GENERAL SYMPOSIA | FUNCTIONAL ADDITIVES AND REACTIVE PROCESSING

Thin Films from Modified Poly(Glycolic Acid) with Excellent Water Vapor Barrier

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Abstract: Commercial biodegradable polymers that combine high oxygen and water vapor barrier properties are scarce. In the packaging industry multilayer materials are usually used to achieve the barrier requirements, however they are usually not recyclable and will not biodegrade when discarded. The outstanding barrier properties of poly(glycolic acid) (PGA) make it an excellent candidate for a biodegradable oxygen and water vapor barrier packaging material. At the same time, its processability into films using standard converting equipment is a major challenge. Low melt strength, high processing temperatures, and fast crystallization at the die limit its use in conventional packaging applications. Chain extenders are typically used to improve the melt strength of polymers and thereby the overall processability, however they may affect the intrinsic barrier properties of the material. This work studied the reactivity of PGA with different chain extenders. It found that by using less than 2% reactive chain extenders the processability of PGA could be highly improved while keeping the intrinsic barrier properties of the material. After compounding PGA with the chain extenders Joncryl and carbodiimide, stable flat sheet extrusion of the material was possible resulting in sheets thinner than 10 μm. The multidirectional stretchability of the melt was improved, showing an increase in the melt strength of the polymer. Barrier properties were measured, and it was found that the water vapor transmission rate (WVTR) is not affected by the addition of the chain extender. This improvement in the processability of PGA offers a promising solution for biodegradable high-barrier packaging materials.

Keywords: Poly(glycolic acid) (PGA), Barrier properties, Chain Extenders, Thin Films

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Introduction

Poly(glycolic acid) (PGA) is a remarkably interesting polyester for film and coating applications due to its excellent barrier properties and its fast biodegradability in natural environments [1,2]. In recent years more cost-effective production technologies were installed at an industrial level which resulted in a reduction in market price. PGA is now an interesting material for cost-competitive markets such as packaging. As a result, multiple PGA producers have appeared in the commodity market [3,4]. In addition, innovative technologies have been developed to derive PGA from biomass, which aids the decoupling of plastic products and packaging from fossil resources [5].

However, PGA's processability in conventional thermoplastic equipment is a challenge. PGA has a high melting point; therefore, it needs to be processed at temperatures above 200°C [6]. It also has high crystallinity [7] and poor melt strength [8]. These properties limit the production of films and sheets from this material with conventional processing equipment.

Copolymerization of glycolic acid, for example with lactic acid, offers the possibility to reduce processing temperatures. It also influences the crystallinity of the polymer which, in turn, improves processability. However, when changing the molecular structure, the gas and water vapor barrier properties (highly dependent on the crystallinity) will be reduced. Even though barrier properties reported for these copolymers can be comparable to other bench market polymers, they are outperformed by the PGA homopolymer [7].

Mixing polyesters with other polymers is a conventional approach that is used to improve processability and/or mechanical properties. However, there are practical and theoretical risks in this approach. One potential issue is the possible de-mixing of the blend due to non-compatibility of the polymers. Another challenge, specific to PGA, is that few other biodegradable polymers can be processed at its high processing temperature. The alternative of blending PGA with non-biodegradable polymers will completely negate the unique selling point of the material. The final and most critical issue is the potential negative effect of blending on the excellent intrinsic barrier properties of the PGA. Until now, studies on PGA enhancement have focused on improving mechanical properties without looking into the effect on the barrier properties [9-11].

Chain extenders are known to improve polyesters' processability. A chain extender will connect the different polymer chains by reacting with the end-groups. In the case of PGA, it is expected that there are hydroxyl and/or carboxyl end-groups available for reacting. Literature show that isocyanate-based chain extenders in amounts up to 3 wt.% are more efficient than methacrylate-based ones due to differences in reactivity, resulting in improved thermal stability [8]. Furthermore, chain extenders have been proven to reduce hydrolytic degradation, resulting in improved material and product lifetime [12]. To obtain more insights on the effect of chain extenders on both processability and functionality, this study investigates five different chain extenders for PGA. Results on processability into thin sheets and barrier properties of the resulting products are reported.

