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Additives to Prevent the Formation of Surface Defects During Poly(vinyl chloride) Calendering

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Abstract

Gas checks are visible fleck-shaped defects that occur on the surface of poly(vinyl chloride) (PVC) films during industrial calendering. Films containing these surface defects often do not meet minimum product specifications and therefore must be disposed of or recycled, resulting in increased cost and material waste. Currently, gas checks are controlled by keeping film gauge low and through trial-and-error modifications of processing parameters by calender operators. In this work, our group developed a series of chemical additives that can be blended with PVC to prevent the formation of gas check defects. We found that a series of poly(caprolactone) (PCL)-based compounds with diester linkers and alkyl chain cappers were all effective at preventing the formation of gas checks during calendering, with additive concentrations as low as 8 phr producing films with no gas checks. We found that the blends produced with our additives had higher melt viscosities than those produced with additives that do not remove gas checks, suggesting that viscosity plays an important role in preventing gas check defects.

Key words: Poly(vinyl chloride), Additives, Calendering, Surface defects, Rheology

Introduction

Calendering is an industrial process in which a polymer melt is passed through a system of heated rolls (i.e., the calender), producing a continuous film with controllable thickness [1]. This technique is commonly used in the production of poly(vinyl chloride) (PVC) films [2], which are used in a wide variety of applications including packaging, construction, and automotive manufacturing [3]. Example products made with PVC films include seepage barriers such as swimming pool and water reservoir liners, automotive seat coverings, hospital blood and intraveinous (I.V.) bags, roofing materials, and meat packaging films among many others [4, 5]. The global demand for PVC continues to grow yearly and the global market is projected to reach USD 72.0 billion by 2025, with almost a quarter of this market share belonging to films and sheets [6].

Calendered PVC films can contain a number of surface defects that reduce overall film quality, resulting in inferior products that are often rejected and discarded during the manufacturing process. One type of defect pictured in Figure 1 is called a 'gas check'. Such defects are also often referred to as specks [7], gas entrapments [8], air bubbles, air inclusions [9], or flecking [4]. They are thought to be caused by air entrapped in the calender bank, which is the area of polymer-buildup just above the narrow gap separating consecutive calender rolls, thereby producing blemishes on the surface of the film. Gas checks can occur at different size scales and appear elongated in the direction of calender flow. These visible defects frequently interfere with PVC sheet processing and can cause local reductions in film mechanical properties at the defect site, sometimes resulting in perforation of the films [9]. In addition, for many PVC film applications, such as furniture covers, automotive trim, and swimming pool liners, the appearance and surface finish of the films are crucial for their marketability. The presence of gas checks renders the films unusable and causes delays and inefficiencies in production as manufacturers must recycle or dispose of films containing these defects. Despite the prevalence of gas checks in calendered film products throughout the plastic manufacturing industry, the mechanisms of gas check evolution during film production is unknown. Therefore, in order to produce high quality films without gas checks and increase overall process efficiency while reducing waste and costs, it is essential to gain a broader understanding of this phenomenon so that measures can be taken to minimize or eliminate them.

Figure 1. Gas check defect on a PVC film.

In the very few publications that exist on controlling the formation of gas checks during calendering [8-11], there have been no studies on the use of additives to prevent gas checks. The number of gas checks in a film has previously been related to the pressure in the calender bank, which can be controlled by the nip opening (i.e., the distance between two consecutive rollers, which determines the final gauge of the film) and calender speed. It has been hypothesized that operating under conditions of smaller nip distances and higher calender speeds, and using polymer blends of higher viscosities would reduce or eliminate gas checks in the final film [9, 10]. Therefore, to avoid the formation of gas checks, current industrial practice requires calender operators to manually manipulate processing parameters such as roll speed and nip distance, and yet even the most experienced calender operators still produce films containing gas checks. Additionally, the downside of manipulating processing parameters to obtain films with satisfactory properties is that it requires operators to work within certain limits that will affect the properties of the final product. For example, it is well known that gas check defects are particularly significant when producing higher gauge, i.e. thickness, films [9]. Using a smaller calender nip distance is proven to reduce the occurrence of gas checks, however it also results in the production of films with a lower thickness. Therefore, there is currently an upper limit to the thickness of film that can be produced industrially through calendering, with industrial calenders typically only being used to produce films below ~0.01 to 0.02 in (0.25 to 0.5 mm) in thickness [11, 12]. This has led to work-arounds such as ‘plying-up’ multiple layers of low-gauge films when the production of a thicker film is required. In these cases, two or more smaller gauge films must be calendered separately and then laminated to form a defect-free, high-gauge film. Being able to calender high-gauge film in a single step would increase the efficiency of film production and improve profitability.

Our research group has previously worked extensively on the development of alternative ‘green’ plasticizers for PVC to replace environmentally-problematic phthalate plasticizers [13-20]. Poly(ε-caprolactone) (PCL) and succinate-based compounds have both shown good compatibility with PVC [21-23]. Over the course of this work, while screening a new PCL-based oligomeric additive for compatibility with PVC film formulations, we observed that the addition of this compound, even in very small concentrations, prevented the formation of gas checks entirely in calendered films produced at the lab-scale. Given the important impact that these surface defects have on the calendering industry, this observation motivated the current study to explore how gas check formation can be avoided in PVC films through the use of additives.

In this work, we report the development of a series of chemical additives that can be used in PVC formulations to prevent the formation of gas checks during the calendering process, without having to alter processing parameters. We investigated the effect of additive concentration and molecular structure (including molecular weight, diacid group type, alkyl chain length, and branching) on the formation of gas checks. We sought to explain the mechanism of gas check removal by investigating the effects of viscosity and surface tension of the individual liquid additives and overall polymer melts. To the best of our knowledge, this is the first reported study on controlling gas check formation through means of a chemical additive, rather than through modifying calendering process parameters.

Experimental

Materials

Poly(ε-caprolactone) (PCL) triol (M_n = 300, 540) (99%) was purchased from Scientific Polymer Products Inc., NY, USA. PCL triol (M_n = 900) (99%), PCL diol (M_n = 530) (99%), fumaric acid (99%), oxalic acid (98%), adipic acid (99%), 1-butanol (99%), 1-decanol (98%), *n*-heptanol (99%), and succinic acid (99%) were purchased from Sigma Aldrich, Missouri, USA. Sulfuric acid (96%) was purchased from Fisher Scientific, New Hampshire, USA. Diheptyl succinate (DHPS) was synthesized in accordance with the method previously described by our group [23]. Diisononyl phthalate (DINP) (99.8%), PVC resin (70K suspension), antimony oxide Hi-Tint (99.68%), silica (99%), stearic acid (99%), barium/zinc stabilizer (1.046 specific gravity at 20°C), and acrylic processing aid (99.8%) were supplied by Canadian General-Tower Limited (CGT Ltd.). All chemicals and reagents were used as received without further purification.

