

Delft University of Technology

Influence of moisture and $\rm CO_2$ on the material behavior of thermoplastic elastomers for beer bottle closures

Turan, Deniz; Poulis, Johannes A.

DOI 10.1016/j.polymertesting.2020.106875

Publication date 2020 **Document Version** Final published version

Published in Polymer Testing

Citation (APA)

Turan, D., & Poulis, J. A. (2020). Influence of moisture and CO₂ on the material behavior of thermoplastic elastomers for beer bottle closures. *Polymer Testing*, *92*, Article 106875. https://doi.org/10.1016/j.polymertesting.2020.106875

Important note

To cite this publication, please use the final published version (if applicable). Please check the document version above.

Copyright Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy

Please contact us and provide details if you believe this document breaches copyrights. We will remove access to the work immediately and investigate your claim.

Contents lists available at ScienceDirect

Polymer Testing

journal homepage: http://www.elsevier.com/locate/polytest

Analysis Method

Influence of moisture and CO₂ on the material behavior of thermoplastic elastomers for beer bottle closures

Deniz Turan^{*}, Johannes A. Poulis

Structural Integrity Group, Faculty of Aerospace Engineering, Delft University of Technology, P.O. Box 5058, 2600, GB Delft, the Netherlands

ARTICLE INFO ABSTRACT Keywords: Metal closures with a polymer-based sealing for beer bottles have been known since the late nineteen-sixties. Elastomer However, to what extent which parameter of the polymer sealing gasket plays a role in closure performance Seal to keep the beer quality to a highest level possible is not fully understood. For this purpose three thermoplastic DMA elastomer (TPE) liners were investigated by differential scanning calorimetry (DSC), Fourier transform infrared Vibration (FTIR) spectrometry, dynamical mechanical analysis (DMA), scanning electron microscopy (SEM) and surface Leakage roughness in order to understand the effect of relative humidity (RH) and carbon dioxide (CO₂) on their physical SEM and chemical properties as well as their macromolecular structures. The TPEs' viscoelasticity in the frequency domain under different isothermal conditions was evaluated. RH and CO₂ were effective for changes in thermomechanical and surface properties. Liner C was found to have lower seal performance attributed to its relatively higher crystallinity, stiffness, weaker bond structure and rougher surface. Vibrations can lead to seal leakage in Liner B due to its higher damping behavior during production and transportation. Liner A outperforms others due to stabile behavior within the operational temperature range.

1. Introduction

Beer is an oxygen-sensitive beverage and has been packaged preferably in glass bottles with a metal closure worldwide. The quality of the beer tends to deteriorate during storage by oxygen ingress because oxygen leads to chemical processes decreasing the shelf life and flavor quality of the beer [1]. The metal caps used for bottled products need a suitable sealing gasket for effective sealing. To achieve a good sealing property the polymer seal for metal closures mainly needs to prevent gas leakage. Thus, it should possess a low and rather constant elastic modulus under a wide range of temperatures and be resilient to maintain a good seal for several months [2,3]. Until now, polyvinylchloride (PVC) containing sealing gaskets have been widely used [3]. However, there is considerable concern about PVC due to potential harm to human health for which reason new thermoplastic elastomer (TPE) seals have been introduced which show high deformability and shape recovery [4]. A challenging problem which arises in this domain is the closure of bottles with sealed metal caps with hardly any leakage. However, the performance is expected to vary with the process conditions of the closed bottle such as at the pasteurization temperature and the internal bottle environment; the relative humidity (RH) and carbon dioxide (CO₂)

pressure. Preventing CO₂ loss during pasteurization is essential, since CO₂ contributes to sensory outcomes, beer foam, mouthfeel, and the shelf stability of beer. Besides this, the transportation of the bottle may have an influence on the leaking. To our knowledge, no study on the influence of these parameters has been done so far. TPEs combine the rubber-like properties with thermoplastic processability and as such close the gap between the elastomeric and thermoplastic materials. In the next few years TPEs are therefore likely to become more important in plastics technology. TPEs can essentially be separated into two groups: Block copolymers and polymer blends. Block copolymers contain both the hard (thermoplastic) and soft (elastomeric) segments that chemically form a macromolecule. Representatives of this group are thermoplastic styrene elastomers (TPS) and thermoplastic polyamide elastomers (TPA) [5]. The elastomeric segments can be formed from unsaturated (poly(styrene-b-isoprene-b-styrene) (SIS); poly(styrene-bbutadiene-b-styrene) (SBS)) or saturated (poly(styrene-b-(ethy lene-co-propylene)-b-styrene) (SEPS), poly(styrene-b-(ethylene-co-buty lene)- b-styrene) (SEBS)) blocks [6]. In the case of polymer blends, the thermoplastic and the elastomer are physically mixed in a two-phase system. In polymer blends the elastomeric phase can either be present in so-called TPE-based olefins without cross-linking (TPO) or

* Corresponding author. E-mail address: d.kunter@tudelft.nl (D. Turan).

https://doi.org/10.1016/j.polymertesting.2020.106875

Received 15 May 2020; Received in revised form 27 August 2020; Accepted 24 September 2020 Available online 28 September 2020

0142-9418/© 2020 Elsevier Ltd. All rights reserved.







Table 1

Properties of supplied thermoplastic elastomer (TPE) liners.

Sealing Compound	Shore Hardness	Melt Flow Index (dg/ min)	Density (g/ cm3)
Liner A	A 68	7	0.92
Liner B	A 88	30	0.92
Liner C	D 50	20	0.93

Liner A Liner B

Liner C



Fig. 1. Injection molded dog-bone shaped specimens of three TPE liners for tensile tests.

dynamically cross-linked thermoplastics (thermoplastic vulcanize (TPV)) [5].

Existing researches have only focused on the thermomechanical properties of materials [5,7–10]. Glass transition temperature (Tg) values determined with DMA, DSC methods are typically used to judge the expected behavior of the actual components. However, this approach has been inadequate in predicting the failure of seals at higher temperatures [4]. It would therefore be of special interest to obtain the temperature range for a safe sealing function. There is also a lack of data concerning frequency-based properties of TPE materials. In particular, few researchers have considered the polymers' viscoelasticity in the frequency domain under isothermal conditions for O-ring seals. Researchers showed that the seal material can lead to leakage at high frequencies due to the loss of a so called leak-tightness [11,12]. During the production process and transportation by either trucks, trains, and/or ships, bottled beer is being exposed to changing temperatures, vibrations and shocks up to 150 Hz [13]. We therefore investigated whether seal performance/leakage can be partly explained by changes in the polymer's material behavior under static and dynamic loading with respect to temperature in the presence of moisture and CO₂. The aim of this study is to understand which physical and chemical phenomena might be (most) responsible on the seal performance, using differential scanning calorimetry, Fourier transform infrared spectrometer, dynamic mechanical analyses, scanning electron microscopy and surface roughness analyses. As a suitable TPE for sealing applications should preferably be selected on the basis of fundamental knowledge of material behavior.

Table 2

Compounding	and	injection	molding	parameters	of	thermoplastic	elastomer
(TPE) liners.							

Parameters	Liner A	Liner B	Liner C
Processing temperature (°C)	175	160	205
Mixing time (min.)	2	2	2
Screw speed (rpm)	80	80	80
Barrel temperature (°C)	180	165	210
Mold temperature (°C)	40	30	45
Injection pressure (bar)	12	10	14
Holding time (sec.)	5	5	5



Fig. 2. A schematic setup of carbonation chamber.