Materials and Methods

This research is conducted in two phases: phase 1 in 2021 with virgin PGA (V-PGA) with MFI of 18 g/10 min, and phase 2 in 2023 with the same batch PGA aged over time (A-PGA) with MFI of 66 g/10 min. In the meantime, PGA is stored in a vacuum sealed bag at 4°C. PGA Vytal J116 with batch code 20210515-G-0304 supplied by PJChem is used in both phases. Carbonyl bis caprolactam (CBC) supplied by DSM, Pyromellitic dianhydride (PMDA) supplied by Sigma Aldrich, Joncryl ADR-4400 and Joncryl ADR-4468 supplied by BASF, and Carbodiimide Nexoll CDI/W supplied by Euro-Chemicals are used as chain extenders. Zinc stearate supplied by Sigma Aldrich is used as catalyst. V-PGA, A-PGA and their compounds are dried at 120°C in a Gerco dry-air desiccant dryer. All additives are dried at 40°C in a vacuum oven for at least 4 hours prior to any type of processing.

A Haake Rheomix Polylab kneader is used to screen the reactivity with different agents. The kneader is set to 225°C. The PGA is kneaded for 5 to 7 minutes (ensuring all material is melted), then the additives are added and the mixture is kneaded for a total of 30 minutes. The following amounts are added to V-PGA for the reactivity study: 0.5 wt.% CBC, 0.5 wt.% PMDA, 0.2, 0.5 wt.% Joncryl ADR-4400, 0.2, 0.5, and 1wt.% Joncryl ADR-4468.

The compounding is performed on a twin screw Berstorff ZE 25*40D extruder at a throughput of 5k g/h, 300 rpm screw speed with the following temperature profile: 20/80/160/180/190/190/200/205/205/205/215°C. V-PGA extruded only once without additives (VE-PGA) is also analyzed. The following compounds are made V-PGA with 0.2 wt.% and 0.5 wt.% Joncryl ADR-4468 (V-0.2J and V-0.5J respectively), both with and without zinc stearate (V-0.2JZ, V-0.5JZ). A-PGA is compounded with 0.5 wt.% Joncryl ADR-4468 (A-0.5J) and 1.5 wt.% carbodiimide (A-1.5C). Melt flow index (MFI) of the pure and produced compounds is measured according to ISO-1133 with Zwick MFLOW MFI. All samples are measured using a standard weight of 2.16 kg and a temperature of 230°C.

Sample sheets are produced on a Dr. Collin tech line A20T single screw extruder equipped with a 150 mm wide adjustable slit die. The line extruder is run at 80 rpm with a temperature profile per zone of 210/233/240°C and die temperature per section of 225/229/230°C.

Water vapor transmission rate (WVTR) is measured according to ASTM method E96-16 following the desiccant method: silicate gel inside the cup, store cup with sample in room with higher relative humidity. Samples are kept under controlled conditions (climate chamber) and weighed with analytical balance (3-digit number). Weight gain or weight loss are plotted against time. Linear regression analysis allows the results to be expressed in g (water)/m^2 (foil) day or corrected to 100 μm foil thickness. WVTR is applied at the temperature and specific relative humidity gradient shown in the data.

Oxygen transmission rate (OTR) is measured according to ASTM D3985-17 for dry condition and ASTM F1927-14 at a specific relative humidity using an Ametek Mocon machine. Automatic controlled relative humidity testing range is between 0 and 90% ± 3%. Standard film test area ($50cm^2$) and film thickness: up to 3 mm. Result are expressed in $mlO2/m^2$. day.bar and corrected to 100μm thickness.

Results and Discussion

Reactivity of Poly(glycolic acid)

Kneading experiments are performed to verify the reactivity of the selected additives with PGA at the chosen temperature. Amounts chosen are based on known amounts typically used for PET, because of the similar polymer end-groups and the high processing temperature. For the V-PGA evaluated without additives, it was observed that at 225°C, 5 minutes are needed for complete melting of the polymer and homogeneous viscosity distribution. This value is set as the minimum processing time to study the reactivity with the different additives.