Synthesis of PCL-based additives

The syntheses of the star-shaped PCL analogs, listed in Table 1, were performed via two-step reaction in a single flask. In the first step, PCL triol (1 stoichiometric equivalent) was massed directly into a three-necked round-bottom flask followed by the diacid reagent (3 equiv.). Benzene was then added to the flask, and the mixture was stirred at room temperature for 5 minutes. Catalytic amounts of sulfuric acid (0.15 equiv.) were then added dropwise to the reaction mixture. The reaction flask was fitted with a Dean-Stark apparatus (to collect water) and a condenser, then placed in a pre-heated oil bath at 100 °C. After two hours, the mixture was cooled to room temperature. In the second step, the alcohol reagent (3 equiv.) was added to the same flask equipped with the Dean-Stark apparatus and condenser, and the mixture was re-heated to 100 °C in an oil bath. After two hours, the flask was cooled to room temperature. The mixture was then concentrated using a rotary evaporator to remove the benzene and obtain the star-shaped PCL analogs as viscous oils. The code names for the PCL analogs listed in Table 1 will be used for all succeeding discussion.

In the first step of the synthesis of the linear PCL compound, listed in Table 1, PCL diol (M_n=530, 1 stoichiometric equivalent) was massed directly into a three-necked round-bottom flask followed by the diacid reagent (2 equiv.) and catalytic amounts of sulfuric acid (0.15 equiv.), and subjected to the same conditions described above. In the second step, heptanol (2 equiv.) was added to the same flask and subjected to the same reaction conditions described above. Linear-PCL$_{530}$-Succ-C7 was obtained as a viscous oil.

Table 1. PCL-based additives

PCL-based additive name	Code	# of PCL branches	M_n (g mol^{-1})
Poly(caprolactone) triol	PCL$_{540}$-triol	3	540
Triacetate-terminated poly(caprolactone)	PCL$_{540}$-Acet	3	666
Triheptylsuccinate-terminated poly(caprolactone)	PCL$_{300}$-Succ-C7	3	897
	PCL$_{540}$-Succ-C7	3	1137
	PCL$_{900}$-Succ-C7	3	1497
Tributylsuccinate-terminated poly(caprolactone)	PCL$_{540}$-Succ-C4	3	1009

Tridecylsuccinate-terminated poly(caprolactone)	PCL_{540}-Succ-C10	3	1261
Triheptyloxalate-terminated poly(caprolactone)	PCL_{540}-Oxa-C7	3	813
Trihepylfumarate-terminated poly(caprolactone)	PCL_{540}-Fum-C7	3	891
Triheptyladipate-terminated poly(caprolactone)	PCL_{540}-Adi-C7	3	981
Diheptylsuccinate-terminated poly(caprolactone)	Linear-PCL_{530}-Succ-C7	1	928

Film Production

All blend components were weighed according to the formulations reported in Table 2, to a total mass of 300 g, and manually premixed in a bowl. Every blend contained 100 parts per hundred resin (phr) PVC 70K suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid. 'phr' is a way of measuring additive concentration in relation to the total amount of polymer resin (in this case PVC) by expressing the weight of any component relative to 100 parts per weight PVC resin. The pre-mixture was blended using a Hartek two-roll mill HTR-300 (d=120 mm, T=160°C, 45 rpm). The mill was pre-heated for a minimum of 1 hour after which time the pre-mixture was added to the mill. Mixing was performed for 7 minutes, starting from the time of film formation on the mill rolls. The milled film was cut into four pieces, each of which was fed separately into the lab-scale calender (d=180 mm, T=160-170°C, P=45 psi hps, 50 rpm). The calender nip distance was set to achieve a film gauge of 0.4 mm +/- 0.05 mm. Each of the four pieces was mixed for 1 minute on the calender before being removed. Each blend resulted in 3 or 4 sheets of film.

Table 2. Formulations for PVC film blends prepared in this study. 'Gas check additive' represents the compounds that were tested for their ability to prevent the formation of gas checks. DINP was used as the primary plasticizer in all blends other than those in which the gas check additives were added at 55 phr.

Blend Formulations					
DINP 55	**DINP 65**	**4 phr**	**8 phr**	**10 phr**	**55 phr**
55 phr DINP	65 phr DINP	55 phr DINP	55 phr DINP	55 phr DINP	---
---	---	4 phr gas check additive	8 phr gas check additive	10 phr gas check additive	55 phr gas check additive
Every blend contains: 100 phr PVC 70K suspension resin, 7 phr antimony oxide Hi-Tint, 1 phr silica, 1 phr stearic acid, 4 phr barium/zinc stabilizer, and 1 phr acrylic processing aid.					

Counting Gas Checks

A 7 cm x 7 cm grid was used to count gas checks on each film. The gas checks within the grid were manually counted from three regions on each film; the top left corner, the center, and the bottom right corner of the film. The number of gas checks counted in each area was then averaged to calculate the number of gas checks per film. This was repeated for all 4 films. The average number of gas checks was normalized per m^2 of film.

Rheology

Liquid additive viscosities were measured by steady-shear tests using a strain-controlled rheometer (Anton Paar MCR 302, Anton Paar Canada, St-Laurent, Quebec, Canada) with parallel plate geometry (25 mm plate diameter) with a CTD 540 convection oven and double gap geometry for low-viscosity samples. Shear rate was increased logarithmically from 0.1 s^{-1} to 100 s^{-1} at 25°C (±0.3°C).

Polymer melts were characterized by measuring storage modulus (G′), loss modulus (G″), damping factor (tanδ) and complex viscosity (η*), through dynamic oscillatory tests using the same rheometer described above. Parallel plate geometry (d=25 mm) and a CTD 450 convection oven were used, operated under nitrogen to prevent PVC degradation. A strain amplitude (5%) within the linear viscoelastic range was applied over a frequency range of 0.01 to 100 $\text{rad} \cdot s^{-1}$ at 170°C. Anton Paar RheoCompass^{TM} software (version 1.23, 403-Release, Anton Paar Germany, Ostfildern, Germany) was used for the analysis of all rheological results.

