
Dibasic lead phosphate	0.4	–	–
Neutral lead stearate	0.8	–	–
Paraffin wax (drop point 106–112 °C)	0.3	0.16	–
Synthetic paraffin (m.p. 73 °C)	0.1	0.46	–
LDPE-wax (drop point 103–110 °C)	–	0.10	0.6
Oxidised PE-wax	–	–	0.1

speed combination of the torque rheometer has to be selected that will permit the test to be completed within a reasonable time span [20]. The suggested temperature/rotor speed combination for rigid PVC is 197 °C/60 rpm. However, this applies to sufficiently stabilised PVC compounds. Since in our case *unstabilised* PVC test compounds were used, lower temperatures of the chamber (175–197 °C) and a lower rotor speed (40 rpm) were chosen to prevent cross-linking and severe degradation.

2.2. PVC compounds: composition and additives

Table 1 lists the composition of the rigid PVC test compounds used in this study. The lead (Pb) formulation was a standard pipe formulation, which was used as rheological standard, *e.g.* reference PVC formulation. Formulation 1 was a basic rigid PVC formulation containing only additives essential for kneader processing, and no thermal stabilisers. Formulation 2 also contained no primary thermal stabilisers, but was rheologically more comparable to the reference lead (Pb) formulation (Fig. 1).

Pre-mixes were supplied by Chemson Polymer-Additive AG (Table 2). Additives were mixed with the PVC powder in a Papenmeier mixer for 10–15 min at 30–40 °C and a tip
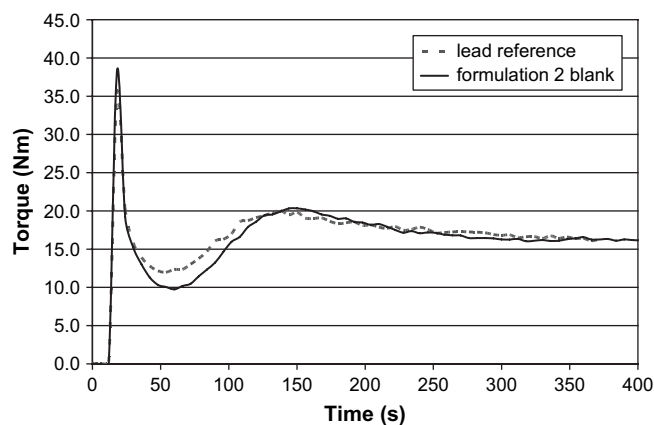

Fig. 1. Rheology of formulation 2 (190 °C) *vs.* the lead-based reference (blank).

Table 2
Additives used in the PVC test compounds

Additive	Description	Supplier
Erythritol	Natural polyol, crystalline	Aldrich
Xylitol	Natural polyol, crystalline	Aldrich
Sorbitol	Natural polyol, crystalline	Cerestar
Isosorbide	Natural rigid diol, crystalline	Cerestar
Mannitol	Natural polyol, crystalline	Aldrich
Di-glycerol	Semi synthetic polyol, viscous liquid	Solvay
Tri-glycerol	Semi synthetic polyol, viscous liquid	Solvay
di-TMP	Synthetic polyol, crystalline	Perstorp
Alcamizer 1®	Synthetic hydrotalcite, carbonate form	Kiowa
Alcamizer 4®	Zinc-containing synthetic hydrotalcite, carbonate form	Kiowa
Alcamizer 5®	Synthetic hydrotalcite, perchlorate form	Kiowa
Zeolite 4A®	Synthetic zeolite	Tessenderlo Chemie
Laponite RD®	Synthetic nano-clay	Rockwood
Paraloid K-125®	Acrylic PVC processing aid	Rohm&Haas
Paraloid KM-355®	Acrylic PVC impact modifier	Rohm&Haas

speed of 32 m/s. The mixture was then heated to approx. 120 °C and subsequently cooled to ambient temperature in 5–10 min.

Prior to kneading, the additives under investigation were manually mixed into the pre-mix compound. All kneader experiments were performed in twofold, and showed a high degree of reproducibility. The torque rheometer curves displayed in the figures are based on the averaged data of two independent experiments.

2.3. Heat stability tests

Rigid PVC sheets were obtained with a Collin two-roll-mill (type W110E, two frequency controlled electric motors, 2×3 zone electrical heating); width 22.5 cm, circumference 35 cm, rotation front/back: 19/23 rpm. Preheating: 204–204 °C (front-rear: set-temperature 207–206 °C); slit-width 0.3 mm. The PVC compound (100 g) was put on the roll-mill and mixed for 3 min by manual cutting and kneading. After an additional 30 s the sheet was removed from the mill.