2. Materials and method

2.1. Materials

The thermoplastic elastomer (TPE) liners in pellet form which are rubber-plastic blends were supplied by Actega DS GmbH (Bremen, Germany). Hardness (based on ASTM D 2240–05), melt flow index (based on ISO 1133:2005, 5 kg, 190 °C) and density (based on ASTM D 792–98) values of the different materials provided by the supplier are listed in Table 1. The hard phase of Liner A consists of a low density polyethylene (LDPE) and the soft phase of a styrene-ethylene-butylene-styrene (SEBS). Liner B is TPE-S (styrene butadiene copolymer) modified polyethylene (blend of LDPE and styrene-butadiene-styrene (SBS)). The hard phase of a high-density polyethylene (HDPE) and the soft phase of a butyl rubber (IIR).

2.2. Sample preparation

Dog-bone shaped specimens of 25 mm gauge length, 5 mm neck width and 1 mm thickness as shown in Fig. 1 were prepared according to specimen type IV as shown in the ASTM D638 standard [14]. They were obtained from commercially available TPE liner compounds by melt compounding and injection molding. A vertical, co-rotating twin-screw micro-compounder (DSM Xplore 15 ml, Geleen, The Netherlands) and a micro 10 cc injection molding machine (DSM-Xplore, Geleen, Netherlands) were used for melt mixing and injection molding, respectively. The compounding and injection molding parameters applied for the specimen production are listed in Table 2.

Prior to testing, the TPE specimens were exposed to relative humidity (RH) and carbon dioxide (CO₂) atmospheres under four conditions: (1) samples were placed and dried in a desiccator with freshly dried silica gel at room temperature (20–23 °C for 3 days); (2) samples were kept inside a desiccator with 97% RH prepared using a saturated salt solution of potassium sulfate (K₂SO₄) at room temperature (20–23 °C) for 3 days until the samples reached a constant weight. The humidity and temperature were monitored by an OMEGA EL-USB-2 data logger; (3) samples were placed into a designed carbonation chamber (Fig. 2) then pressurized with 1 bar CO₂ gas (Linde industrial gasses, The Netherlands, food-grade) at 20 °C and allowed to equilibrate for 3 days.



The Leaking Pressure (bar)



samples were placed into the carbonation chamber with a saturated salt solution of potassium sulfate at 97% RH and pressurized with 1 bar CO_2 gas during 3 days. The saturated samples were tested immediately after removal from the desiccator and carbonation chamber.

2.3. Characterization of TPEs

In order to evaluate the sealing performance of the liners, the leakage pressure of a metal closure profile sealed with three different liners for pasteurized bottles was measured by using a leaking pressure equipment designed, constructed and modified by HEINEKEN and a local metal construction company. For each liner, 45 bottles were closed with the same crimp molds dedicated for the closure with a standard thickness of 0.22 mm. During the seal leaking pressure test method, the metal closure on the filled bottle is pierced with a needle device connected to a pressure generator and immersed in a small basin filled with tap water at room temperature. Through the needle device the pressure inside the bottle is increased with 3 bar/min. Once gas bubbles escape from the sealed bottle (gas bubbles appear in the basin), the leaking pressure is recorded.

The thermal behavior and physical changes of elastomer pellets kept at condition 1 (0% RH- 0 bar CO2- 20 °C) and their injection molded samples were kept at four different conditions recorded by a differential scanning calorimeter (DSC 8000, PerkinElmer, USA). Each sample (about 11 mg) was put into an aluminum crucible and closed by pressing an aluminum counterpart which was pierced by a needle on the top for degassing. The samples were cooled down at a rate of 10 °C/min to -70 °C and then heated up at 10 °C/min to 200 °C in a nitrogen atmosphere. This cycle was repeated. The thermal response of the heat flow as a function of temperature was recorded in this process. The fractional crystallinities were compared based on the fusion enthalpy (ΔH_m) as determined from the area under the melting endotherm. The degree of crystallinity (X_c) can be calculated from a differential scanning calorimetry curve by dividing the measured heat of fusion by the heat of fusion of 100% crystalline material, and the calculation of X_c is shown as:

$$Xc = \frac{\Delta Hm}{\Delta H_{100}} x \ 100\%$$

where, ΔH_m is the enthalpy absorbed by the test sample during the heating process, ΔH_{100} is the enthalpy absorbed by the sample during the crystallization-melting process. The ΔH_{100} of polyethylene is 293 J/g, regardless of the density [15]. Two measurements were run independently for each sample.

The attenuated total reflectance (ATR) method of the Fourier transform infrared spectrometer (PerkinElmer FTIR, Spectrum 100 Series; Waltham, USA) with the provided Spectrum 10^{TM} spectroscopy software was used in this study as a qualitative method in order to identify the chemical changes of the elastomer based on its specific absorption bands. The spectra were recorded at a resolution of 4 cm⁻¹ in the range of 4000–600 cm⁻¹ with 32 iteration scans at ambient conditions ($T = 20 \ ^{\circ}C$, RH = 50%). The absorbance spectra were normalized between 0 and 1 with the help of Origin 16 (Origin Lab, Northampton, MA, USA) software to compare the spectrum of liners. The method was performed twice for each sample.

The dynamic mechanical properties of the injection molded elastomer samples after conditioning were determined in tension mode using a dynamic mechanical analyzer (DMA RSA-G2 Solids Analyzer, TA Instruments, USA) since tension experiments are far easier for the interpretation of the correct material behavior in complex situations caused by RH and CO₂ [8]. Measurements of the storage modulus E', the loss modulus E'' and the dissipation factor tan δ were carried out in the temperature range of -100 °C to 100 °C at a heating rate of 2 °C/min at ambient conditions. Samples (25 mm × 5 mm × 1 mm) were vibrated in tension mode at a frequency of 1 Hz and a strain amplitude of 0.02%. Like in the temperature sweep, the variation of storage modulus (E'), loss modulus (E'') and loss factor (tan δ) as a function of frequency (0.1–150 Hz) were recorded at a fixed dynamic strain of 0.02% and at temperatures of 20 °C, 40 °C and 60 °C. Two analysis were carried out for each sample.

The surface morphologies of the TPE samples were studied using a JOEL JSM – 7500F (Tokyo, JAPAN) scanning electron microscope (SEM) at an accelerating voltage of 5 kV and a probe current of approximately 10 μ A. The elastomer surfaces were coated with gold for 90 s at a at a coating thickness of 2 nm using a sputter coater (Quorum Q300T, East Sussex, UK) for enhanced conductivity to reduce static loading during the SEM experiments. To investigate the influence of CO₂ and RH on the surface properties of the TPE samples, the surface roughness was

Table 3

DSC results of thermoplastic elastomer (TPE) liners.