The PVC disks used for rheological testing were made using a hot press (Carver Manual Hydraulic Press with Watlow Temperature Controllers, Carver Inc., Wabash, IN, USA) and a corresponding mold. The calendered films were punched into 25 mm diameter circles. A stack of 8 film cut-outs was pressed into circular disks of approximately 1 mm thickness and 25 mm diameter at 165°C (329ºF). The samples were pressed at 5 tons of clamping force for 1 minute, then at 20 tons of clamping force for 4 minutes. Samples were cooled using circulating cold water at 20 tons of force, until they reached room temperature. The disks were removed from the mold and placed in a desiccator (filled with Drierite^{TM} obtained from Fisher Scientific, Montréal, QC, Canada) for a minimum of 48 hours before the evaluation of their rheological properties.

Surface tension

The interfacial tension between the liquid additives and air was measured using the pendant drop method [24]. A typical pendant drop apparatus was developed for this purpose, similar to previously reported apparatuses [25-27], and used to obtain the profile of the pendant drop. The apparatus consists of an illuminated experimental chamber with a syringe insert, a viewing system consisting of a camera and lens, and an attached computer used for data acquisition. The software used to analyze the drop profile was Image J (version 1.52q) with the open source Pendant Drop plug-in [28].

The pendant drop method requires the sample density to be known. A 25 mL specific gravity bottle pycnometer was used to measure unknown liquid densities. Three measurements were taken for each liquid, and an average value was used.

Statistics

To establish whether the additives had a significant effect on gas check removal, GraphPad Prism version 8.0 was used to perform a one-way analysis of variance (ANOVA) followed by Tukey's multiple comparison post hoc test (α=0.05) to evaluate whether there were any significant differences in gas check removal between DINP, DHPS, PCL_{540}-Acet, and PCL_{540}-Succ-C7. Similarly, to investigate the effect of additive concentration on gas check removal, a one-way ANOVA was used followed by Tukey's multiple comparison test (α=0.05).

Results and Discussion

Preventing gas check formation using additives

During the screening of our PCL-based additives for their compatibility with PVC, it was observed that blends containing PCL_{540}-Succ-C7 resulted in the production of calendered films with remarkably few surface defects, as shown in Figure 2.

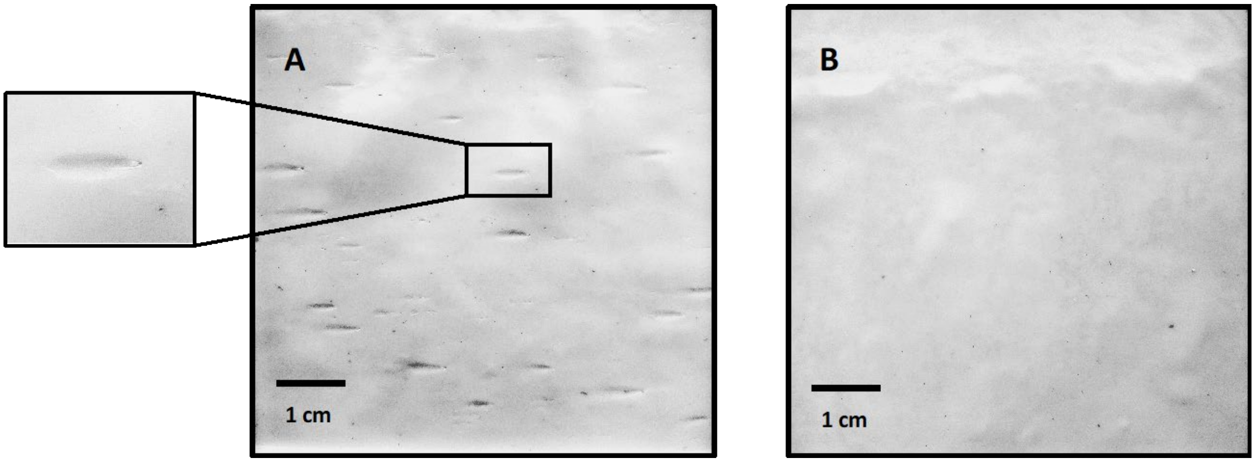
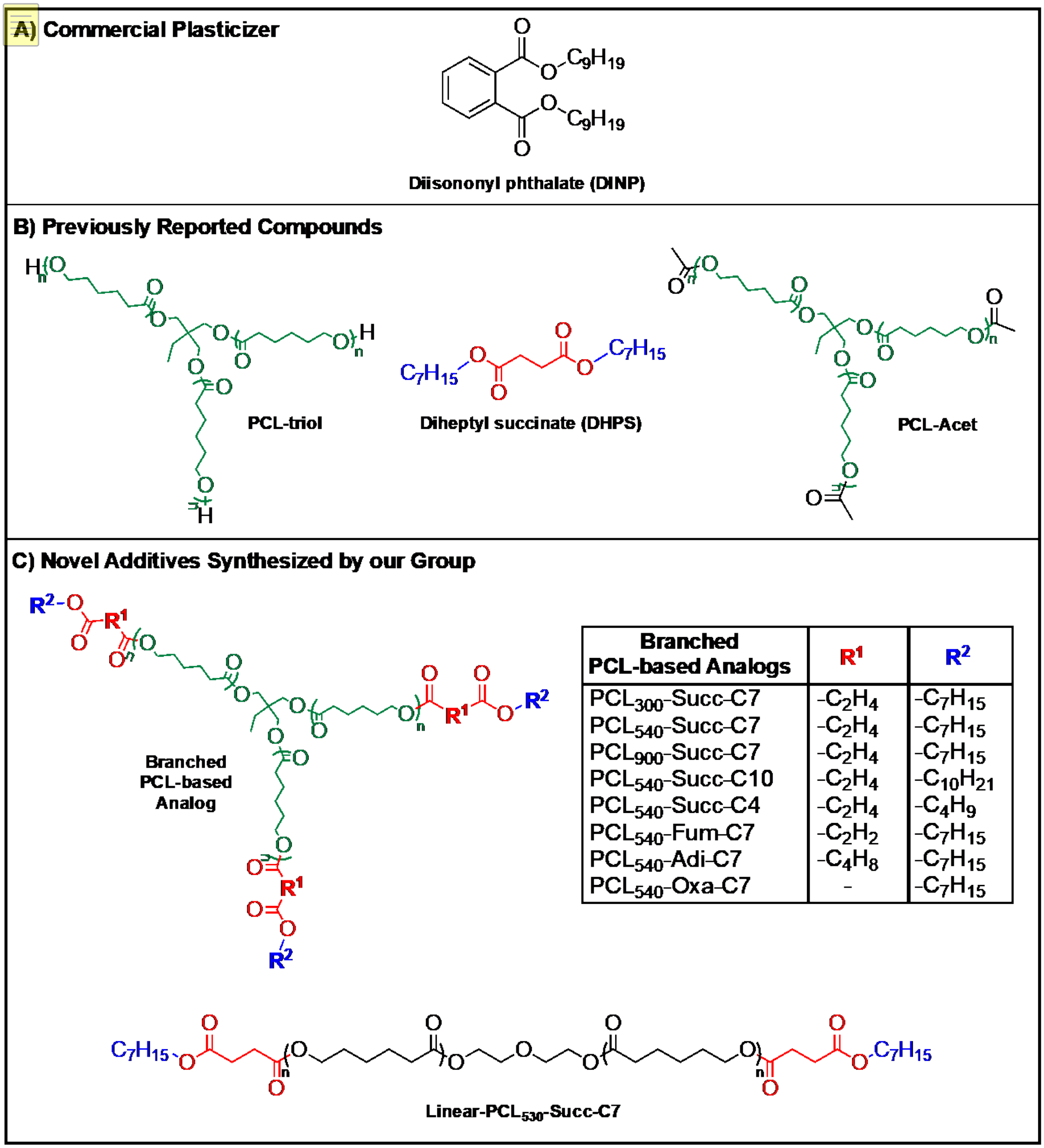