Static heat stability measurements were performed on PVC strips (26×3 cm) cut from the roll-milled PVC sheets. The PVC strips were subjected to heating in a Mathis oven (Mathis thermotester LTE-T; ventilation speed 1250 rpm, temperature 200 °C, total time 30 min).

3. Results and discussion

To investigate the applicability of natural polyols as heat stabilisers for rigid PVC compounds, their influence on plate-out was studied. The preferred way to study plate-out behaviour would be by long-term extruder processing of polyol containing PVC formulations, followed by a detailed chemical analysis of the solid deposits found on the processing

equipment. However, in order to study a broad range of different polyols this would take up a disproportionate amount of resources and time. Since it is known that lubrication has significant influence on plate-out, it was expected that polyols could affect plate-out similarly to lubrication [17]. Changes in lubrication, which can lead to plate-out formation, usually also influence the rheology of the PVC compound. This can be studied with a torque rheometer. Processing of PVC as observed with a torque rheometer consists of a number of different phases, which are related to morphology changes in the PVC caused by heating and shear. An unprocessed PVC grain (diameter approx. 100 μm) contains several globules (microparticles) of a diameter of approx. 1 μm [18,20,21]. The globules, in turn, consist of nodules with a diameter of approx. 10 nm (submicro-particles). At temperatures up to 190 °C, the PVC grains are broken down to globules (plastification process). At 180 °C, the globules in turn are altered and compacted. After significant interdiffusion, the boundaries of the nodules disappear and a three-dimensional network of polymer chains is formed [6,22]. This process is known as fusion.

Fig. 2 shows an example of a plastogram. When the PVC sample is charged into the system, the torque rises. Subsequently, the torque begins to drop sharply because of free material flow before the globules starts to compact (valley torque). Next, the torque starts to rise again and generates the fusion peak. At this point, the material reaches a void-free state and sets on to melt at the interface between the compacted material and the hot metal surface. When the sample is melted and fused for an extended period of time in the mixer, the temperature increases slightly because the sample absorbs more energy. A higher melt temperature will result in a decrease of the melt viscosity of the molten sample. Therefore, the torque eventually decreases in time.

Internal lubricants, _e.g._ glycerol monostearate (GMS) [19], decrease the fusion time (the period of time to reach the fusion peak), but have little influence on the valley torque. Whereas internal lubricants will also decrease the melt viscosity and will enhance polymer flow [22], external lubricants (_e.g._ PE-waxes [18]) will reduce both the valley and fusion torque, and will delay the fusion time. External lubricants migrate
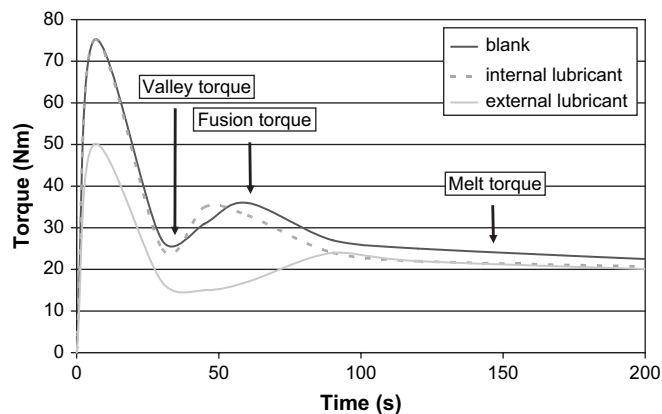

Fig. 2. Schematic torque rheometer curves for an internal and an external lubricant.

out of the PVC compound and form a layer between the polymer and the surface of the processing equipment, thereby lowering the friction between the polymer melt and the melt surface [23]. Well-known problems resulting from over-lubrication are surging of the extruder, lumpiness of the extrudate, incomplete fusing, and the necessity to employ a high barrel temperature. Common problems found in the end products are low impact strength and acetone failure. In contrast, under-lubrication leads to rough extrudate, adhesion to metal surfaces, melt fracture and abnormally low barrel temperatures.

3.1. Influence of internal and external lubricants on rheology

Kneader experiments with formulation 1 and various known lubricants indeed showed that when processed at 185 °C and 40 rpm, addition of either 1 phr internal lubricant, *i.e.* glycerol monostearate (GMS) [19], or 1 phr external lubricant, *i.e.* PE-wax [18], resulted in the expected torque rheometer curves (Fig. 3).

Since the melt viscosity of a polymer depends on the temperature of the polymer melt, the melt temperature for all PVC compounds containing internal and/or external lubricants was recorded. Melt temperatures were found that were highly comparable with those obtained for the blank PVC compound lacking the lubricants. Consequently, differences in melt viscosity (see Fig. 3) are not caused by differences in melt temperature, but due to lubrication effects. Therefore, for all other rheometer experiments of PVC compounds containing polyols (*vide infra*) melt temperature curves were also independently measured. In all instances no significant differences were discernible between the blank PVC compound and the PVC compounds containing polyols. Hence for all investigated samples, the observed differences between the torque rheometer curves are directly related to lubrication effects.

