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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

Daan S. van Es [a], Johan Steenwijk [a,b], Guus E. Frissen [a], Hans C. van der Kolk [a], Jacco van Haveren [a], John W. Geus [b], Leonardus W. Jenneskens [b,*]

[a] *Wageningen University and Research Centre, Bio-based Products, P.O. Box 17, NL-6700 AA Wageningen, The Netherlands*
[b] *Chemical Biology and Organic Chemistry, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, The Netherlands*

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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.

Keywords: Additives; Rheology; Poly(vinyl chloride) (PVC); Renewable resources; Polyols; Stabilization

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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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[*] Corresponding author. Tel.: +31 30 2533128; fax: +31 30 2534533.
E-mail address: l.w.jenneskens@chem.uu.nl (L.W. Jenneskens).

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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 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.

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

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

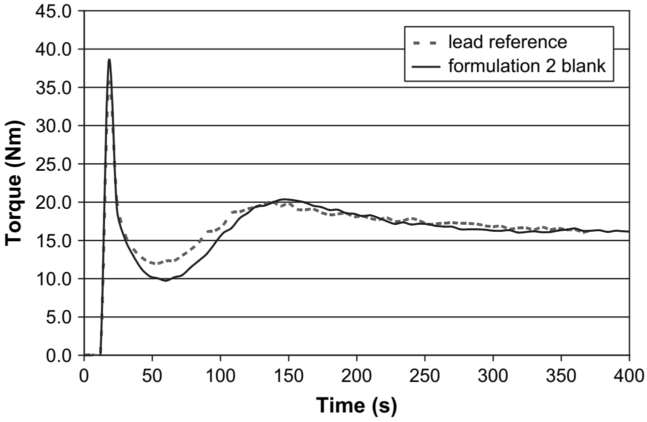

Fig. 1. Rheology of formulation 2 (190 °C) *vs.* the lead-based reference (blank).