Figure 2. Calendered PVC film (A) with gas check defects (no additive used, 55 phr DINP plasticizer) and (B) without gas check defects through use of PCL_{540}-Succ-C7 as an additive at 10 phr (55 phr DINP plasticizer).

In fact, it was found that using PCL_{540}-Succ-C7 in PVC blends at 55 phr resulted in the production of calendered films with no gas checks (n=3). In contrast, the use of DINP, which is the current industrial plasticizing standard, in PVC blends at 55 phr resulted in films with an average of 5115 gas checks per m^2 of film (n=6). The chemical structures of PCL_{540}-Succ-C7 and DINP are shown in Figure 3.



Branched PCL-based Analogs	R^1	R^2
PCL$_{300}$-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL$_{540}$-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL$_{900}$-Succ-C7	$-C_2H_4$	$-C_7H_{15}$
PCL$_{540}$-Succ-C10	$-C_2H_4$	$-C_{10}H_{21}$
PCL$_{540}$-Succ-C4	$-C_2H_4$	$-C_4H_9$
PCL$_{540}$-Fum-C7	$-C_2H_2$	$-C_7H_{15}$
PCL$_{540}$-Adi-C7	$-C_4H_8$	$-C_7H_{15}$
PCL$_{540}$-Oxa-C7	-	$-C_7H_{15}$

Figure 3. Chemical structures of compounds investigated for their ability to remove gas checks: (A) current industrial standard for film plasticization (DINP), (B) previously reported compounds used as 'building blocks' for our novel additives, (C) novel PCL-based analogs synthesized in this study.

After the initial observations that our parent molecule eliminated gas check surface defects, we sought to investigate which of the molecular components or 'building blocks' (Figure 3b) that make up PCL$_{540}$-Succ-C7 were responsible for the effect. In line with this, two separate PVC blends were prepared: one containing diheptyl succinate (DHPS) and one with PCL$_{540}$-triol, both at 55 phr. A one-way ANOVA test followed by a Tukey post-test was performed to determine whether there was any statistically significant change in the number of gas checks for blends made with the building blocks compared to the parent compound. It can be seen in Figure 4 that DHPS, one of the building blocks of PCL_{540}-Succ-C7, was not able to prevent the formation of gas checks when blended with PVC at 55 phr, with an average of 6241 gas checks per m^2 of film, showing no decrease compared to DINP ($P>0.05$). PCL_{540}-triol was found to be incompatible with PVC which was evidenced by several observations including: (i) significantly delayed film formation rate on the mill compared to other blends; (ii) extremely poor quality of the final film, which was very brittle, with many cracks and holes, and exhibited similar physical properties to unplasticized PVC; (iii) the material coming off the mill was covered in a thick oily layer, further suggesting the immiscibility of PCL_{540}-triol with PVC. Therefore, we added acetate groups to cap the ends of the PCL_{540}-triol, producing PCL_{540}-Acet, a known compound that is compatible with PVC [22, 29]. Due to the similarity in structure between PCL_{540}-Acet and PCL_{540}-triol, PCL_{540}-Acet was used as a compatible substitute to investigate the contribution of the PCL_{540}-triol group to gas check removal. Upon blending PCL_{540}-Acet with PVC at 55 phr, it was observed that film formation occurred during regular time frames, resulted in no oily residue on the film, and the film was flexible, thereby confirming its compatiblity with PVC, as reported by Choi et al. [29]. However, similarly to DHPS, PCL_{540}-Acet did not remove gas checks, producing films with an average of 6122 gas checks per m^2 of film (Figure 4). Taken together, these results suggest that the observed phenomenon of gas check-free films had arisen due to the unique chemical structure of PCL_{540}-Succ-C7 alone, and not due to its individual constituents.

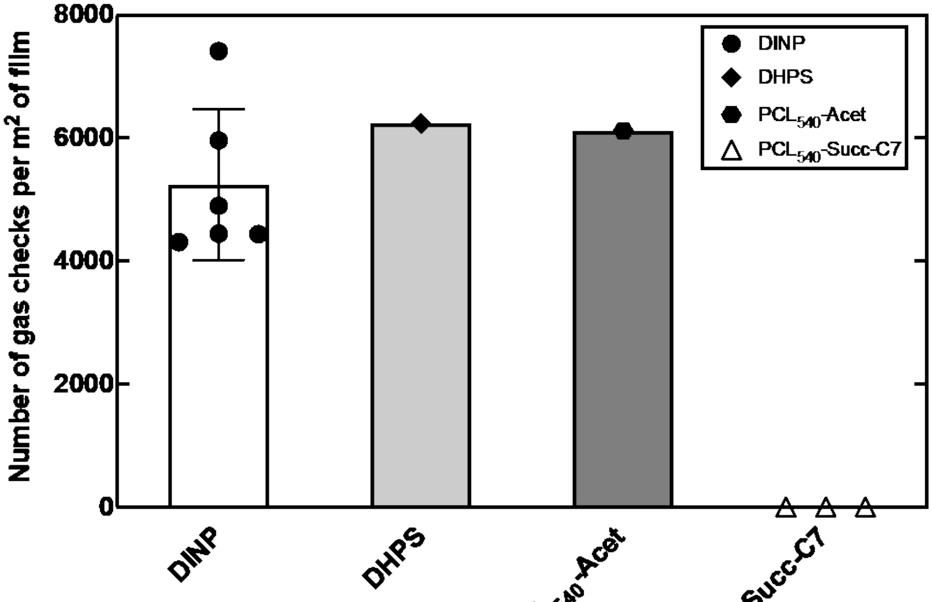


Figure 4. Number of gas checks per m^2 of calendered film with DINP, DHPS, PCL_{540}-Acet and PCL_{540}-Succ-C7 blended at 55 PHR. Film gauge was 0.4 mm +/- 0.05 mm for all films.

