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Evaluation of the Surface Tension of Poly(vinyl butyral) Using the Pendant Drop Method

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Summary: In this work the surface tension of poly(vinyl butyral) was evaluated for temperatures ranging from 240 to 260 °C, using the pendant drop method. The surface tension values obtained were in the same range as the ones obtained for other molten polymers; However the variation of surface tension with temperature was more than ten times larger than for other molten polymers. This difference was attributed to a chemical change of the polymer during the surface tension measurement.

Keywords: pendant drop method; poly(vinyl butyral); tension surface

Introduction

Poly(vinyl butyral), PVB, is a random copolymer of vinyl butyral, vinyl alcohol, and vinyl acetate. Its chemical structure is shown in Figure 1. The interest in PVB is based on its structure, which consists of hydrophilic and hydrophobic polymer units in a ratio that can vary over wide ranges. Usually, commercial PVB presents 17–22 wt% of vinyl alcohol units and 1–3 wt% of vinyl acetate units. The hydrophobic vinyl butyral unit gives the terpolymer good thermoplastic processibility, toughness, elasticity, and compatibility with many polymers and plasticizers. The hydrophilic vinyl alcohol and vinyl acetate units are responsible for the high adhesion to inorganic materials such as glass.[1–3] Poly (vinyl butyrals) have been used as raw material for paints, as binders in special paints and in ceramic suspensions, in adhesives, and recently, in blends with other polymers.[1–10] However, the most important field of application of PVB is still the manufacture of laminated safety glass, for which PVB is almost without competition. PVB terpolymer is normally used as a blend of 30 wt% of a plasticizer and PVB to form a film. The plasticizers most frequently used are alkyl phthalate, dibutyl sebacate, and di-2-ethylhexanoate of triethylene glycol.[1–3] The PVB film is used in laminated safety glass which are used in automotive industry and construction.[1,2] Laminated safety glasses consist of a ‘‘sandwich’’ of a PVB film between two sheets of glass.[1] A bad adhesion between the PVB and glass can lead to rejection of the laminated safety glass. In turns, the adhesion between PVB and glass is a function of the materials structure and can be influenced by external phenomena such as water adsorption onto the surface of laminated glasses for example.[11] This adhesion can be quantified by the knowledge of interfacial energy between the glass and PVB at the temperature at which the laminated glass are prepared. However, to our knowledge neither the interfacial adhesion nor the surface tension of PVB at temperatures above softening temperatures have been evaluated, most likely due to the experimental difficulties encountered in evaluating this parameter for PVB which is often used as mentioned above as a blend.

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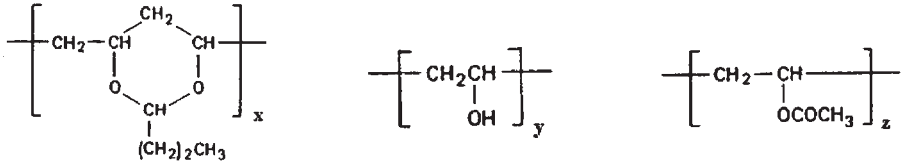

(vinyl butyral) (vinyl alcohol) (vinyl acetate)

Figure 1.
Structure of the poly(vinyl butyral) terpolymer. x, y and z can vary over wide ranges.

The pendant drop method has been widely used to measure surface and interfacial tension of liquids. This method involves the determination of the profile of a drop of one liquid suspended in another liquid (air in the case of surface tension measurement) at mechanical equilibrium. The balance between gravity and surface forces determines the shape of the drop, and through image analysis of the drop profile the interfacial/surface tension can be evaluated. More details about the pendant drop method can be found in Demarquette.[12]

In this work the possibility of evaluating the surface tension of molten PVB film using the pendant drop method has been investigated. The obtained results were explained in light of infrared spectroscopy measurements.

Experimental

Materials

A commercial PVB film normally used in laminated glasses supplied by Solutia do Brasil (Saflex RB41) was used in this work. The plasticizer used in the PVB film was di-2-ethylhexanoate of triethylene glycol.