Conditions	Sealing Compound	$T_m (^{o}C)^{a}$	$T_c (^{o}C)^{a}$	$\Delta H_m (J/g)^a$	Xc (%)	$\Delta H_c (J/g)^a$
Pellet form	Liner A	115.7 ^{yW}	101.4 ^{yW}	8.4 ^{zW}	2.9^{zW}	-11.4^{zW}
0% RH- 0 bar CO ₂ - 20 °C	Liner B	105.1 ^{zW}	92.3 ^{zW}	23.3^{yW}	8^{yW}	-34.6 ^{yW}
	Liner C	130.4 ^{xW}	116.5 ^{xW}	118.2 ^{xW}	40 ^{xW}	-118.3^{xW}
1- 0% RH- 0 bar CO ₂ - 20 °C	Liner A	103.9 ^{yX}	90.3 ^{yY}	8 ^{zW}	2.7^{zW}	-9.3^{zX}
	Liner B	95.3 ^{zY}	82.2 ^{zX}	22.5^{yX}	7.8 ^{yX}	-31.5^{yX}
	Liner C	119.6 ^{xX}	104.8 ^{xX}	108.1^{xY}	36.9 ^{xY}	-111.4^{xY}
2–97% RH- 0 bar CO ₂ - 20 °C	Liner A	103.6 ^{yX}	88.8 ^{yZ}	8.1 ^{zW}	2.8^{zW}	-9.6^{zX}
	Liner B	95.4 ^{zY}	82 ^{zX}	22.3 ^{yX}	7.6 ^{yX}	-31.1^{yX}
	Liner C	120 ^{xX}	104.7 ^{xX}	122^{xW}	41.6 ^{xW}	-117.4^{xX}
3- 0% RH- 1 bar CO ₂ - 20 °C	Liner A	104.4 ^{yX}	90.5 ^{yY}	7.9 ^{zW}	2.7^{zW}	-9.5^{zX}
	Liner B	95.6 ^{zXY}	81.9 ^{zX}	21.9 ^{yX}	7.5 ^{yX}	-29.7^{yY}
	Liner C	119.6 ^{xX}	104.5 ^{xX}	112.6 ^{xX}	38.4 ^{xX}	-106.7^{xZ}
4–97% RH- 1 bar CO ₂ - 20 °C	Liner A	104.6 ^{yX}	91.3 ^{yX}	7.6 ^{zW}	2.6^{zW}	-9.1^{zX}
	Liner B	96.1 ^{zX}	81.9 ^{zX}	23.5 ^{yW}	8^{yW}	-14.9^{yZ}
	Liner C	121.3 ^{xX}	104.3 ^{xX}	120.1 ^{xW}	41 ^{xW}	-117.2^{xX}

 T_m : the melting temperature, T_c : crystallization temperature, ΔH_m : heat of fusion, X_c : the degree of crystallinity and ΔH_c : absolute value of crystallization enthalpy. Different lowercase letters (x, y, z) in the columns indicate significant differences within each condition between sealing compounds according to Tukey tests (p < 0.05). Different uppercase letters (W, X, Y, Z) in a column indicate significant differences between conditions according to Tukey tests (p < 0.05).

^a The presented data are the averaged values of two independent samples.

measured with a 3D profilometer VR-5000 produced by Keyence (Osaka, Japan) for surface parameters R_a (arithmetic mean surface roughness) and R_z (surface roughness depth). The surface analysis was performed five times for each sample.

2.4. Statistical analysis

Statistical analysis was performed using a Minitab 16.0 (Minitab Inc, State College, PA, USA) for DSC and DMA results. Based on a fullfactorial design of experiment, the influence of carbon dioxide and moisture atmosphere on material behaviors was investigated using 1 mm thick samples, which were produced by injection molding. Data were obtained from a general full factorial design with 2 replicates. There were 2 levels for carbon dioxide, 2 levels for relative humidity, and 3 levels for TPE material. The data were subjected to analysis of variance (ANOVA) to determine the main effects and interactions, and the Tukey's HSD (honestly significant difference) test was used to evaluate the differences between the treatments' means.

3. Results and discussion

The seal leaking pressure test was carried out in order to investigate the performance of liners and seal integrity. The range of leaking pressure of Liners A and B was between 7 and 12 bar. However, Liner C showed a significantly lower mean leaking pressure than the other two liners (Fig. 3) meaning that Liner C shows a lower quality of sealing performance.

A differential scanning calorimetry (DSC) study was carried out in order to investigate the effect of the RH and CO₂ environment on the crystallization and melting behavior of the injection molded elastomers. The thermal characteristics of the elastomers in pellet form before the injection molding was also studied by DSC. Table 3 shows the results of DSC measurements during the second heating step of all samples which allows for a direct comparison of the crystallization behavior of different materials after erasing the thermal history through the first heating scan. Both the melting temperature (T_m), crystallization temperatures (T_c), heat of fusion ΔH_m (a proportional indication of the level of crystallinity), degree of crystallinity (Xc) and absolute value of crystallization enthalpy ΔH_c (proportional to the amorphous content) are displayed in Table 3. It can be seen that the thermal properties of pellet form of liners (Liner A, Liner B and Liner C) are significantly different (p < 0.05). The melting temperature, the corresponding heat of fusion and the degree of crystallinity for Liners A and B are significantly lower than that of Liner C. Liner B and C in pellet form showed a melting temperature of 105 and

130 °C, respectively. After the injection molding process a clear decrease in melting temperatures was observed. Such a drop in T_m, shows, in part, that the elastomers do not crystallize to the same extent as the unmolded ones. This feature of melting point depression may be accounted for as a result of the configurational defects in the backbone chain including dislocations, chain disorder and amorphous defects independent from the crystal structure and the rate of crystallization [16]. In addition, in Liner C this drop in the T_m is accompanied by a decrease in the ΔH_m value, meaning the total degree of crystallinity of Liner C decreased after the injection molding. This was the effect of the time being too short for Liner C to rearrange itself into the crystalline structure compared to the unmolded liner, since it has the lowest crystallization rate among the liners due to the highest T_c value. The total degree of crystallinity of Liner A showed no significant change. The slightly lower T_c of all sealing compounds upon injection molding can be attributed to the loss of nucleation efficiency in the elastomer [17]. It is known that the mechanical behavior of TPEs depends on their composition (e.g. ratio of soft to hard phase), selected process and existing process conditions. The process conditions lead to different states of distribution, stretching and dispersion of the elastomeric phases during processing. As a result the mechanical behavior of injection molded TPE components also exhibit an anisotropic character [5]. In this study the significant differences in results between the studied elastomers in pellet form and molded shape clearly gives an indication of the need for injection molding process optimization for each liner material.

A very high relative humidity (RH) caused a significant increase in melting (ΔH_m) and crystallization enthalpy (ΔH_c) of Liner C (Table 3, condition 2). Such an increase in ΔH_m and ΔH_c can be assigned to the perfection and growth of crystals in a humid environment compared to a dry condition (condition 1). H₂O molecules occupy the intermolecular spaces between molecular chains, and function as a plasticizer by which the amorphous molecular chains are activated to increased micro-Brownian motions. With the increase of temperature, the molecular chains will realign, resulting in an increased amount of crystallization. Finally, this crystallization process ends after the H₂O molecules have disappeared and are evaporated from the bulk material [18]. The ΔH_c of Liner B and C, conditioned under CO₂ atmosphere (condition 3), showed a decrease compared to that of in condition 1. The ΔH_m of Liner C increased with an increased concentration of CO_2 , while the ΔH_m of Liners A and B showed no significant change. Liner A among elastomers conditioned under humid and CO2 atmosphere (condition 4) showed no significant change in terms of thermal properties. However, the ΔH_m of Liners B and C increased. While the ΔH_c of Liner B decreased, the ΔH_c of Liner C showed a significant increase with humidity and CO_{2.} Although



Fig. 4. ATR-FTIR spectrum of (A) all TPE materials at dry conditions; (B) Liner A; (C) Liner B; (D) Liner C at different conditions; (E) Liner B zoomed in 2960–2820 cm⁻¹ and (F) Liner C zoomed in 2960–2820 cm⁻¹ at different conditions (G) Liner B zoomed in 710–740 cm⁻¹ at different conditions H) Liner C zoomed in 710–740 cm⁻¹ at different conditions. The data presented are the average of two independent samples.

studies on the effect of CO_2 on crystallization kinetics are limited, our findings support the phenomenon that dissolved CO_2 molecules increase the crystallization through the reduction of the dissipation energy required for the crystallization and plasticization effect. As such increasing the molecular mobility, so that the molecular chains can be easily rearranged. Similar results have been reported in the literature [19,20]. The negative correlation between leaking pressure of liners and the degree of crystallinity is worth mentioning because the higher crystallinity level of Liner C resulted into a lower sealing performance due to higher rigidity, which may reduce the compressive stress, the compliance or resilience and increases the possibility of seal leakage occurrence. The significant difference between crystallinity of the liners alone can thus attribute to seal failure. The found results, showing an increased degree of crystallinity (X_c) at a high relative humidity and CO_2 gas pressure, may raise concerns about the sealing quality of Liner C.