When sorbitol was added to formulation 1 the rheology effects were comparable to those found after addition of an external lubricant (compare Figs. 3 and 4). A dosage level of 1 phr of polyol was chosen as this yielded a sufficiently

Fig. 4. Torque rheometer curves (185 °C) for formulation 1 containing sorbitol.

quantitative and reproducible effect. Note that in real rigid PVC formulations polyol addition levels rarely exceed 0.1–0.2 phr.

Next, a range of alditols (natural linear polyols of the general formula $(CH_2OH)_n$, Fig. 5) were tested for their effects on the rheology of formulation 1. Addition of either 1 phr of erythritol (C4-alditol) or xylitol (C5-alditol) leads to fusion torque depression (Fig. 6). The most significant results were obtained with the two isomeric C6-alditols, sorbitol and mannitol. Although both hexitols contain six hydroxyl groups the effect of 1 phr of mannitol is comparable to the addition of 2 phr of sorbitol.

The marked differences can be attributed to differences in reactivity of both hexitols under the applied PVC processing conditions during which HCl is released. Most alditols can undergo acid-catalysed intramolecular cyclodehydration reactions yielding cyclic ethers and water (*cf.* Scheme 1) [2,4]. In the PVC matrix HCl can act as catalyst in this reaction. Whereas all alditols tested here are capable of forming cyclic ethers, their relative cyclodehydration rates differ substantially. Barker has reported that in 2 N HCl at 100 °C the reaction from sorbitol to 1,4-sorbitan proceeds 39 times faster than the related formation of 1,4-mannitan from mannitol [24]. The 2,5-anhydro mannitol isomer (2,5-sorbitan) is formed at a comparable rate to the 1,4-anhydro isomer. Bock et al. have found that in H_2SO_4 the complete cyclodehydration of sorbitol proceeds approx. five times faster than that of mannitol [25]. As a result, the average concentration of sorbitol in the PVC matrix will be significantly lower than that of mannitol.
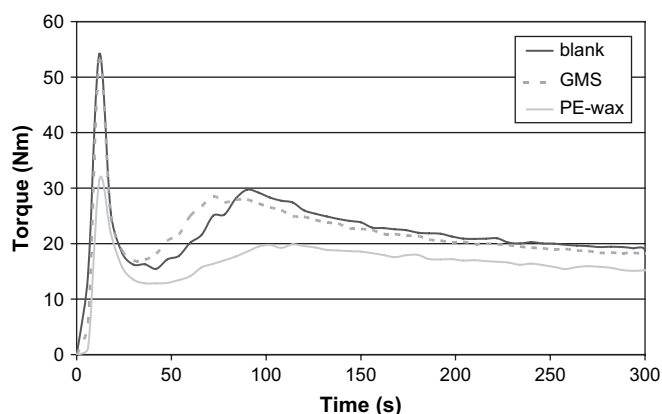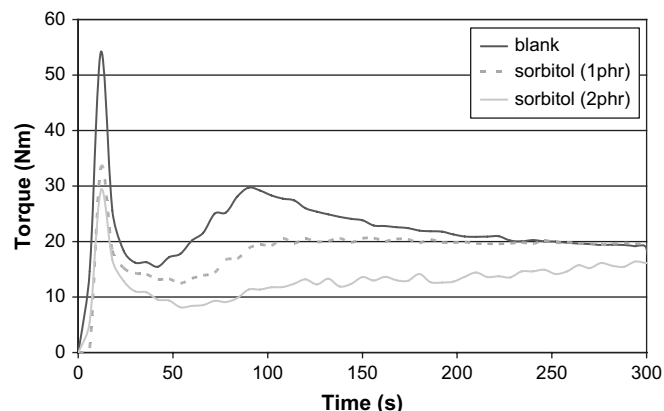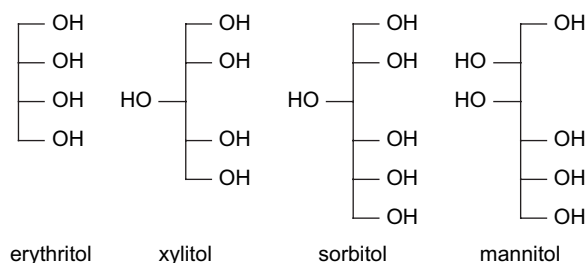