Chain extenders used are known to react either with the carboxyl or with the hydroxy groups available in the PGA. The functional epoxide groups of Joncryl react with the carboxyl groups of PGA polymers. In the case of carbodiimide, the carboxyl group will directly form an amide bond with the primary or secondary amine. CBC and PMDA connect to the hydroxyl groups, CBC as a monofunctional chain extender and PMDA as a multifunctional.

From the executed tests, it can be derived that additives reacting with carboxyl end-groups are the most efficient when adding them in the same amount (1%). Figure 1 shows the torque measured at the kneader for two trials with 1 wt.% PMDA and 1 wt.% Joncryl ADR-4468. When adding 1 wt.% Joncryl ADR-4468, a huge increase in torque at around 10 minutes (7 times higher than the molten PGA) is observed. In contrast, for PMDA a decreasing line is observed; this shows that by adding 1 wt.% PMDA at this temperature, no reaction takes place. After 30 minutes of kneading, the torque with Joncryl is twice as high as the initial molten PGA, despite the expected thermal degradation (torque decline with time). It was suspected that 1 wt.% of this type of Joncryl might be too high to process the compound into sheets via sheet extrusion due to abundant crosslinking. Therefore, lower amounts are used for further experiments. Enough reactivity is seen when adding 0.2 and 0.5 wt.%, but significantly lower torques are observed. The reactivity is lower because less amounts of molecules with reactive groups are available.

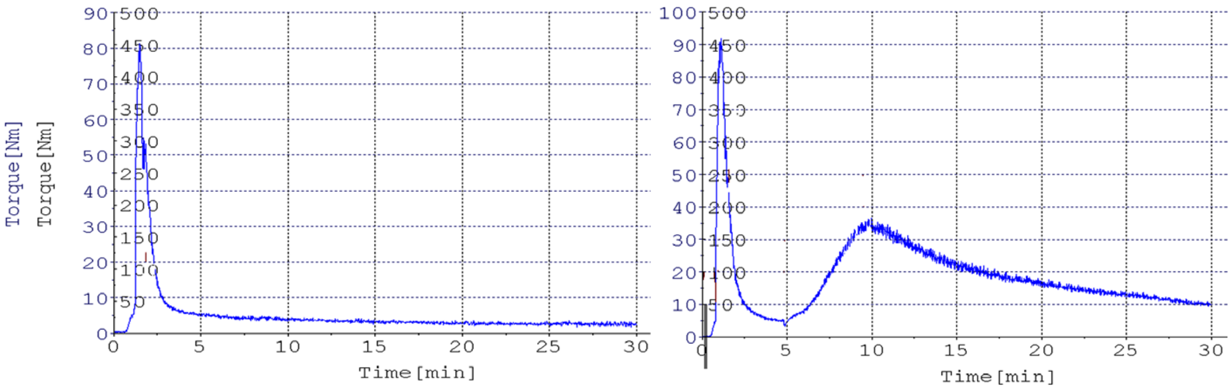

Figure 1. Torque (Nm) vs time (min) as measured by the kneader. Left: PGA with 1 wt.% PMDA and no reaction, right: PGA when 1wt.% Joncryl ADR-4468 is added.

Amounts of 0.2 wt.% and 0.5 wt.% of Joncryl ADR-4400 did not show any reactivity with the PGA. Joncryl ADR-4400 has only 5 functional epoxide groups, while Joncryl ADR-4468 has 9 epoxide groups available for reacting. Apparently, these amounts of Joncryl ADR-4400 are not enough.

When adding 0.5wt.% CBC or PMDA, no increase in torque was observed. This shows that no reaction took place at the temperature and amounts used. It could be either that not enough hydroxyl groups are available or that the required reaction temperatures are higher than the used temperature. PMDA and CBC are typically used in the chain extending of PA6 and PET, usually processed at higher temperatures, above 230°C [6]. These tests were performed at a maximum temperature of 225°C to avoid extensive thermal degradation of PGA, while reducing the viscosity enough to allow mixing.