In order to determine the chemical changes induced in the TPEs, ATR-FTIR analysis was undertaken on injection molded materials. The main interesting features of the ATR-FTIR normalized spectra were the differences in spectral composition of the chemical functional groups between the TPE materials. As seen in Fig. 4a, common peaks at 2918 cm⁻¹ and 2848 cm⁻¹ corresponded to asymmetric and symmetric stretching vibration of methylene in the saturated hydrocarbon

Table 4

Frequency (cm ⁻¹)	Sealing Compound	Assignments and observations
699	Liner A & B	Styrene characteristic band. Out-of-plane bending of the –C-H groups in the aromatic ring, all the 5 hydrogen carbons oscillating in phase.
		Typical for mono-substituted aromatic ring. Strong and well evidenced in all copolymers [40]
720	All liners	CH ₂ plane rocking modes of ethylene groups in ethylene-polypropylene rubber [40]
730	All liners	Bending vibrations (wagging) of the –C-H groups in the cis- polybutadiene units [40]
911	Liner B	Out-of-plane (wagging) vibrations of the hydrogen atoms correspond to the trans C=C unsaturation (vinyl) in polybutadiene. Strong and well
		evidenced in all copolymers [41]
965	Liner B	Out-of-plane (wagging) vibrations of 1,2 butadiene terminal vinyl C–H band [41]
1019	Liner C	C–O stretching vibrations of carboxylic groups [42]
1045	Liner C	Stretching vibration of $O-CH_{2^-} + C-CH_3$ or $C-C$ chain [40]
1230	Liner C	Mainly due to C–O stretching of ester [43]
1365 & 1391	Liner C	C–H stretching bands of the t-butyl groups of the forming polyisobutylene [44]
1377	Liner A & B	CH ₂ wagging, and C–C chain stretching vibrations [40]
1473 & 1463	All liners	CH ₂ bending deformation [24]
2848	All liners	Symmetrical stretching vibrations of the CH ₂ groups [40]
2918	All liners	Asymmetrical stretching vibrations of the CH ₂ groups [40]

backbone, respectively [21]. These C-H stretching bands occurred higher absorbance in Liner C, Liner B and Liner A, respectively. Different features have also been observed in the 1470-1350 $\rm cm^{-1}$ domain, where absorption bands correspond to scissoring vibrations of the methylene group (1463 cm⁻¹ in all TPE materials spectra) and to symmetric deformation of the methylene group (1377 cm^{-1} in Liner A and B spectra) [22]. The appeared peaks in 1377 cm⁻¹ band for Liner A and B can be attributed to the presence of side chain branches of polyethylene which is further confirmed as LDPE by the reviewed literature [23,24]. These differences in spectral composition affect the crystallinity and both the thermal and mechanical properties of the liner materials, e.g. more side chain branches first in Liner A and then in Liner B, causing a reduction of crystallinity. Supplementary, for all, a doublet with maxima at 730 and 719 cm⁻¹ where bending and rocking vibrations of crystalline and amorphous methylene group is encountered [25]. Thus, high absorbance noted in the IR spectral region of 730-720 cm⁻¹ for Liner C, Liner B and Liner A, respectively proves to show the incremental crystallinity in the sense of the reduction in the ordered phase content which correlates very well with the found DSC results (Table 3, condition 1, the highest X_c data). Fig. 4b show typical spectral changes observed in the Liner A in the region 4000-600 cm^{-1} after conditioning in the RH and CO2 environment. Two characteristic water vapor absorption patterns were observed in the 4000–3500 cm^{-1} and 2000–1200 cm^{-1} ranges after storage at elevated humidity (blue shift, condition 2). These are the results of rotation-vibration transitions, associated with the stretching and bending vibrations of H₂O, respectively. Furthermore, changes are observed in the C=C stretching at 1645 cm⁻¹ (Fig. 4b). An increase in O-H and C=C bonds when bonded water molecules are present is consistent with results of previous studies [26,27]. Moreover, a CO₂ absorption band at around 2350 cm⁻¹ was seen, involving CO₂ antisymmetric stretching after storage under CO₂ environment (red shift, condition 3). After storage at elevated humidity and under CO₂ (orange shift, condition 4), absorption patterns were observed at 2000-1200 cm⁻¹ associated with the bending vibrations of H₂O, meaning Liner A demonstrates a greater affinity for polar substances like H₂O. The crystallinity of a TPE sample can be determined from the ratio of the 730 to 719 cm⁻¹ peak [10]. The ratio of these peaks didn't change with conditioning, meaning no change in crystallinity. In Fig. 4c, a broad hydroxyl absorption is observed at 3410 cm⁻¹ in the Liner B after storage at elevated humidity (condition 2). A slight increase in the CO₂ absorption band around 2350 cm⁻¹ was observed after storage under CO_2 environment (condition 3). The ratio of the 730 to 719 cm⁻¹ peak was found to be unchanged at condition 2 and 3. However it was increased slightly for Liner B after storage at elevated humidity and under CO_2 (condition 4) due to decrease in band at 719 cm⁻¹ associated with the amorphous segment. In Fig. 4d, a slight increase in water vapor

absorption is observed at 3380 cm⁻¹ in Liner C after storage at elevated humidity (condition 2). The O-H stretching vibrations exhibited by all liner materials is purely due to invaded water molecules which have formed hydroxyl functional groups in the polymer matrix [22]. Evidence of this was the blue shift of the O-H stretching band which occurs higher absorbance in Liner A and B than Liner C, meaning Liner A and B both demonstrate a greater affinity for polar substances. Highly polar molecules such as H₂O can be prevented from entering the pores of Liner C by its higher crystallinity. Contribution of the relatively stronger O-H bonds [28] to the elastomer structure can thus possibly increase its chemical and thermal resistance. Unlike Liner A and B, no CO2 absorption band around 2350 $\rm cm^{-1}$ was observed in Liner C after storage under the CO₂ environment (condition 3). The presence of relatively higher crystallinity in Liner C would be expected to hinder CO₂ mobility. Fig. 4d also shows that the ratio of the 730 to 719 cm^{-1} peak associated with the degree of crystallinity was found to decrease for Liner C after storage at elevated humidity (condition 2), under CO₂ (condition 3) and RH-CO₂ environment (condition 4), respectively. Moreover, the bond appears as a doublet near 1019 and 1045 cm⁻¹ with a maximum intensity at 1019 cm^{-1} in the Liner C. These spectra might be an alternative indicator for changes in the ordered structure as the crystalline phases decreased [29] with decremented band absorption in the same order like the 730 to 719 cm^{-1} peak. Unlike Liner A and B, the normalized ATR-FTIR data for Liner C contradicts with data from the DSC measurements regarding the changes in degree of crystallinity with respect to the elevated RH and CO₂ conditions. It is well known that DSC is a direct method to obtain the crystallinity of a semi-crystalline polymer from the area of the endothermal peak on the DSC curve. However, during the heating-cooling process, further crystallization may occur. Consequently, FTIR can provide a direct evaluation of the crystallinity [30]. The incremental degree of crystallinity of the Liner C with conditioning, determined from DSC, might be attributed to further crystallization during heating in the DSC study. Therefore, we can propose ATR-FTIR as an effective and non-destructive tool to evaluate crystallinity of TPEs to study the effect at elevated humidity and CO₂ conditions. Moreover, Table 4 summarizes the main functional group frequencies observed in each elastomer. Our findings seem to imply that Liner C has relatively weaker bonds than Liner A and B such as C-O and C-C which might decrease its performance as a sealing material, particularly its chemical and thermal resistance.