Additive concentration

To investigate the effect of PCL_{540}-Succ-C7 concentration on eliminating gas checks, we blended the additive at increasing concentrations from 4 phr to 55 phr. All blends (except for the 55 phr PCL_{540}-Succ-C7 blend) contained 55 phr DINP as a primary plasticizer with PCL_{540}-Succ-C7 added at concentrations of 4 phr, 8 phr, and 10 phr (Figure 5). A one-way ANOVA and Tukey post-test were performed to determine whether the observed reduction in gas checks with concentration was statistically significant. It was found that at 4 phr there was no significant effect of the PCL_{540}-Succ-C7 on gas check removal ($P>0.05$), with an average of 4807 gas checks per m^2 counted on the film. At 8 phr, there was a significant reduction in the number of gas checks compared to the DINP control and 4 phr films, with an average of 877 gas checks per m^2 ($P<0.05$, $P=0.0013$ and $P=0.0098$, respectively). There was no statistically significant difference in the number of gas checks between the 10 phr and 55 phr films ($P>0.05$), with virtually no gas checks in any of the films. Therefore, it was established that PCL_{540}-Succ-C7 could be used as a processing aid at concentrations of 10 phr and above in conjunction with a primary plasticizer to effectively remove gas checks.

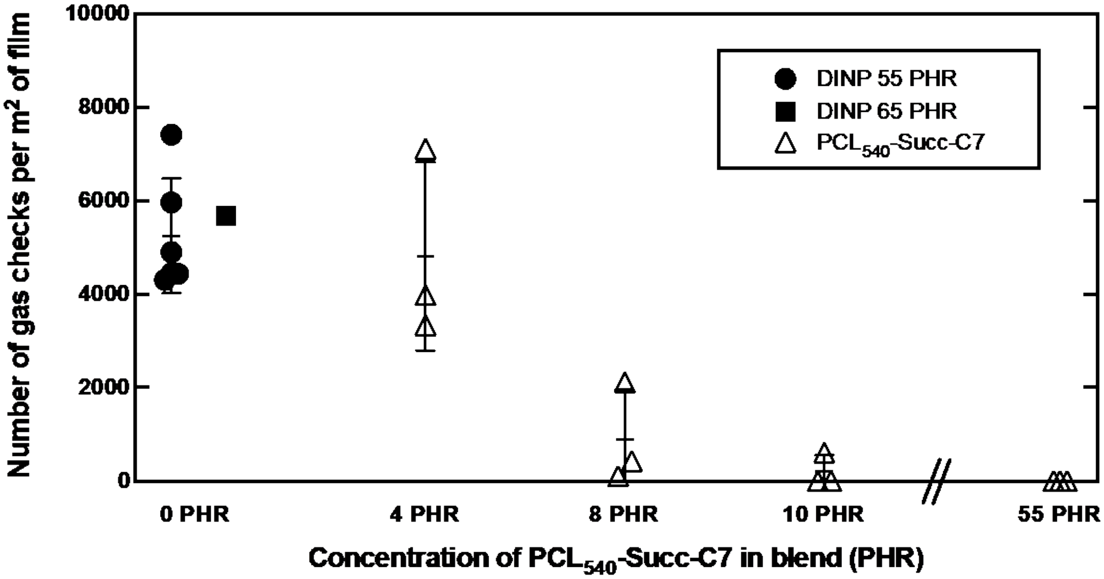


Figure 5. Effect of concentration of PCL-Succinate-C7 on gas check removal.

A film with 65 phr DINP was also calendered for comparison, in order to determine whether the simple addition of an extra 10 phr of additive could be the reason for gas check removal. It was found that the 65 phr DINP film still contained an average of 5680 gas checks per m^2 of film (Figure 5). Therefore, the observed effects in blends where PCL_{540}-Succ-C7 was incorporated as an additive are due to PCL_{540}-Succ-C7 specifically rather than the presence of extra compound.

Molecular structure

Having demonstrated the efficacy of PCL_{540}-Succ-C7 in preventing gas checks at concentrations as low as 10 phr, while its constituents showed no effects, we wanted to further investigate the structural features responsible for this observed effect. We aimed to perform a structure-function analysis by synthesizing a small library of structural analogs. A total of 9 novel additives were synthesized, shown in Figure 3c. A series of star-shaped and linear PCL analogs were made using commercially available PCL-triols (M_n = 300, 540, 900) and PCL-diol (M_n = 530) as building blocks to study the effect of molecular weight and degree of branching. Several diacids were screened as ester linkers. 1-butanol, *n*-heptanol, and 1-decanol were screened as end-capping agents to study the effect of carbon chain length. The performance of these additives in preventing gas checks was compared with previously known compatible additives: DINP, PCL_{540}-Acet, and DHPS.

The PCL-triol oligomer that we used to synthesize PCL_{540}-Succ-C7 had an average molecular weight (M_n) of 540 g/mol. PCL-triols with identical structures (Figure 3b) but with different M_n of 300 g/mol and 900 g/mol were used to synthesize PCL_{300}-Succ-C7 and PCL_{900}-Succ-C7. We found that both PCL_{300}-Succ-C7 and PCL_{900}-Succ-C7 prevented the formation of gas checks in calendered films completely at 55 phr with no difference in effetiveness at 4 phr, 8 phr, and 10 phr compared to PCL_{540}-Succ-C7 (see Supporting Information, Figure S1). Therefore, we conclude that at values between 300 and 900 g/mol, the molecular weight of the PCL-triol oligomer core had no effect on gas check removal during calendering.

Next, the central PCL-triol (with an M_n of 540 g/mol) was kept constant, while the diacid group was varied from a succinate group to a fumarate, oxalate, or adipate group, shown in red in Figure 3c. All of the new molecules that were synthesized (PCL_{540}-Fum-C7, PCL_{540}-Oxa-C7 and PCL_{540}-Adi-C7) completely removed gas checks at 55 phr, as shown in Table S1 of the Supporting Information. Therefore, between the analogs tested, the type of diacid did not influence their activity.

Previous studies have shown that succinate and maleate performance as plasticizers was correlated with the alkyl chain length of the molecules [16]. Optimal performance was observed at chain lengths of six to eight carbons, with decreasing performance noted at ten carbons. Thus, the chain length of the alkyl group at the end of our PCL molecule was modified to determine whether chain length also has an effect on gas check removal. The alkyl chain length was modified from its original C_7 (heptanol) to C_4 (butanol) and C_{10} (decanol), as shown in blue in Figure 3, while keeping the PCL_{540}-triol core and succinate elements constant. This resulted in the synthesis of two additional analogs, namely PCL_{540}-Succ-C4 and PCL_{540}-Succ-C10, both of which removed all gas checks at 55 phr and behaved similarly to PCL_{540}-Succ-C7 (see Supporting Information, Table S1). Therefore, we conclude that within this range, alcohol chain length did not influence the prevention of gas check formation.