Pendant Drop Equipment

The pendant drop apparatus used in this work was the same as the one described by Arashiro and Demarquette.[13] It basically consists of three parts (Figure 2):

1. *An experimental cell* where the pendant drop is formed.
2. *An optical system* to monitor the evolution of the drop.
3. A *Data acquisition system* to infer the surface tension from the geometrical profile of the drop.

Sample Preparation and Description of Experimental Procedures

Surface Tension Experiment

PVB film was cut into pieces of about 4 cm long and 1.5 cm wide. All samples remained under vacuum at a temperature of 120 °C for 2 hours prior pendant drop measurements. It was observed that this treatment was necessary if one wants to avoid bubbles in the drops that would prevent the surface tension measurement. The samples were then cut and inserted carefully into the needle necessary to form the drop. More details can be found in Arashiro and Demarquette.[13] The syringe was then inserted in the pendant drop apparatus and left to anneal at the temperature at which the experiment was performed. Before forming the drop it was necessary to leave the polymer into the syringe for 2 hours to prevent the formation of air bubbles. After this time, the pendant drops were formed slowly until reaching an adequate volume of around 10 mm^3. The pendant drops were then left to reach mechanical equilibrium. The experiments were performed under argon atmosphere to avoid thermal degradation.

In order to evaluate the surface tension of molten polymers using the pendant drop method it is necessary to evaluate the density of the material at the temperature at which the surface tension is evaluated. The density of PVB used in this work was

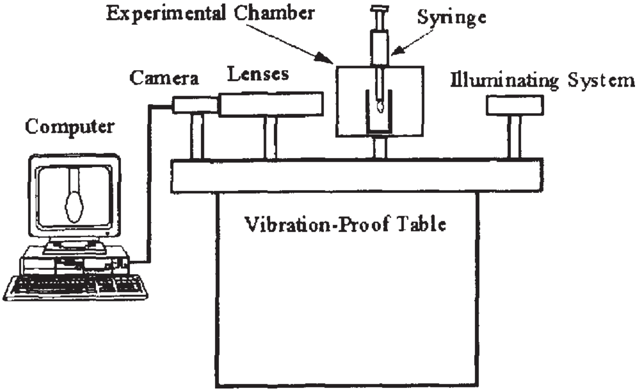

Figure 2.
Schematic representation of the pendant drop apparatus (refs. 12 and 13).

evaluated using PVT (Pressure, Volume, Temperature) analysis.

PVB Film Characterization
The drops after surface tension analysis (kept roughly five hours at the temperature at which surface tension was determined in a argon atmosphere – see below) were examined for any change in their functional groups using a Nicolet 560 IR-Magna infrared spectrophotometer with DRIFTS (diffuse reflectance infrared transform spectroscopy) technique, and 4 cm^{-1} resolution.

Results and Discussion

Figure 3 shows typical droplet images. Figure 3 (a) shows a pendant drop of PVB film at the beginning of the experiment and Figure 3 (b) shows the pendant drop after 5 hours. It can be seen that the drop is obtained without any bubble and evolves from a round to a more elongated shape. This type of evolution is typical when measuring surface tension of molten polymers.[12]

Figure 4 shows a typical graph of the value returned by the image analysis of the pendant drops as a function of time. Once the drop has reached mechanical equilibrium, this values levels off and corresponds to the value of surface tension. In this case it is shown the analysis of a PVB film droplet at 245 °C. The duration of the experiment was of 5 hours although mechanical equilibrium was reached after around 100 minutes, which corresponds to the equilibrium times found when measuring the surface tension of molten polymers using the pendant drop method.[12,13]

The values of the surface tension, as well as the experimental densities obtained for the poly(vinyl butyral) film are presented in

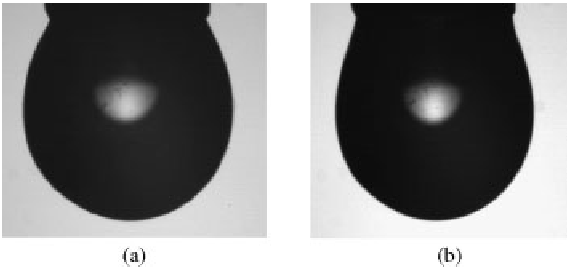

Figure 3.
Evolution of a pendant drop. (a) at the beginning of the experiment (b) after 1.5 hour.