The response of elastomers to an applied energy can be storing and/ or dissipating of this energy. For sealing materials, the elastic component is the highly important. However, around the glass transition temperature the mechanical properties of the polymer change dramatically. For this reason DMA was conducted to determine the T_g of the TPE material samples. This analysis method investigates the material's



Fig. 5. Storage modulus measured at 1 Hz a) DMA graph of all TPE material samples as a function of temperature, b) DMA graph of Liner A as a function of temperature, c) DMA graph of Liner B as a function of temperature, d) DMA graph of Liner C as a function of temperature, (e) interval plot for Liner A at 20 °C, (f) interval plot for Liner A at 60 °C, (g) interval plot for Liner B at 20 °C, (h) interval plot for Liner B at 60 °C, (i) interval plot for Liner C at 20 °C, (j) interval plot for Liner C at 60 °C. The data presented are the average of two independent samples.

Fig. 6. DMA graphs of loss tangent (tan δ) measured at 1 Hz as a function of temperature for a) all TPE material samples, b) Liner A, c) Liner B, d) Liner C. The data presented are the average of two independent samples.

physical properties at different temperatures by applying sinusoidal stresses resulting in a sinusoidal strain of the elastomeric polymer responsible for the sealing performance. With the amplitude and phase shift of the recorded sinusoidal strain, information about the mechanical changes inside the elastomer can be gathered including its complex elastic modulus and, subsequently, the storage (E') and loss modulus (E'') as well as the loss factor (tan δ). The curves presented in Fig. 5 are the averaged values of two samples. Fig. 5a shows the temperature dependence of the storage modulus (E') of these TPE samples at 1 Hz. All the curves show three distinct regions: a glassy high modulus region where the segmental mobility is restricted, a transition zone where a substantial decrease in the E' values with an increase of temperature and a rubbery region (the flow region) with a drastic decay in the modulus with temperature. At very low-temperatures (between -100 °C and -70 °C), the sealant material is in its glassy state and is both stiff and brittle. In the glassy state, the polymer shows higher storage modulus which decreases with increasing temperature. It is important to mention that the modulus in the glassy state is determined primarily by the strength of the intermolecular forces and the way the polymer chains are packed. The ability of a sealant to dissipate stresses is governed by its low-temperature stiffness. Therefore, Liner B is expected to be more capable of dissipating stresses than Liner A and to have better field performance at low-temperatures. The storage modulus of the blend in the glassy region is due to the high strength polymer matrix. If the inservice temperature of a sealant is lower than its glass transition

temperature, the sealant will become very stiff (glassy state), and an increase in sealant cohesion failures and adhesion failures may occur [31]. E' of Liner A was relatively low in the temperature range from 0 to 60 °C. For this reason, Liner A might be widely used as the material for the sealing gaskets of pry-off caps for glass bottles, because it shows flexible and stable behavior at operational temperatures. However, because a clear relaxation process exists at ~ 0 °C, the E' modulus of Liner C drops drastically around 700 MPa, meaning that there may be an increased risk of leakage upon drop impact at low temperatures. As a result, it looks like the Liner C should not be used as a sealing material, especially when subjected to temperature changes between 20 and 60 °C which is inevitable due to pasteurization. The E' of all TPE samples at 60 °C was over 20 MPa, indicating that the elastomer had enough heat resistance to endure the harsh condition during pasteurization. Previous study pointed 1.8 MPa as limit of E' for heat resistance [3]. The DMA measurement showed that E' of Liner C (Fig. 5d) is almost 10-fold higher than that of Liner A in a temperature range of 0–60 °C. Hence, Liner C is not desirable to apply as a sealing material for beer bottle closures because it shows a stiff and unstable behavior at operational temperatures. Fig. 5b and c shows that the initial E' of Liner A and B decreased by increasing RH and increased by an increasing CO2 gas pressure environment (meaning embrittlement). In contrast, the E' of Liner C didn't change significantly in the temperature range of -100 °C-100 °C at either increasing RH or CO₂ gas pressure, compared to samples at dry condition (condition 1) (Fig. 5d). When we have a closer look to the

Fig. 7. DMA graphs at 20, 40 and 60 °C as a function of frequency a) storage modulus of all TPE material samples, b) storage modulus of Liner A, c) storage modulus of Liner B, d) storage modulus of Liner C, e) loss tangent (tan δ) of all TPE material samples, f) loss tangent (tan δ) of Liner B, h) loss tangent (tan δ) of Liner C. The data presented are the average of two independent samples.

Fig. 8. Interval plot of loss tangent (tan δ) value at 10 Hz for a) Liner A at 20 °C, b) Liner A at 40 °C, c) Liner A at 20 °C, d) Liner B at 20 °C, e) Liner B at 40 °C, f) Liner B at 20 °C, g) Liner C at 20 °C, h) Liner C at 40 °C, i) Liner C at 20 °C, b) Lin

influence of the conditions on the E' behavior of the liners, it can be seen that E' of Liner A increased with RH at 20 °C (Fig. 5e). On the other hand, E' of Liner B and C decreased (Fig. 5g and i, respectively). At 60 °C, CO₂ was found effective in increasing E' of Liner A and Liner B (Fig. 5f and h, respectively). In contrast, E' of Liner C decreased (Fig. 5j). The correlation between the FTIR and DMA results at 20 °C is striking, because liners with stronger atomic bonds show a higher elastic modulus (increased stiffness) than liners built up with weaker atomic bonds. We know that the mechanical properties of polymers depend on the type of atomic bonds. The bonds in polymers can be divided into two major groups: the primary bonds (ionic and covalent bonds) and the secondary bonds (hydrogen bonds, dipole and van der Waals interactions). Primary bonds include the strong covalent intramolecular bonds. Typical covalent bonds in polymers are C–H bonds, corresponding to a bond disso-ciation energy level of 410 kJ mol^{-1} [32]. For instance, relatively stronger covalent bonds such as O-H groups (with a bond dissociation energy level of 460 kJ mol⁻¹) and C=C groups (bond dissociation energy level of 611 kJ mol⁻¹) formed in the Liner A structures after storage at elevated humidity is probably responsible for its higher storage modulus at condition 2. Moreover, at the high RH environment increasing the relatively weak C-O bonds in the range of 1000-1120 cm⁻¹ in the Liner B structure would be responsible for the decrease in its storage modulus. There is also satisfactory agreement between the change in the chemical bonds of Liner C and its storage modulus as a result of the internal beer bottle environment (high RH and CO₂ gas). Decreasing the ratio of the 730 to 719 cm^{-1} peak associated with the degree of crystallinity would be responsible for decreasing the storage modulus with increasing RH and CO2. Overall, Liner A and B when conditioned under a high RH in a CO₂ environment, their storage modulus had increased at operational temperatures (0 °C-60 °C). While Liner A underwent moisture-hardening, Liner B indicated clearly a CO2-hardening behavior. Although Liner C showed a lower E' after exposure to a high RH and CO2 environment at 60 °C pasteurization temperature, its storage modulus was found to be high compared to that of Liner A and B. Thus even the environment inside the beer bottle may not help Liner C to show enough resilience to reduce the risk of seal leakage to occur at operational temperatures.