The final structural element that was investigated was the role of branching in the additive molecule. All of the aforementioned structures, including the original PCL_{540}-Succ-C7 have a 3-armed star shaped structure (Figure 3c). We synthesized a new linear molecule from a PCL-diol core, keeping the succinate diacid and heptanol end groups constant (Figure 3c). We observed that the Linear-PCL_{530}-Succ-C7 removed all gas checks at 55 phr, similarly to the star-shaped molecules, suggesting that branching was not the reason for gas check removal (see Supporting Information, Table S1).

Thus, it was concluded that a molecular arrangement consisting of a PCL core structure with an attached diacid and alcohol effectively prevented gas check formation, whereas, remarkably, each component on its own did not. We discovered a series of additives with varying molecular weights of the PCL central group, different acid linkers (succinic, fumaric, adipic and oxalic) and alcohol capping units of varying lengths (n-butyl to n-decyl) that are effective at removing gas checks during calendering when blended with PVC.

Viscosity

We sought to investigate whether the inclusion of the ester linkage along with the alkyl chain and PCL core altered the viscosity of our compounds, which could produce favorable pressures to remove gas checks. Bourgeois et al. previously reported that the occurrence of gas checks in calendered film was related to the presence of air inclusions in the calender bank, which was in turn related to pressure [9]. They found that at pressures below 120 bar the calender bank contained air inclusions in the backflow and distributed along the flow streams, which corresponded to gas check defects in the final calendered sheets. At pressures above 120 bar, only a few microbubbles were observed in the calender bank, and the corresponding PVC sheets were found to be free of gas checks. Pressure in the calendar bank is related to shear rate and consequently melt viscosity [30] and, hence, Bourgeois et al. hypothesized that calendering under conditions of high calender speed, small nip opening, and high apparent viscosity of the polymer would avoid the formation of gas check defects. Since we maintained constant calender speed and nip opening in the production of all our films yet saw a significant decrease in the number of gas checks depending on our film composition, we sought to investigate the effect of viscosity on gas check removal.

As a first step, the viscosities of our novel additives were measured at 25°C, shown in Figure 6. It can be seen that the viscosities of the additives that remove gas checks when blended with PVC are higher than those of the additives that do not remove gas checks. DINP, DHPS, and PCL_{540}-Acet (which do not remove gas checks) have viscosities that range from approximately 10 cP to 115 cP. The viscosities of the PCL-based additives (which all remove gas checks) range from approximately 315 cP for Linear-PCL_{530}-Succ-C7 to 3100 cP for PCL_{540}-Fum-C7. This trend suggests that viscosity plays a role in the additives' ability to prevent gas checks from forming. It is worth noting that PCL_{540}-triol, which was found to be incompatible with PVC, has a high viscosity. Despite having a viscosity within the 'favorable' range, it is not a suitable additive to remove gas checks since it does not blend well with PVC and drastically reduces film quality, making the resulting product unusable.

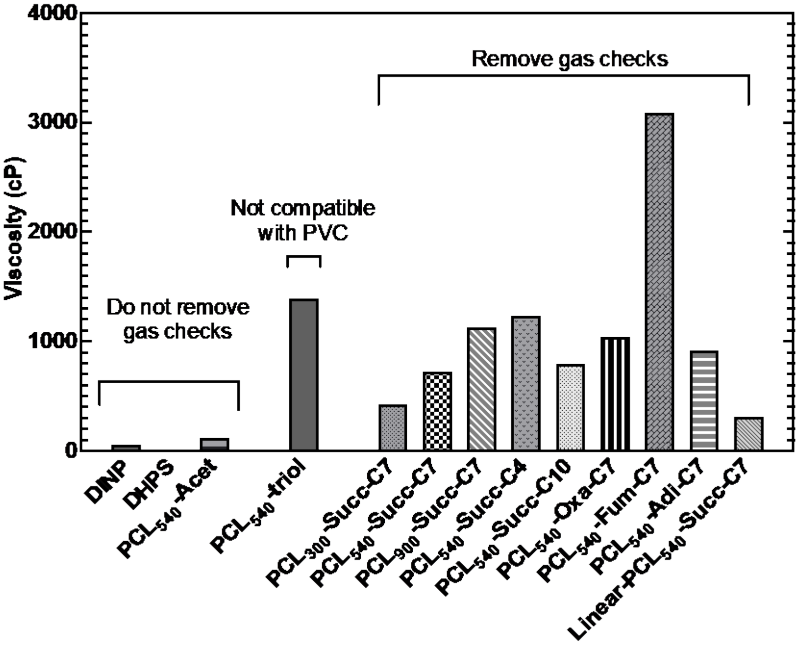


Figure 6. Liquid viscosities of additives at 25°C. Steady-shear measurements were taken between 0.1 and 100 s^{-1}.

We subsequently performed rheological tests, shown in Figures 7 and 8, on the PVC blend melts at 170°C to see if the melt viscosities also corresponded with the prevention of gas check formation. Figure 7 shows the complex viscosities of blends made with additives that do not prevent gas checks. It can be seen that DHPS has the highest complex viscosity of this group. Figure 8 shows the complex viscosities of blends made with additives that prevent gas checks. It is notable that all of these blends have higher complex viscosities when compared to the blends that do not prevent gas checks, using DHPS as a visual comparison. G′, G″, and tanδ also followed a similar trend and are shown in Figures S2-S7 of the Supporting Information. Both G′ and G″ were higher for the blends that were found to prevent gas checks. The melt rheology of the blends further supports our hypothesis that these additives alter the apparent viscosity of the polymer blends during calendering, resulting in higher pressures in the calender bank, thus preventing gas check formation in films produced under the same processing conditions of temperature, nip distance, and roller speed.