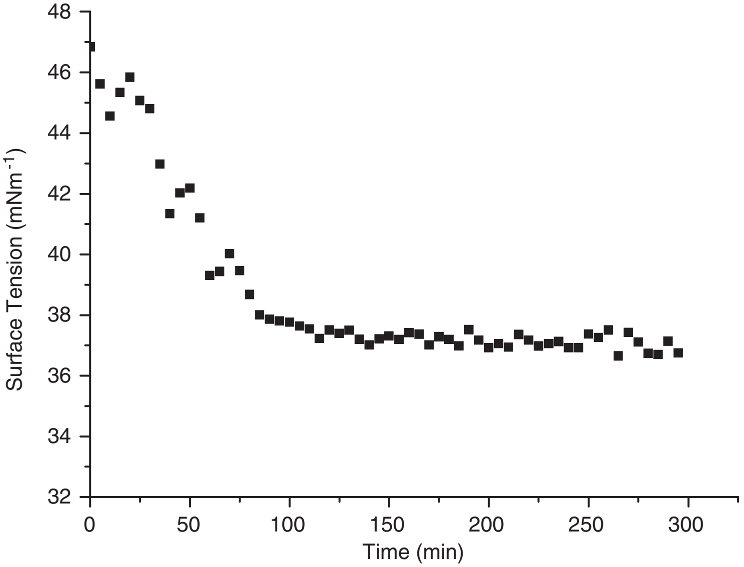

Figure 4.
Typical graph of surface tension as a function of time for poly(vinyl butyral) film at 245 °C.

Table 1. These values correspond to the average of the results obtained performing three to five different experiments.

The values presented in Table 1 are in the same order of magnitude than the ones for other molten polymers.[12–14] Figure 5 shows the surface tension of PVB film as a function of temperature. The symbols represent the experimental data. The straight line represents the best fit obtained by linear regression. It can be seen that the surface tension of PVB film decreases linearly when the temperature is increased, what is expected thermodynamically. The equation of the straight line obtained fitting the surface tension as a function of temperature is:

$$Y(T) = 187.0476 - 0.6275\,T \quad R^2 = 0.9772$$

Table 1.
Experimental values of the surface tension and density obtained for the PVB film.

Temperature (°C)	γ (mN · m^{-1})	ρ (cm^{-1})
240	36.4 ± 0.2	0.87
245	32.0 ± 0.3	0.86
250	30.6 ± 0.1	0.86
255	26.4 ± 0.3	0.86
260	23.4 ± 0.2	0.85

$-\frac{\partial\gamma}{\partial T}$. The surface tension temperature coefficient is 0.6 mN · m^{-1} which is much larger than values reported for other polymers.[13,14]

Figure 6 shows a comparison between the Infrared spectra of the pendent drops, the virgin PVB film and the film that has been dried in a vacuum oven prior to surface tension measurement (see experimental section). The infrared spectra present a broad band at 3600 cm^{-1} corresponding to –OH group, together with the C–H stretching at 2975 cm^{-1} and 2870 cm^{-1}. The spectra also present a peak at 740 cm^{-1} corresponding to C–H stretching originated from cyclic hydrocarbon within the vinyl butyral units of PVB, a strong C=O absorption peak at 1740 cm^{-1}, corresponding to the vinyl acetate units of PVB and ester units of plasticizer (di-2-ethylhexanoate of triethylene glycol). It can be also observed the symmetric and asymmetric axial stretching of C–O–C group at 1050 and 1175 cm^{-1}, respectively, present in the structure of PVB (vinyl acetate units) and of plasticizer (ester groups).[15]

It can be seen from Figure 6 that the spectra for the virgin and the film of PVB

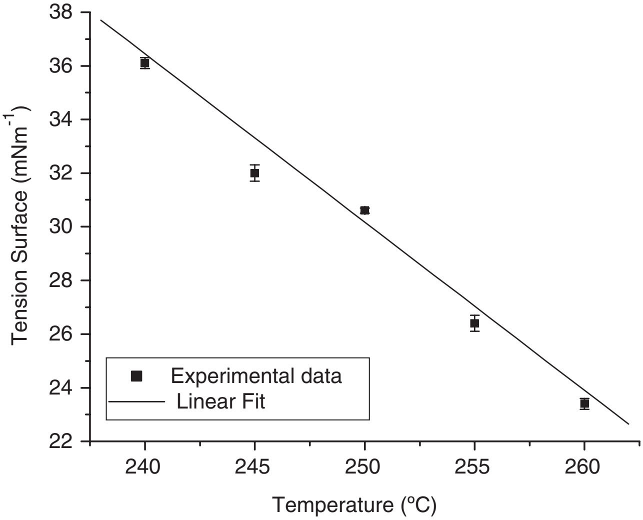

Figure 5.
PVB film surface tension in function of temperature.