For polylactic acid, it is well known that zinc stearate can be used as a catalyst in combination with Joncryl to accelerate its reaction time. Trials were done to confirm if the use of this catalyst will also work with PGA. When adding 0.5 wt.% Joncryl ADR-4468, the measured reaction times with PGA were as long as 7 minutes. By adding 150 ppm zinc stearate, the reaction times could be decreased from 7 to approximately 3 minutes. Torque graphs are shown in Figure 2, where reaction times are indicated between the orange lines.

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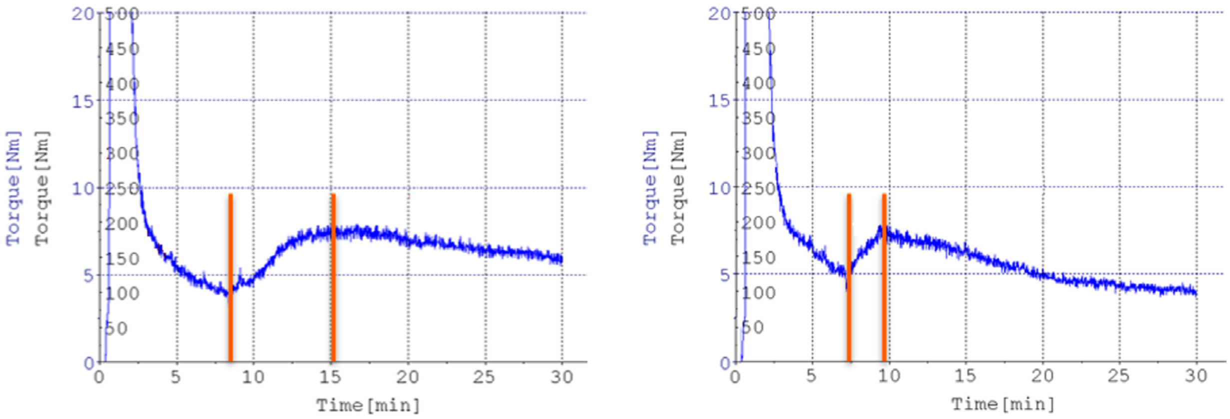

Figure 2. Kneader raw data showing the torque vs. time (blue curves) with the reaction time (between orange lines). Left: PGA with 0.5 wt.% Joncryl ADR-4468, right: PGA with 0.5 wt.% Joncryl ADR-4468 and 150 ppm zinc stearate.

Melt Flow Properties

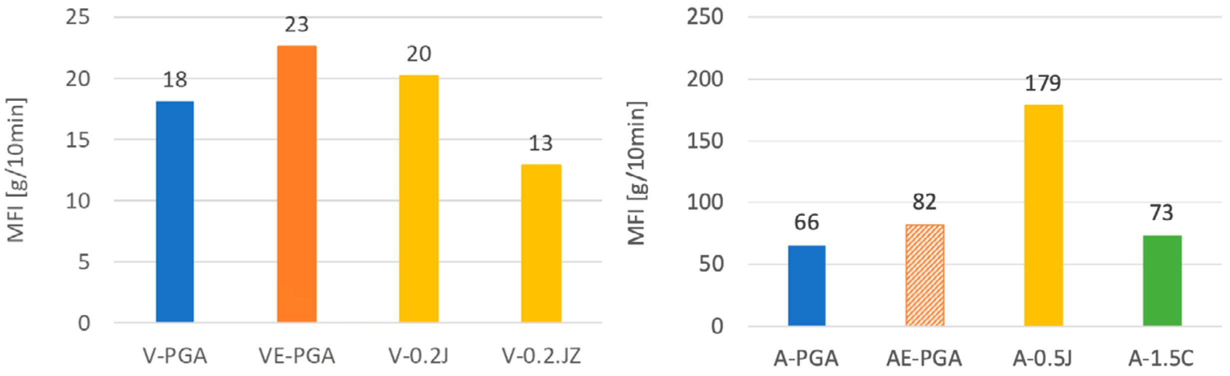

Figure 3. Melt flow index–MFI (230°C 2.16 kg) of the different pure and modified PGA materials. Top: Results for virgin PGA (phase 1). Down: Results for aged PGA (phase 2). The pattern filled bulk corresponds to a predicted value since no data is available.