Fig. 6 shows the temperature dependence of the loss tangent (tan δ) of these TPE samples at 1 Hz. The ratio of the loss modulus (E") to the storage modulus (E') is referred to as internal damping or loss tangent $(\tan \delta)$ of the provided seal. The main peak of the loss tangent curve is frequently associated to the glass transition temperature (T_g) [33]. From Fig. 6a, it is clear that the T_g of Liner B as being -86 °C was far lower than that of Liner A and Liner C (being around -60 °C). This suggests that Liner B with a peak at lower temperature has a better capability to maintain its elastic properties at lower temperatures than the other two liner materials. For this reason Liner B is preferable for low temperature applications. However, for liners aimed to be used as beer bottle sealants, the magnitude of the tan δ over the operating temperature range is important. At an operating range of 0-60 °C, Liner A showed a low and constant flat curve across the vast majority of this range. On the other hand, the tan δ curve of Liner B and Liner C showed an upturn with temperature increase at the operational range which is associated with material softening. As the macromolecular chains rearrange to reduce the stored energy, a loss of sealing force occurs. The tan δ value at the T_g is decreased for all TPE material samples conditioned under high RH and CO₂ (Fig. 6a). Due to the presence of a plastic phase as the continuous matrix, the restriction is imposed on the rubber chain mobility leading to a reduction in the tan δ at $T_g.$ Our findings on the value of the tan δ of Liner A at the operating range of 0–60 °C shows that neither RH nor CO₂ has any significant effect (Fig. 6b). However, tan δ or internal damping of Liner B first increased with increasing RH and CO₂ gas pressure, but over 40 °C, the RH and CO₂ caused a decrease in tan δ (Fig. 6c). Moreover, Liner C revealed in a lower tan δ curve as a result of the effect of RH and CO₂ at the operating range (Fig. 6d). The experimental results lead to similar conclusions where Liner A outperforms the others

because a flatter and lower tan δ curve is more desirable within the operational temperature range.

In addition to the static tests, dynamic viscoelastic behavior of the TPE materials was investigated in the frequency domain under different isothermal conditions in order to understand sealing behavior under vibrations which are introduced into beer bottles in the course of the production line and transportation. For this reason the dynamic storage modulus (E') and loss tangent (tan δ) as a function of frequency within a range from 0.1 Hz to 150 Hz are shown in Fig. 7. This frequency range is chosen because bottled beer is being exposed to vibrations and shocks to a frequency up to 150 Hz during the production line and transportation by truck, train, or ship [13]. Fig. 7a indicates that the dynamic storage modulus of all liners increase with a higher frequency and the dynamic stiffness decreases at higher temperatures. This means that high vibrational impact during pasteurization may not result in leakage. However, increase in vibrations during cooling may result in leakage due to loss of flexibility of the liner material. Previous study on beer bottle vibrations during transport revealed that beer bottles packaged in plastic crates show amplified vibrations when the frequency rises. According to the study results, the bottles in the highest crate are subject to vibrations between 75 and 150 Hz with up to nine times the amplitude of the pallet vibrations [13]. Moreover, packages can be subjected to vibrations up to 100 Hz during sea transportation [34]. Thus, it is important to note that the stiffness of Liner C increased significantly after 100 Hz at 20 °C. Fig. 7b, c and 7d show details of the effect of internal parameters in the beer bottle on liner stiffness in the frequency domain. Results in Fig. 7b demonstrate that when both RH and CO₂ are increased (condition 4), an increment in E' of Liner A is observed at 20 °C. However, only RH was effective to increase the dynamic stiffness of Liner A at 40 and 60 °C. We observe from Fig. 7c that RH and CO2 caused an increase in E' of Liner B at 20 and 40 °C, however, the effect of RH and CO₂ on Liner B's dynamic stiffness was found to be insignificant at 60 °C. Fig. 7d indicates a significant increase in dynamic stiffness of Liner C with increasing RH and CO_2 at 60 °C. The results on tan δ of all liners in the frequency domain at 20, 40 and 60 °C are compared in Fig. 7e. Liner C shows a low damping characteristic due to the low tan δ values at 20 $^\circ\text{C}$ as a function of frequency, meaning low energy dissipation, hence the material behavior is nearly elastic. However, in contrast, at 60 °C an increase in dynamic tan δ of Liner C was observed above 60 Hz. Previous study showed that temperature rise up to 60 °C is possible in sea transport containers [35]. The increase in dynamic tan δ as a function of frequency corresponds to a higher increase in E" compared to E'. This higher increase in E" corresponds to the material becoming more viscoelastic when loaded at higher frequencies, which, in turn, could result in higher stress relaxation and higher seal leakage for Liner C during transportation when bottled beer is exposed to higher temperatures [36]. From Fig. 7f we can note that the effect of RH and CO₂ on the dynamic tan δ of Liner A at 20 °C was not significant. However, at higher temperatures and higher vibrations (100 Hz) presence of RH and CO₂ helps Liner A act more elastic response by decreasing its dynamic tan δ value meaning prevention of leakage when bottled beer is being exposed to changing temperatures and vibrations during transportation. Liner B demonstrates high tan δ values at 40 °C, however RH and CO₂ causes decrease at high frequencies (Fig. 7g). Liner C shows low tan δ values at 20 °C (high resilience), whereas the CO_2 gas causes an increase in tan δ after 60 Hz and CO₂ together with RH causes an increase in tan δ after 20 Hz, which means more energy dissipation potential at high frequencies. On the other hand, at higher temperatures presence of RH and CO₂ helps Liner C act more elastic response by decreasing its dynamic tan δ value resulting in similar possibility of leakage in beer bottles exposed to 20 °C or 60 °C at higher vibrations during transportation (Fig. 7h). Low tan δ means that the separation between liner and glass bottle surface is small due to high resilience of liner material on glass bottle so the leakage is small because separation causes leakage [12]. Previous findings on vibrations for packaged beer research concluded that beer bottles packaged in cardboard boxes are subjected (and vulnerable) to transport

Fig. 9. SEM images of a) Liner A, b) Liner B, c) Liner C placed in dry environment, d) Liner A, e) Liner B, f) Liner C conditioned with 97% relative humidity (RH), g) Liner A, h) Liner B, i) Liner C conditioned with carbon dioxide (CO₂) gas, j) Liner A, k) Liner B, l) Liner C conditioned both with RH and CO₂.

Fig. 10. Surface analysis results of molded liner materials a) average roughness (R_a) and b) mean peak-to-valley height (R_z) values.

vibrations lower than 25 Hz [13]. Bottles can also vibrate or sway in the production line at frequencies up to 40 Hz [37]. Therefore, Fig. 8 pinpoints the differences in tan δ values at 10 Hz as the most possible vibration frequency during transport and in the production line. Tan δ of Liner A was significantly high at 20 °C after storage at elevated humidity under CO₂ (Fig. 8a). At 40 °C, Liner A showed similar tan δ values (Fig. 8b) and at 60 °C, its tan δ was significantly low regarding to CO₂ (Fig. 8c). Fig. 8d and e shows that both RH and CO₂ caused a significantly high tan δ for Liner B at 20 and 40 $^\circ\text{C},$ respectively. At 60 $^\circ\text{C},$ tan δ values of Liner B at different conditions were similar (Fig. 8f). Tan δ of Liner C was significantly high at 20 °C when it was conditioned under RH (Fig. 8g). At 40 °C, Liner C also showed similar tan δ values (Fig. 8h) and at 60 °C, its tan δ was significantly low regarding to RH and significantly high regarding to CO₂ (Fig. 8i). During pasteurization the pressure in the container is expected to increase. This is partly due to the temperature rise acting on the headspace, the CO₂ gas volume increase and partly due to the vibration, which encourages CO₂ to be released from the liquid. There is a strong probability that Liner B can leak during the pasteurization process at 60 °C, during the cooling at 40 °C and also at 20 °C due to having higher tan δ values with the effect of RH and CO₂ in the headspace of the beer bottle at vibrations during transport and during production. The results also point to the probability that Liner C can leak during the pasteurization process and transportation.