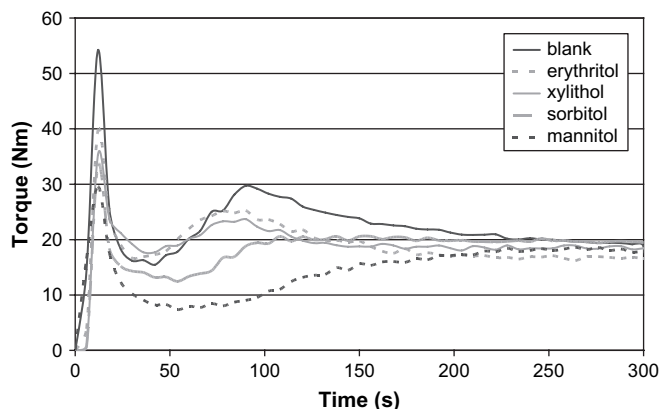Fig. 3. Measured torque rheometer curves (185 °C) for formulation 1 containing an additional 1 phr of either an internal lubricant (GMS) or an external lubricant (PE-wax).

Fig. 5. Alditols tested in formulation 1.

Fig. 6. Torque rheometer curves (185 °C) for formulation 1 containing various alditols at 1 phr.

Fig. 7. Torque rheometer curves (185 °C) for formulation 1 containing sorbitol and isosorbide (*cf.* Scheme 1) at 1 phr.

Furthermore, the final intramolecular cyclodehydration products also differ. Whereas the hexitol sorbitol is transformed into the diol isosorbide, mannitol is converted into a mixture of the diol isomannide and the tetrol 2,5-sorbitan. The latter is incapable to undergo further intramolecular cyclodehydration. The mannitol containing PVC compound will therefore contain significantly more hydroxyl groups than the sorbitol containing PVC compound. Reduction of the number of hydroxyl groups from six in sorbitol to two in isosorbide has dramatic consequences for the rheological behaviour of a PVC compound. It is clear that addition of 1 phr of isosorbide to
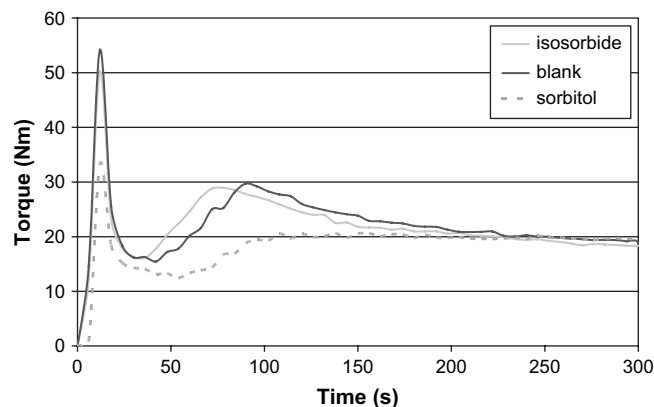
formulation 1 results in an effect comparable to the addition of an internal lubricant (compare Figs. 3 and 7). Acid-catalysed intramolecular cyclodehydration of sorbitol to isosorbide (Scheme 1) should results in a reversal in rheological behaviour as the reaction proceeds during processing. Addition of linear polyols to formulation 1 evidently leads to rheological behaviour comparable to over-lubrication with an external lubricant. Lubrication is documented to have a significant effect on plate-out, depending on the types and amount of lubricants applied in a PVC formulation. The effect increases with increasing size of the alditols (and thus the number of hydroxyl
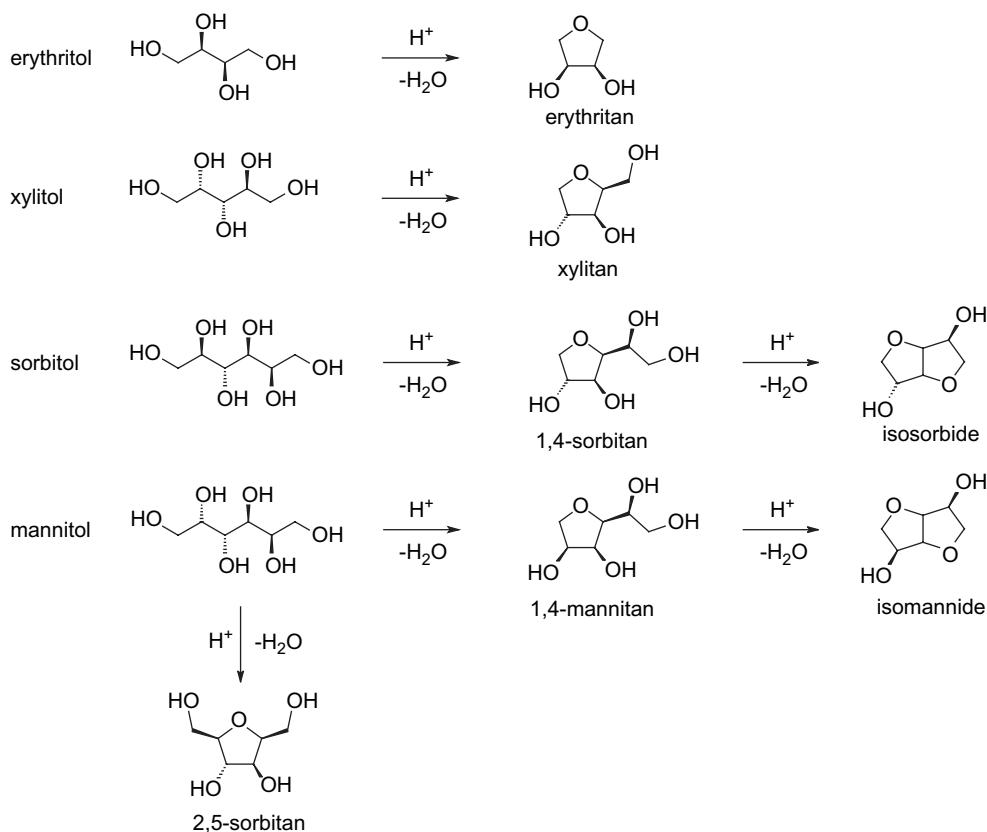
Scheme 1. Acid-catalysed cyclodehydration reactions of alditols tested in formulation 1.