Figure 3 shows the MFI results of a selection of manufactured PGA samples. The results of the virgin PGA trial (phase 1) show that the compounding step has a significant effect on the polymer viscosity. MFI increases by more than 20% which can be attributed to thermal degradation. The decrease in MFI of this PGA after extrusion with the addition of Joncryl shows the effect of the chain extender on the viscosities, probably due to crosslinking. In phase 2 of this study, PGA has aged over time as the MFI more than tripled. This indicates a drastic decrease in molecular weight over time. This is probably due to the rapid hydrolysis of PGA despite storing it at low temperatures and in sealed bags.

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The addition of 0.5 wt.% Joncryl ADR-4468 to the aged PGA does not counteract the ongoing thermal degradation, it even seems to increase it. However, the addition of 1.5 wt.% carbodiimide (not used in phase 1) has a significant effect, counteracting the ongoing thermal degradation.

PGA Flat Sheet Processing

The PGA grades and modified PGA compounds were processed via flat sheet extrusion where the maximal sheet-width of 15 cm is achievable. The thickness, highest achievable width and width variation of the produced sheets can be found in Table 1. Some example sheets are also shown in Figure 4. The processing of the virgin PGA leads to very narrow sheets that do not reach 5 cm at a thickness lower than 20 µm. The intrinsic low melt strength of the PGA results in a large variation in thickness and width. At similar or lower thickness than the virgin PGA, the Joncryl modified sheets showed to be much more stable with less necking, resulting in wider sheets with small variation. These are the thinnest sheets that have been produced up to now with modified PGA.

Unfortunately, this effect was not observed for thicker sheets made with the aged PGA (A-0.5J). This could be explained by the reaction speed of Joncryl, which could be too slow when competing with the extremely fast thermal degradation at the extruder for these aged materials with expected low molecular weights.

Sheets using combinations of Joncryl and zinc stearate could not be analyzed further. Though zinc stearate helped increase the reaction speed of Joncryl ADR-4468, as seen in Figure 2, the flat extrusion process is very unstable for thin sheets, so unstable that it was not possible to collect samples for further analysis. Also, specks were seen in the sheets, probably due to alter crystallization mechanisms during re-processing.

Due to the low viscosity of the aged PGA, it was necessary to drastically increase the thickness of the sheets to values around 100 µm, this is why A-0.5J and A-1.5C are thicker as well. Again, a large variation in the width of the sheets for the pure PGA can be observed and surprisingly also for the Joncryl modified sheets. However, when modifying the aged PGA with carbodiimide, the sheet extrusion process stabilizes and sheets at full width with small width variations are obtained. The MFI of the modified aged PGA grade showed to be slightly higher than the aged PGA. Most probably, the viscosity is at the level of the predicted value of the extruded aged PGA or even lower. Figure 4 shows an example of three typical sheets with lengths of around 20 cm and a maximum width of 12 cm, only obtained for the sample A-1.5C.

Figure 4. Left A-PGA, middle A-0.5J, right A-1.5C.

Table 1. Dimensions of flat sheets produced.

Material	Thickness (μm)	Highest achievable width (cm)	Width variation (cm)
V-PGA	10 to 20	<5	~ 2.5
V-0.2J	6	11	< 0.5
A-PGA	80	9.5-13	~ 4
A-0.5J	100	8-11	~ 4
A-1.5C	70	12	< 0.5