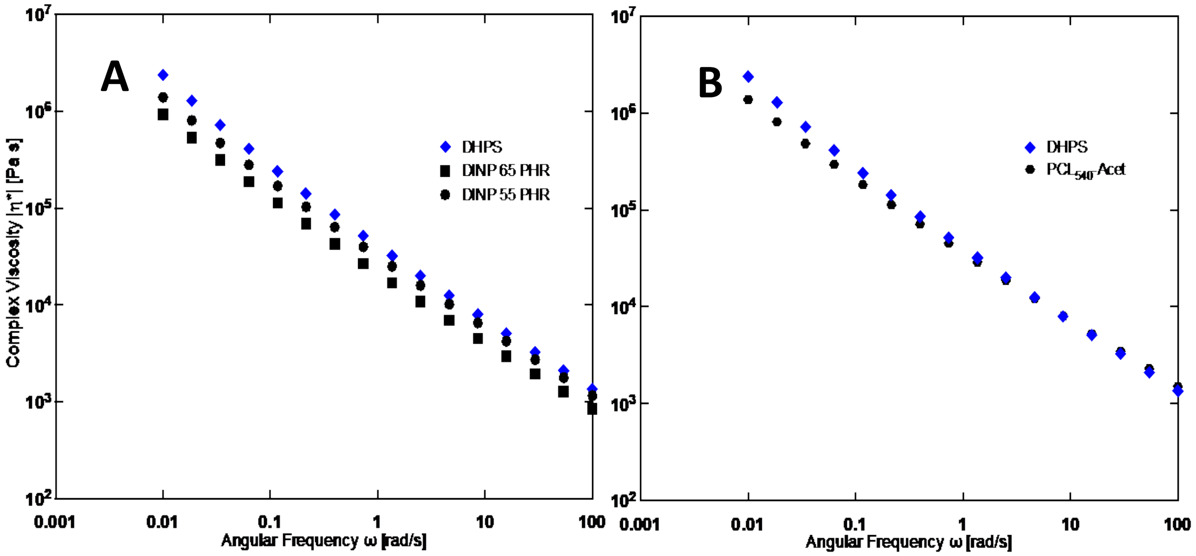


Figure 7. Complex viscosity as a function of frequency at 170°C for PVC melts made with additives that do not prevent gas check formation: (A) DINP at 55 and 65 phr and (B) PCL$_{540}$-Acet at 55 phr. All additives are shown in comparison to DHPS at 55 phr (shown in blue) which also does not prevent gas check formation.

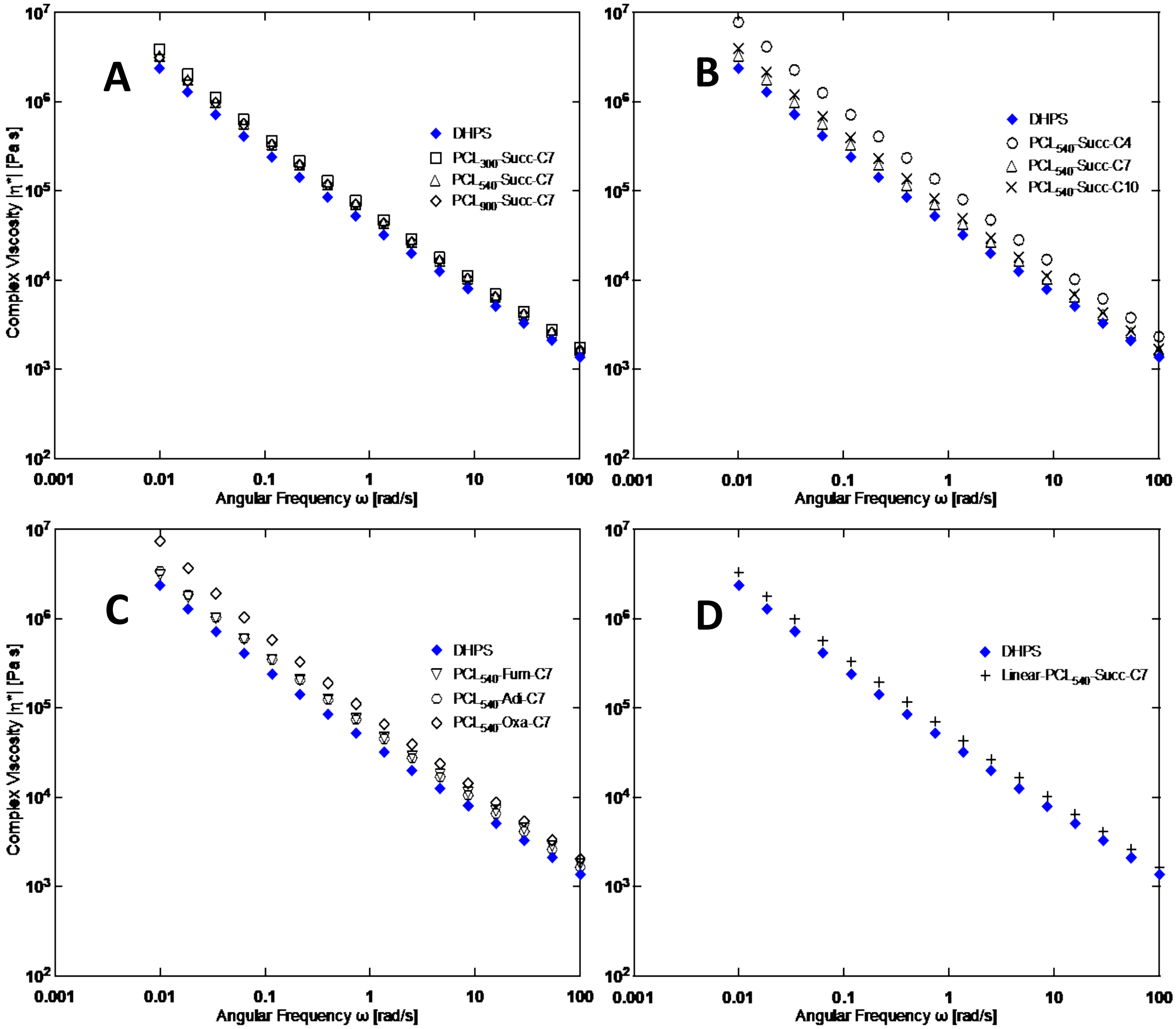


Figure 8. Complex viscosity as a function of frequency at 170°C for PVC melts made with additives that effectively prevent gas check formation: (A) PCL$_{300}$-Succ-C7, PCL$_{540}$-Succ-C7, PCL$_{900}$-Succ-C7 (B) PCL$_{540}$-Succ-C4, PCL$_{540}$-Succ-C7, PCL$_{540}$-Succ-C10 (C) PCL$_{540}$-Fum-C7, PCL$_{540}$-Adi-C7, PCL$_{540}$-Oxa-C7 (D) Linear-PCL$_{530}$-Succ-C7. All curves are shown in comparison to DHPS (shown in blue, which does not prevent gas check formation). All additives were blended at 55 PHR.