groups), and can be related to their propensity towards acid-catalysed intramolecular cyclodehydration of the respective alditols.

One possible explanation of the observed effects might be that the highly polar polyols migrate out of the polymer melt due to their incompatibility with the PVC matrix (which increases with an increasing number of hydroxyl groups), and form a layer between the metal surface of the processing equipment and the polymer melt. However, all of the alditols used in this experiment (and their respective intramolecular cyclodehydration products) have melting points below the applied processing temperatures, which render them improbable candidates for the formation of solid deposits.

Another, more viable explanation could be that polyols force other (in)organic additives, including lubricants, out of the polymer matrix to the surface of the processing equipment. Chemical analysis of plate-out deposits has shown that the major part (*ca.* 70%) consists of inorganic substances, the remaining part being organic materials [8,10–12]. The highly polar polyols will increase the bulk-polarity of the polymer melt, which leads to an increased incompatibility of the polymer melt with various apolar additives. Furthermore, polyols and their intramolecular cyclodehydration products could increase the mobility of some of the inorganic components in the compound, effectively transporting them out of the polymer matrix.

Based on the initial results with the C4–C6-alditols in formulation 1, new experiments were performed with a different set of polyols in formulation 2 (Table 1 and Fig. 8). In this case an addition level of 1.5 phr of polyol was chosen to obtain significant and reproducible torque rheometer results. Also under these conditions sorbitol displayed a pronounced external lubrication effect compared to the blank. In order to investigate the influence of the number and type of hydroxyl groups three other polyols were compared to sorbitol, *e.g.* di-trimethylol-propane (di-TMP), di-glycerol and tri-glycerol (Table 3 and Fig. 8). Di-TMP has four primary hydroxyl groups and a relatively high molecular weight. Di-glycerol has two primary and two secondary hydroxyl groups and has a molecular weight comparable to that of sorbitol. Tri-glycerol has a molecular weight comparable to that of di-TMP and has a number and type of hydroxyl groups comparable to sorbitol. None of the three synthetic polyols are expected to yield significant acid-catalysed intramolecular cyclodehydration products under the applied conditions.

When processed with the torque rheometer in formulation 2 the effect of adding 1.5 phr of di-TMP was surprisingly small (Fig. 9). In contrast, di-glycerol exerts a more pronounced external lubricant effect. This difference could be due to the fact that on a molecular basis 50% more di-glycerol was added than di-TMP. Given the negligible difference in molecular weight between di-TMP and tri-glycerol, the significant external lubrication effect of tri-glycerol can only be attributed to the difference in the number and type of hydroxyl groups. When going from tri-glycerol to sorbitol, again a striking increase in external lubrication effect is observed. This can, at least in part, be explained by the difference in molecular weight; on a molecular basis 30% more sorbitol was added than tri-glycerol. Furthermore, the increase in the total number of hydroxyl groups probably also will contribute to the effect. Dramatic is the difference between di-glycerol and sorbitol. Given their comparable molecular weights the difference in rheological behaviour can only be due to the difference in number of hydroxyl groups.