Scanning electron microscopy (SEM) was used to study the morphology of dry and conditioned liner samples at elevated humidity and under CO_2 environments. Besides this, surface roughness analysis was performed for the interpretation of the SEM micrographs. SEM micrographs and surface roughness results of the liner samples are presented in Fig. 9 and Fig. 10, respectively. Surface roughness is commonly determined by using average roughness (R_a) and mean peak-

to-valley height (R_z) values. While R_a gives average surface roughness, R_z can give information for any pore, hole or surface deformities detrimental to strength. The R_a and R_z values presented in Fig. 10 are the average values of five samples. Molded Liner C shows a less wrinkled surface morphology (Fig. 9c) than that of Liner A and B (Fig. 9a and b, respectively) in dry a condition (condition 1). This finding is supported by the lowest R_a values of Liner C (Fig. 10a). Moreover, some flow lines from the injection molding process can be observed on the Liner A and C surfaces due to their higher melt viscosities (respectively lower melt flow index-MFI shown in Table 1) with a longer molecule chain causing a higher resistance to flow during the molding process. Fig. 9d, e and 9f demonstrate the transition to lamellar morphology showing incremented regions protruding from the surface in high RH environments (condition 2) for Liner A, B and C, respectively. This finding was also supported by incremented R_a values, meaning increased roughness with moisture absorption and swelling due to an increased number of hydroxyl groups. Liner A exhibited some discontinuous paths with cavities and cracks as a result of the exposure effect of CO₂ (condition 3) in Fig. 9g. A significant increase in R_z values of Liner A after storage under CO₂ clearly indicates this finding (Fig. 10b). Volume increase under the influence of CO₂ might be an explanation for the cavities in the Liner A. Previous researchers also hypothesize that the CO₂ molecules, absorbed in the polymer during treatment, increase the free volume of the material [38]. The surface of Liner B became relatively smoother with CO₂ (Fig. 9h) and Liner C showed a relatively flat and smooth surface (Fig. 9i) which is also shown by no significant changes in R_a and decreasing R_z values of Liner C. A decrease in the number of fine flow lines and an increment in the number of cavities and cracks could be seen for Liner A exposed to both high RH and CO₂ environment (Fig. 9j), showing no significant change in Ra values and increased Rz values

supporting the increment in pores and cavities. An increase in the number of fine flow lines in the lamellar morphology of Liner B and C was observed with RH together with CO_2 (condition 4) in Fig. 9k and l, respectively. For condition 4, an increase in surface roughness and surface deformities can also be seen from incremented R_a and R_z values for Liner B and C in Fig. 10a and b, respectively. Leakage is a function of surface roughness for molded sealing. Minimum leakage can be obtained when the roughness is minimal [39].

Overall, conditioning leads to changes in surface roughness of TPE liners. Surface roughness changes are associated with dimensional changes owing to swelling–shrinkage. Liner C had the highest surface roughness after storage at elevated humidity and under CO₂, leading to an increase in seal leakage.

4. Conclusions

The effect of RH and CO_2 gas environments on physical and chemical properties of three injection molded TPE liners was investigated in order to understand the sealing behavior of these TPE's under static and dynamic vibrations, as introduced into beer bottles in the production process and during transportation. The dynamic viscoelastic behavior of the TPE materials were investigated in the frequency domain under different isothermal conditions.

The findings of this study indicate that Liner C shows the lowest performance of sealing which can be attributable to its degree of crystallinity, the highest among the tested TPE liners. Optimization of the injection molding process for each liner material is necessary, since the molding process effects the crystallinity and results in melting point depression compared to the elastomers in pellet form. Although ATR-FTIR results correlate with DSC results regarding the crystallinity at dry conditions, the results contradict with each other under elevated humidity and CO₂ conditions due to possible further crystallization during heating in the DSC study. Thus, ATR-FTIR is suggested as an effective and non-destructive tool to evaluate crystallinity of TPEs after storage under RH and CO $_2$ conditions. The main finding of ATR-FTIR is that Liner C has relatively weaker bonds such as C-O and C-C than Liners A and B which might decrease the performance of sealing. While Liner A shows a flexible and stable behavior at operational temperatures (0-60 °C) due to a low and relatively constant storage modulus and damping behavior, Liner C has the stiffest and the most unstable thermomechanical behavior. Although Liner C shows less stiffness under elevated RH and CO₂ environments, its storage modulus still stays higher than that of Liner A and B. Even the internal beer bottle parameters such as RH and CO₂ gas may not help Liner C to have enough resilience to prevent seal leakage. This paper has highlighted that Liner B might show an increased risk of leaking during the pasteurization process at 60 °C, during the cooling process at 40 °C and also at 20 °C (during transportation) due to having higher tan δ values as an effect of high RH and CO₂ in the headspace of beer bottles. Liner C might show an increased risk of leakage during the pasteurization process and during transportation. The surface roughness as a surface property is also a good indicator of the mechanical performance of elastomeric materials. Irregularity in the surface might lead to seal leakage. Although Liner C has a relatively smooth surface at dry conditions, its roughness becomes the highest after storage at elevated humidity and under CO₂. Possibly due to dimensional changes owing to swelling-shrinkage, resulting in seal leakage.

In conclusion, flexibility of the polymer seal is required in terms of good sealing properties of beer bottles, but a high degree of crystallinity should be avoided. To achieve an excellent sealing property, the material used as a gasket should possess a stable, relatively low elastic modulus under a wide range of temperatures and frequencies plus minimum surface roughness. The thermomechanical and surface properties of plastic-rubber blends can be optimized by choosing the right blend composition and molding conditions.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was carried out under project number A17021b in the framework of the Research Program of the Materials innovation institute (M2i) (www.m2i.nl) supported by the Dutch government. The authors very much appreciate the support for material supply by Actega DS GmbH. Authors also acknowledge HEINEKEN for discussions on problem definition. The authors would like to thank the following people Johan Bijleveld, Marlies Nijemeisland, Durga Mainali and Gertjan Mulder for training and making instruments available. All other laboratory staff: Fred Bosch, Victor Horbowiec, and the people from the TU Delft DEMO workshop.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymertesting.2020.106875.