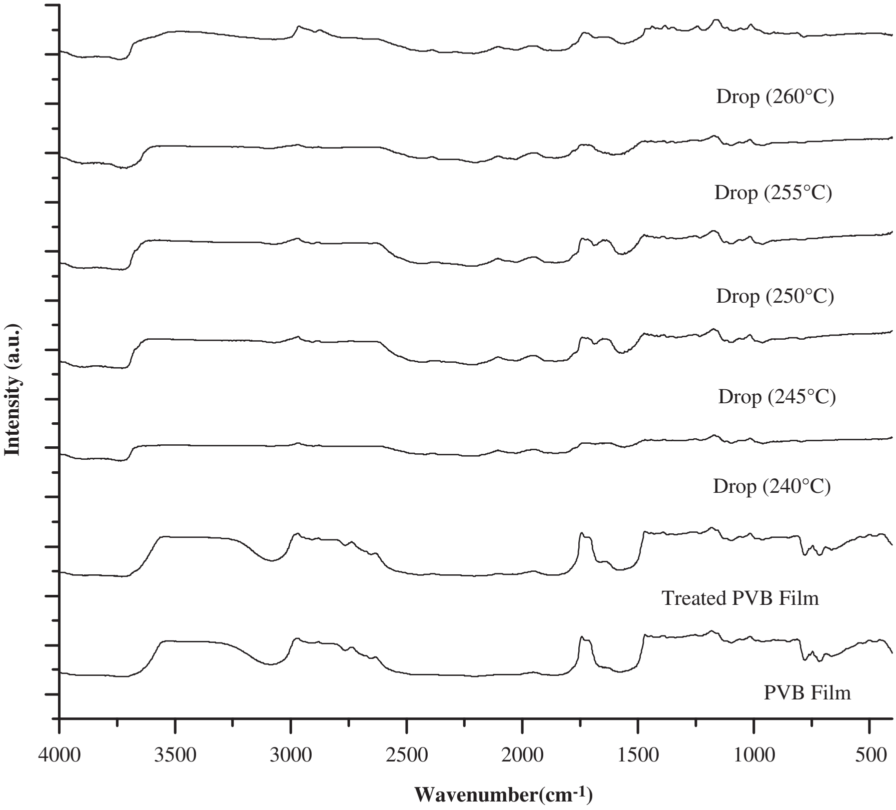

Figure 6.
Infrared spectra of PVB after different thermal treatment.

after treatment in a vacuum oven for 2 hours at 140 °C are identical, indicating that the PVB neither suffered modification in its chemical structure nor lost plasticizer. Comparing the spectra of the PVB of the drops with the one for virgin and treated PVB it can be seen that some chemical modifications occurred during surface tension measurement. In particular, two regions of the spectra were modified: from 800 to 700 cm^{-1} and from 1800 to 1600 cm^{-1}. Figures 7 and 8 show blow ups of Figure 6 for wavelengths ranging from 1000 to 500 cm^{-1} and from 1800 to 1500 cm^{-1}, respectively. As a first analysis, it can be seen from Figure 7 that the intensity of C–H stretching peak of vinyl butyral units of PVB (740 cm^{-1}) decreased as the temperature at which the surface tension was measured increased. That peak almost disappeared for the sample that was used for a surface tension measurement at 260 °C. Most likely, the samples that were submitted to temperatures of 250 and above suffered cleavage of the ring. In Figure 8, it can be noted that the strong C=O peak at 1740 cm^{-1}, corresponding to the vinyl acetate units of PVB and ester group of plasticizer, was broadened and reduced in intensity for all pendant drop samples. Also the band at 1650cm^{-1} corresponding C=C group was increased as the surface tension measurement temperature was increased. The chemical modifications occurring during surface tension measurement corroborate the thermal degradation mechanism proposed by El-Din et al.[2]. According to this mechanism, the initial point of degradation is the vinyl acetate unit, the weakest unit of PVB structure which detaches itself from the main chain. In subsequent steps the molecule suffers scission and the ring of the vinyl butyral unit opens, leading to the formation of chains with C=C double bonds.