Visual inspection revealed that roll-mill processing of formulation 1 containing 1.5 phr of sorbitol led to the formation of a white solid deposit on the surface of the rolls. Processing of a blank PVC compound did not lead to the formation of a deposit; neither did addition of a commercial hydrotalcite (Alcamizer 1, Table 2). Surprisingly, when both sorbitol (1.5 phr) and the hydrotalcite (1.0 phr) were added to the compound also no deposition was observed. This prompted us to investigate the rheological effects upon addition of hydrotalcites to polyol containing PVC compounds in more detail. Kneader experiments with formulation 2 showed that Alcamizer 1[®] had no significant rheological effect (Fig. 10). A combination of sorbitol (1.5 phr) and Alcamizer 1[®] (1.0 phr) led to a dramatic reduction of the external lubrication effect exerted by sorbitol.

Hydrotalcites are currently used in commercial PVC compounds as acid scavenging co-stabilisers, and are also potential stabilisers for heavy metal-free stabiliser formulations [26]. Hydrotalcites are basic magnesium–aluminium carbonates of the general formula $Mg_{1-x}Al_x(OH)_2A_{x/n}^{n-} \cdot mH_2O$, wherein $0 < x \leq 0.5$, m is a positive number, and A^{n-} represents an anion having a valence of n. Hydrotalcites consist of a basic composite layer and an interlayer, in which the anions that compensate the positive charge in the basic layer are accommodated. In case of carbonate ions (CO_3^{2-}) as anions (*e.g.* Alcamizer 1[®], $0.25 < x < 0.33$ ratio Mg^{2+}/Al^{3+} 2/3), reaction with HCl leads to the formation of carbon dioxide (CO_2), water (H_2O) and chloride ions (Cl^-) in the interlayer.

Apart from the commercially available magnesium–aluminium carbonate (Alcamizer 1[®]), two other commercial hydrotalcites were also tested in formulation 2. Alcamizer 4[®] is a magnesium–zinc–aluminium (ratio $Mg^{2+}/Zn^{2+}/Al^{3+}$
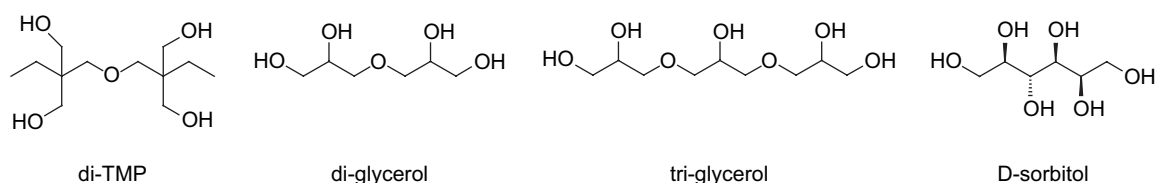

Fig. 8. Polyols tested in formulation 2.

Table 3
Description of polyols tested in formulation 2

Polyol	Prim. OH-groups	Sec. OH-groups	Total OH-groups	Mw
di-TMP	4	–	4	250.33
Di-glycerol	2	2	4	166.17
Tri-glycerol	2	3	5	240.25
Sorbitol	2	4	6	182.17

3/1/2) carbonate, which because of the presence of zinc can act as a primary stabiliser. Alcamizer 5® is a magnesium–aluminium (ratio Mg^{2+}/Al^{3+} 2) perchlorate (ClO_4^-), frequently used in PVC-polyurethane composite materials [27]. When processed in formulation 2, Alcamizer 1® and 4® had no significant effect on the rheology, while Alcamizer 5® appears to exert a moderate internal lubricant effect (Fig. 11). When all three hydrotalcites (1 phr) were processed in combination with sorbitol (1.5 phr) the results were partly unexpected. Whereas Alcamizer 1® and 5® gave comparable results, the curve for the zinc-containing Alcamizer 4® still showed a pronounced external lubrication effect (Fig. 12). This can be rationalised by assuming that as time progresses more zinc becomes available in the PVC melt, acting as a primary stabiliser and thus effectively suppressing HCl formation. This will result in a reduction of the acid-catalysed intramolecular cyclodehydration of sorbitol, leading to a higher effective sorbitol concentration, and hence a more pronounced external lubrication effect (see Scheme 1 and also Fig. 7).

Since all hydrotalcites were capable of neutralising the rheological effects of sorbitol, the question came up whether other inorganic materials could exert the same effect. Zeolite 4A® is a synthetic zeolite which is often used as a cost-effective substitute for hydrotalcites in PVC formulations. When tested in formulation 2 the rheological behaviour of Zeolite 4A®, both neat and in combination with sorbitol, was similar to that of Alcamizer 1®.

Finally, Laponite RD®, a fully synthetic smectite clay, with the empirical formula $Na_{0.7}^+$ $[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]^{-0.7}$, was also tested in formulation 2, and gave results highly comparable to those obtained with Alcamizer 1® (rheometer curves not shown).

Fig. 10. Torque rheometer curves (190 °C) for formulation 2 containing sorbitol (1.5 phr) and/or Alcamizer 1® (1.0 phr).