References

- R.M. Hofeldt, S.A. White, Sealed Containers and Sealing Compositions for Them, Google Patents, 1991.
- [2] D.D. Hundt, E.W. Merrill, Seal for Crown Closures, Google Patents, 1964.
- [3] T. Moriga, N. Aoyama, K. Tanaka, Development of a polyurethane sealing gasket with excellent sealing and opening properties, Polym. J. 47 (2015) 400–407.
- [4] T. Grelle, D. Wolff, M. Jaunich, Leakage behaviour of elastomer seals under dynamic unloading conditions at low temperatures, Polym. Test. 58 (2017) 219–226.
- [5] C. Hopmann, C. Zimmermann, Characterisation of the Quasi-Static Material Behaviour of Thermoplastic Elastomers (TPE) under Consideration of Temperature and Stress State, Journal of Elastomers & Plastics, 2019, 0095244319835868.
- [6] S. Munteanu, C. Vasile, Spectral and thermal characterization of styrene-butadiene copolymers with different architectures, J. Optoelectron. Adv. Mater. 7 (2005) 3135.
- [7] A. Arevalillo, M.E. Muñoz, I. Calafell, A. Santamaría, L. Fraga, J.A. Barrio, Thermomechanical properties linked to rheological features in high molecular weight SEBS copolymers: effect of styrene content and ethylene/butylene proportion, Polym. Test. 31 (2012) 849–854.
- [8] A. Ilseng, B.H. Skallerud, A.H. Clausen, Tension behaviour of HNBR and FKM elastomers for a wide range of temperatures, Polym. Test. 49 (2016) 128–136.
- [9] E. Lainé, J. Grandidier, G. Benoit, B. Omnès, F. Destaing, Effects of sorption and desorption of CO2 on the thermomechanical experimental behavior of HNBR and FKM O-rings-Influence of nanofiller-reinforced rubber, Polym. Test. 75 (2019) 298–311.
- [10] M.B. Zarandi, H.A. Bioki, Thermal and mechanical properties of blends of LDPE and EVA crosslinked by electron beam radiation, Eur. Phys. J. Appl. Phys. 63 (2013).
- [11] T. Grelle, D. Wolff, M. Jaunich, Temperature-dependent leak tightness of elastomer seals after partial and rapid release of compression, Polym. Test. 48 (2015) 44–49.
- [12] B. Tan, L.S. Stephens, Evaluation of viscoelastic characteristics of PTFE-Based materials, Tribol. Int. 140 (2019) 105870.
- [13] A. Paternoster, S. Vanlanduit, J. Springael, J. Braet, Measurement and analysis of vibration and shock levels for truck transport in Belgium with respect to packaged beer during transit, Food Packaging and Shelf Life 15 (2018) 134–143.
- [14] ASTMInternational;, D638-14 Standard Test Method for Tensile Properties of Plastics, ASTM International2014.
- [15] Y. Kong, J. Hay, The enthalpy of fusion and degree of crystallinity of polymers as measured by DSC, Eur. Polym. J. 39 (2003) 1721–1727.
- [16] D.-W. Van der Meer, Structure-property Relationships in Isotactic Polypropylene, University of Twente, 2003.
- [17] R. Uotila, U. Hippi, S. Paavola, J. Seppälä, Compatibilization of PP/elastomer/ microsilica composites with functionalized polyolefins: effect on microstructure and mechanical properties, Polymer 46 (2005) 7923–7930.
- [18] M. He, Z. Wang, R. Wang, L. Zhang, Q. Jia, Preparation of bio-based polyamide elastomer by using green plasticizers, Polymers 8 (2016) 257.

Polymer Testing 92 (2020) 106875

- [19] M. Nofar, W. Zhu, C. Park, Effect of dissolved CO2 on the crystallization behavior of linear and branched PLA, Polymer 53 (2012) 3341–3353.
- [20] M. Takada, M. Ohshima, Effect of CO2 on crystallization kinetics of poly (ethylene terephthalate), Polym. Eng. Sci. 43 (2003) 479–489.
- [21] Z. Lei, Q. Yang, S. Wu, X. Song, Reinforcement of polyurethane/epoxy interpenetrating network nanocomposites with an organically modified palygorskite, J. Appl. Polym. Sci. 111 (2009) 3150–3162.
- [22] J. Charles, S. Muthusamy, Comparative study of butyl rubber (IIR) and Bromobuty1 rubber (BIR) based on FTIR, dielectric and thermal studies, Journal of Applied Science and Engineering Methodologies 2 (2016) 206–211.
- [23] Y. Davies, J. Davies, M.J. Forrest, Infrared Spectra of Rubbers, Plastics and Thermoplastic Elastomers, Walter de Gruyter GmbH & Co, 2019. KG.
- [24] J. Gulmine, P. Janissek, H. Heise, L. Akcelrud, Polyethylene characterization by FTIR, Polym. Test. 21 (2002) 557–563.
- [25] A. Wojtala, K. Czaja, M. Sudol, I. Semeniuk, Weathering of low-density polyethylene grafted with itaconic acid in laboratory tests, J. Appl. Polym. Sci. 124 (2012) 1634–1642.
- [26] A. Barbosa, L. Da Silva, A. Öchsner, Hygrothermal aging of an adhesive reinforced with microparticles of cork, J. Adhes. Sci. Technol. 29 (2015) 1714–1732.
- [27] Y. Diamant, G. Marom, L. Broutman, The effect of network structure on moisture absorption of epoxy resins, J. Appl. Polym. Sci. 26 (1981) 3015–3025.
- [28] M.L. Huggins, Bond energies and polarities 1, J. Am. Chem. Soc. 75 (1953) 4123–4126.
- [29] A. Díaz, L. Franco, F. Estrany, L. Del Valle, J. Puiggalí, Poly (butylene azelate-cobutylene succinate) copolymers: crystalline morphologies and degradation, Polym. Degrad. Stabil. 99 (2014) 80–91.
- [30] P. Pagès, Characterization of Polymer Materials Using FT-IR and DSC Techniques, Universidade da Coruña: Coruña, Spain, 2005.
- [31] H. Soliman, A. Shalaby, Characterizing the low-temperature performance of hotpour bituminous sealants using glass transition temperature and dynamic stiffness modulus, J. Mater. Civ. Eng. 21 (2009) 688–693.
- [32] S. Lampman, B. Bonnie Sanders, N. Hrivnak, J. Kinson, C. Polakowski, Characterization and Failure Analysis of Plastics, ASM International, Materials Park, OH, USA, 2003.

- [33] V. Jovanović, J. Budinski-Simendić, L. Koruguc-Karasz, A. Aroguz, J. Milić, N. Vukić, G. Marković, P. Dugić, Compression Set and Damping Properties of Oil-Extended Elastomers for Sealants Production, vol. 9, The University Thought-Publication in Natural Sciences, 2019, pp. 32–37.
- [34] J. Foley, Transportation Shock and Vibration Descriptions for Package Designers, Sandia Labs., Albuquerque, N. Mex., 1972.
- [35] B. Jaskula-Goiris, B. De Causmaecker, G. De Rouck, G. Aerts, A. Paternoster, J. Braet, L. De Cooman, Influence of transport and storage conditions on beer quality and flavour stability, J. Inst. Brew. 125 (2019) 60–68.
- [36] A. Mata, A.J. Fleischman, S. Roy, Characterization of polydimethylsiloxane (PDMS) properties for biomedical micro/nanosystems, Biomed. Microdevices 7 (2005) 281–293.
- [37] M.F. McGowan, R.-Y.A. Wu, Method and Apparatus for Assisted Heat Transfer for Containers, Google Patents, 2017.
- [38] A. Andersson, W. Zhai, J. Yu, J. He, F.H. Maurer, Free volume and crystallinity of poly (ethylene naphthalate) treated in pressurized carbon dioxide, Polymer 51 (2010) 146–152.
- [39] E. Widder, Gaskets: Surface Finish Effects in Static Sealing, ASME B46 Seminar, 2004.
- [40] B. Pennington, R. Ryntz, M. Urban, Stratification in thermoplastic olefins (TPO); photoacoustic FT-IR depth profiling studies, Polymer 40 (1999) 4795–4803.
- [41] P. Costa, S. Ribeiro, G. Botelho, A. Machado, S.L. Mendez, Effect of butadiene/ styrene ratio, block structure and carbon nanotube content on the mechanical and electrical properties of thermoplastic elastomers after UV ageing, Polym. Test. 42 (2015) 225–233.
- [42] G.L. Shearer, An Evaluation of Fourier Transform Infrared Spectroscopy for the Characterization of Organic Compounds in Art and Archaeology, University of London, 1989.
- [43] M.C. Celina, N.H. Giron, M.R. Rojo, An overview of high temperature micro-ATR IR spectroscopy to monitor polymer reactions, Polymer 53 (2012) 4461–4471.
- [44] J.E. Puskas, M.G. Lanzendörfer, W.E. Pattern, Mid-IR real-time monitoring of the carbocationic polymerization of isobutylene and styrene, Polym. Bull. 40 (1998) 55–61.