Barrier Properties of PGA Sheets

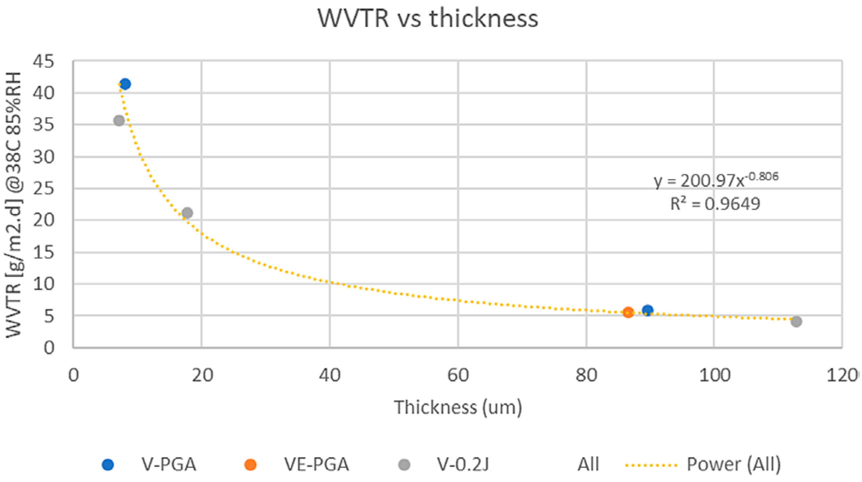

Figure 5. Water vapor barrier properties dependence on the thickness of the film.

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Barrier properties are largely dependent on the thickness of a product; therefore, water vapor and oxygen transmission rates are usually corrected for thickness. However, this relationship is not linear and especially for polyesters, depending on the crystallinity of the material [13]. When looking into flat sheets, crystallinity and therefore barrier properties will also be affected by processing conditions such as temperature and stretching at the die. Linear regression models have been built, for example, for PE to allow the prediction of the minimum required thickness for achieving the peak performance of the material [14]. Figure 5 shows the dependence of uncorrected water vapor transmission rates on film thickness. Even with the limited amount of data input caused by the inability to process all formulations, this model can help predict the layer thickness needed to achieve the desired WVTR. It is interesting to notice that not only the pure PGA is fitted in the model but also the Joncryl modified PGA. Transmission rates corrected for thickness are shown in Table 2.

When correcting the values for thickness, water vapor transmission rates measured at two different conditions are at the same level of around 3 g/m².day for pure and modified PGA (see Table 2). These values are independent of the starting material (virgin or aged) and of the chain extender used. Oxygen transmission rates are only evaluated for virgin PGA, pure and modified. Due to the low OTR, measuring times are lengthy. Results show that the addition of chain extender does not negatively affect the barrier properties. The modification of PGA with the reported chain extenders preserves the excellent barrier properties of PGA. From this, it can be derived that the original crystalline structure of the PGA polymer remains intact. More research into the crystalline and molecular structure of the PGA is recommended to confirm this hypothesis.

Table 2. Top: water vapor transmission rate (WVTR) and bottom: oxygen transmission rate (OTR) at the given conditions corrected for 100μm thickness.

Material	Sheet thickness (μm)	WVTR (23°C, 85% RH) [g/m².day]	WVTR (23°C, 90% RH) [g/m².day]
V-PGA	10-20	3.4 ± 0.5	
V-0.2J	6	2.5 ± 0.8	
A-PGA	80		2.9 ± 0.6
A-0.5J	100		3.0 ± 0.2
A-1.5C	70		2.5 ± 0.1
Material	**Sheet thickness (μm)**	**OTR (25°C, 0% RH, 100% O_2) [mlO_2/m².day.bar]**	**OTR (25°C, 90% RH, 100% O_2) [mlO_2/m².day.bar]**
V-PGA	10-20	0.3 ± 0.1	0.2 ± 0.1
V-0.2J	6	0.3 ± 0.1	0.5 ± 0.2

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Conclusions

The use of Joncryl ADR-4468 and carbodiimide chain extenders to modify PGA has a positive effect on processing properties. Full width sheets could be obtained, achieving for the first-time flat sheets with thickness below 10 μm when using 0.2 wt.% Joncryl as an additive. The water vapor and oxygen barrier properties of the modified PGA are preserved when using Joncryl and carbodiimide as chain extenders, even when the virgin material has aged for two years. CBC and PMDA do not show sufficient reactivity at the concentrations and conditions used in this study. Chain extenders that react with PGA seem to counteract the effect of thermal degradation at the extruder during processing; more research on the exact mechanism is needed. A simple model to predict the WVTR values of flat sheets made of pure and modified PGA is proposed. With this model the thickness of the PGA-layer needed to achieve certain WVTR can be estimated. This study shows how the processing of PGA can be enhanced, which is one of the biggest hurdles to using PGA as functional material in biodegradable barrier packaging products.

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