Since the rheological neutralising effect appeared to be universal for a number of nano-sized inorganic materials, the question rose whether this effect could also be obtained with the aid of purely organic PVC additives. Hence, two well-known acrylates were tested; Paraloid K-125® an acrylic processing aid for PVC and Paraloid KM-355® an acrylic impact modifier for PVC. When added in 1 phr to formulation 2, K-125 caused an increase in the melt-torque, while addition of KM-355 led to a delay in fusion time (Fig. 13). Note that 1 phr is at the low end of the usual addition levels for these types of PVC additives. When tested in combination with sorbitol, Paraloid KM-355® significantly reduced the external lubricant effect, while Paraloid K-125® even outperformed Alcamizer 1® (Fig. 14). A literature survey revealed that the use of small amounts of acrylic resins for the prevention or suppression of plate-out has been suggested before [8,28,29]. Note, however, that the results reported in these papers were based on the use of either lead or barium/cadmium based stabiliser systems. This underlines that there is indeed a correlation between the rheological effects observed with the torque rheometer and the occurrence of actual plate-out on processing equipment.
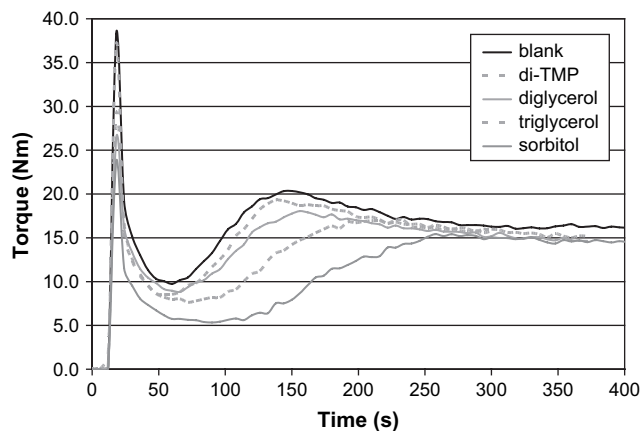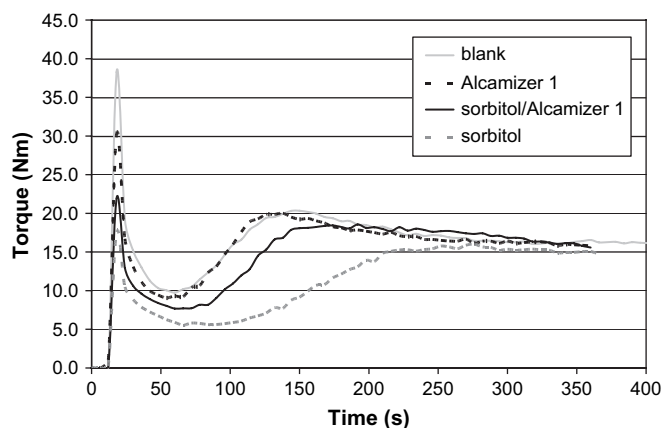

Fig. 9. Torque rheometer curves (190 °C) for formulation 2 containing polyols at 1.5 phr.
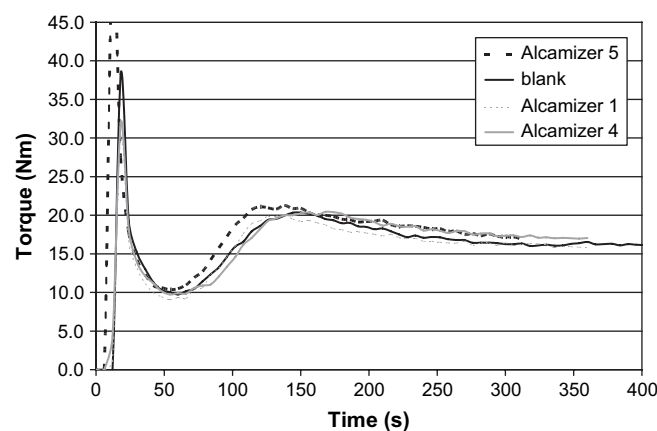

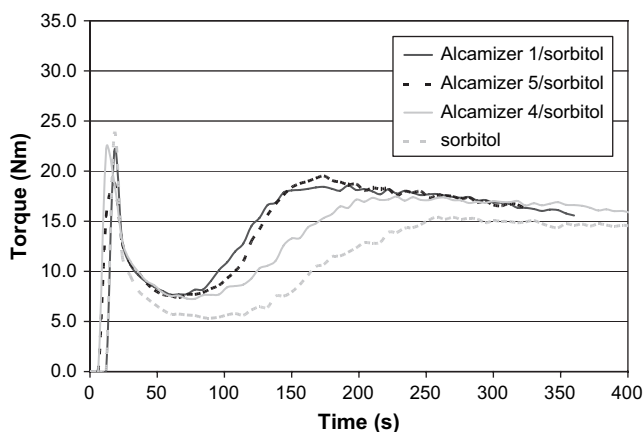Fig. 11. Torque rheometer curves (190 °C) for formulation 2 containing various hydrotalcites (1.0 phr).