Surface Tension

Due to the prominent influence of surface tension in the bubble dissolution model developed by Kontopoulou et al. [31], we measured the surface tension of two of our additives, DHPS (an additive that does not prevent gas checks) and PCL$_{540}$-Succ-C7 (an additive that prevents gas checks), in air at 25°C. DHPS was found to have a surface tension of 30 dynes/cm, and PCL$_{540}$-Succ-C7 was found to have a surface tension of 33 dynes/cm. Similarly to Bourgeois et al. [9], Kontopoulou et al. [31] reported that applying higher pressures accelerated bubble dissolution, in this case due to a hypothesized increased driving force for diffusion. Based on their model, they concluded that the factors that significantly affect bubble dissolution are initial bubble size, surface tension, and air concentration in the melt. Based on the similarity in our measured surface tension values between an additive that does not prevent gas checks and one that does, we suggest that the effect of our additives on preventing gas check formation is more strongly influenced by viscosity than surface tension. In altering melt viscosity, and thus pressure, during calendering, we believe that less air becomes entrapped in the polymer melt during processing. Less entrapped air would lead to fewer defects caused by the escaping air. This is consistent with the findings reported by Kontopoulou et al. [31] that correlate air concentration in the melt with bubble dissolution.

Conclusion

A series of PCL-based additives was developed that can be used to prevent the formation of gas check surface defects during PVC calendering. We found that combining a PCL oligomer core with a diacid linker and alcohol cap consistently produced additives capable of removing gas checks for a range of PCL molecular weights, acid types, and alkyl chain lengths. Viscosity was found to be an important factor in preventing gas check formation; that is, all of the additives that were successful in preventing gas checks had higher viscosities than additives that did not prevent gas check formation. Additionally, we showed that at higher temperatures typically used during processing polymer blends made with additives that prevented defects had higher complex viscosities than blends made with additives that did not prevent defects. Interestingly, it was found that PCL-triol, a high-viscosity oligomer, was not a suitable additive for gas check removal, indicating that viscosity alone is not enough to prevent these defects. Good compatibility with PVC is also an essential feature of any gas check removal additive. Preliminary surface tension mesurements suggested that the influence of bulk viscosity in removing gas checks is stronger than the influence of surface tension-related diffusion. Further investigation of these additives for their plasticizing performance will be important to determine whether incorporating them into blends at low concentrations with a different primary plasticizer is preferable or whether their performance would allow them to be used independently as plasticizers that can also remove defects. We have shown that, as far as removing gas checks is concerned, both of these options would be viable since defect removal was observed at concentrations as low as 10 phr.

References

[1] Z. Tadmor, C.G. Gogos, *Principles of Polymer Processing*, Wiley, (2013).
[2] *Modern Plastics Encyclopedia*, McGraw-Hill, (1991).
[3] W.V. Titow, *PVC Plastics: Properties, Processing, and Applications*, Springer Netherlands, (2012).
[4] M.V. Titow, *PVC Technology*, Springer Netherlands, (2012).
[5] F. Pardos, R.T. Limited, *Plastic Films: Situation and Outlook : a Rapra Market Report*, Rapra Technology Limited, (2004).
[6] M.R. Future, (2020), pp. 140.
[7] A. Schnabel, O. Hissmann, *Kunststoffe*, **97**, 104-111 (2007).
[8] J. Frydel, D. Mewes, S. Luther, R.H. Schuster, *Kautsch. Gummi Kunstst.*, **61**, 286-293 (2008).
[9] J. Bourgeois, J. Agassant, *J. Macromol. Sci., Part B: Phys.*, **14**, 367-385 (1977).
[10] S. Luther, D. Mewes, *Polym. Eng. Sci.*, **44**, 1642-1647 (2004).
[11] F.H. Ancker, U.S. Patent, 3,658,978 (1972).
[12] M.G. Rosato, D.V. Rosato, *Concise Encyclopedia of Plastics*, Springer US, (2012).
[13] R. Jamarani, H.C. Erythropel, J.A. Nicell, R.L. Leask, M. Marić, *Polymers*, **10**, 834 (2018).
[14] H.C. Erythropel, P. Dodd, R.L. Leask, M. Maric, D.G. Cooper, *Chemosphere*, **91**, 358-365 (2013).
[15] H.C. Erythropel, M. Maric, D.G. Cooper, *Chemosphere*, **86**, 759-766 (2012).
[16] H.C. Erythropel, S. Shipley, A. Börmann, J.A. Nicell, M. Maric, R.L. Leask, *Polymer*, **89**, 18-27 (2016).
[17] R. Jamarani, H.C. Erythropel, D. Burkat, J.A. Nicell, R.L. Leask, M. Maric, *Processes*, **5**, 43 (2017).
[18] D.G. Cooper, O.A. Mamer, M. Maric, J.A. Nicell, *Chemosphere*, **77**, 258-263 (2009).
[19] J. Kastner, D.G. Cooper, M. Marić, P. Dodd, V. Yargeau, *Sci. Total Environ.*, **432**, 357-364 (2012).
[20] A. Kermanshahi Pour, O.A. Mamer, D.G. Cooper, M. Maric, J.A. Nicell, *J. Mass Spectrom.*, **44**, 662-671 (2009).
[21] G. Shi, D.G. Cooper, M. Maric, *Polym. Degrad. Stab.*, **96**, 1639-1647 (2011).
[22] W. Choi, J.W. Chung, S.-Y. Kwak, *ACS Appl. Mater. Interfaces*, **6**, 11118-11128 (2014).
[23] B.M. Elsiwi, O. Garcia-Valdez, H.C. Erythropel, R.L. Leask, J.A. Nicell, M. Maric, *ACS Sustainable Chem. Eng.*, (2020).
[24] J.D. Berry, M.J. Neeson, R.R. Dagastine, D.Y. Chan, R.F. Tabor, *J. Colloid Interface Sci.*, **454**, 226-237 (2015).
[25] E. Arashiro, N. Demarquette, *J. Appl. Polym. Sci.*, **74**, 2423-2431 (1999).
[26] E.Y. Arashiro, N.R. Demarquette, *Mater. Res.*, **2**, 23-32 (1999).
[27] J.C. Moreira, N.R. Demarquette, *J. Appl. Polym. Sci.*, **82**, 1907-1920 (2001).
[28] A. Daerr, A. Mogne, *J. Open Res. Softw.*, **4**, (2016).
[29] W. Choi, J.W. Chung, S.Y. Kwak, *J. Polym. Sci., Part A: Polym. Chem.*, **53**, 1134-1142 (2015).
[30] S.L. Dotson, L.B. Simmons, *J. Vinyl Addit. Technol.*, **1**, 76-83 (1995).
[31] M. Kontopoulou, J. Vlachopoulos, *Polym. Eng. Sci.*, **39**, 1189-1198 (1999).