Fig. 12. Torque rheometer curves (190 °C) for formulation 2 containing various hydrotalcites (1.0 phr) and/or sorbitol (1.5 phr).

Fig. 14. Torque rheometer curves (190 °C) for formulation 2 containing Paraloid K-125® or KM-355® (1.0 phr), and/or sorbitol (1.5 phr).

3.2. Effects on static heat stability

As these investigations are part of an ongoing program directed at developing industrially viable alternative environmentally benign stabiliser systems, all additives tested for their effect on rheology were also tested with regard to their effects on heat stability (Mathis oven static heat stability). Addition of acid scavengers like sorbitol or hydrotalcites (and to a lesser extent the Zeolite 4A®) led to the expected improvements in long-term heat stability. The Laponite RD® and both Paraloid® acrylates had no observable adverse effect on static heat stability when added to a suitably stabilised heavy metal-free PVC compound.

4. Conclusions

Previously we have shown that, in contrast to general consensus, (natural) polyols when added to lead- and zinc-free rigid PVC compounds do not necessarily lead to a bad early (initial) colour [2,4]. Now, a second potential drawback of polyols, increased plate-out, was investigated. It was shown that the rheology of unstabilised rigid PVC compounds containing
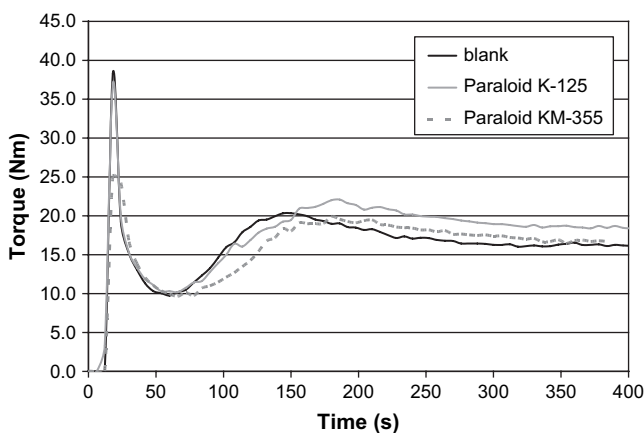

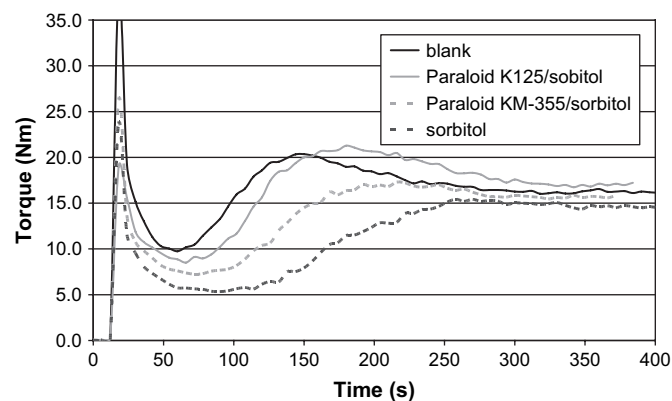Fig. 13. Torque rheometer curves (190 °C) for formulation 2 containing Paraloid K-125® or KM-355® (1.0 phr).

polyols was similar to those of over-lubricated compounds. A relationship was established between the magnitude of the external lubricant effect and the type and number of hydroxyl groups present in the polyol. An increasing number of hydroxyl groups increased the effect on the rheology. Furthermore, a relationship was established between the propensity of a polyol to undergo acid-catalysed cyclodehydration under processing conditions and the external lubricant effect. Based on these results sorbitol is expected to cause less plate-out than mannitol at comparable addition levels. Xylitol, which has previously been shown by us to be an effective heat stabiliser for rigid PVC [2], is expected to have an even smaller effect on plate-out.

In addition it was also demonstrated that the adverse rheological effects caused by the addition of polyols can be countered by the addition of other additives, some of which are already in use as PVC additives and stabilisers.

Long-term extruder processing of some of the compounds tested by us should reveal whether the rheological effects observed in the kneader experiment correspond to reduced plate-out/die build-up during extrusion.

Although we have confirmed that polyols indeed can have dramatic effects on the rheology, our study has also shown that choosing the right polyol based on its molecular structure and choosing the right co-additives can lead to the desired processing behaviour. This opens up new opportunities for natural polyols in next generation stabiliser systems for lead- and zinc-free rigid PVC formulations.

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