The changes of chemical structure undergone by the PVB during surface tension measurement could explain the large value of $-\frac{\partial \gamma}{\partial T}$. During the surface tension measurement, at higher temperatures than 250 °C, PVB degrades through a reduction of vinyl acetate polar units and a creation of C=C double bonds; it becomes less polar, presenting surface tension values typical of apolar polymers such as polypropylene or polyethylene.[14]

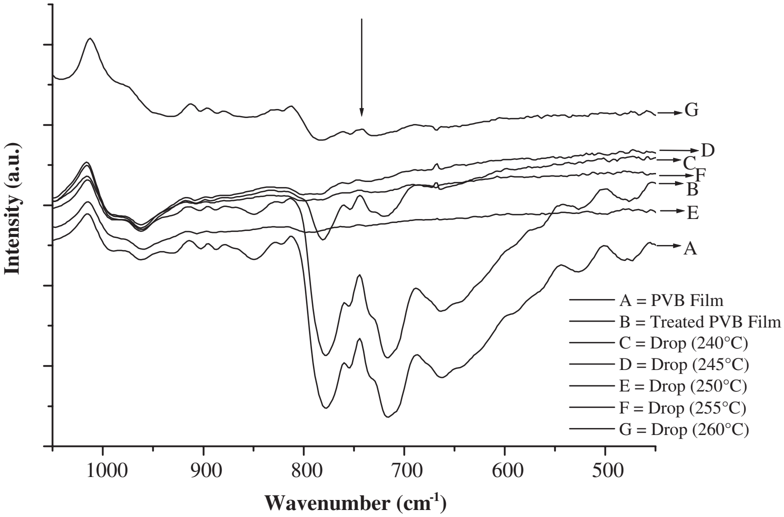

Figure 7.
Infrared spectra of the samples studied for wavelengths ranging from 1000 to 500 cm^{-1}.

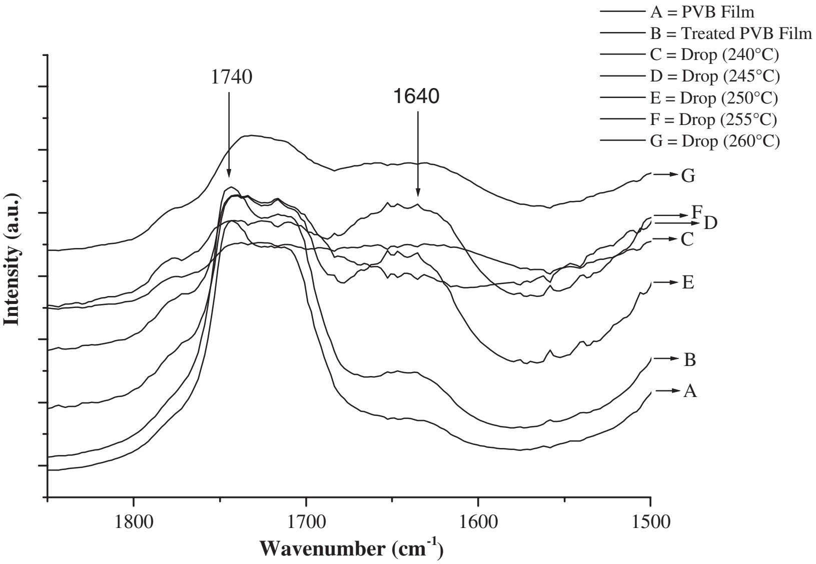

Figure 8.
Infrared spectra of the samples studied for wavelengths ranging from 1800 to 1500 cm^{-1}.

Conclusion

In this work, surface tension of poly(vinyl butyral) (PVB) was evaluated using the pendant drop method for temperatures ranging from 240 °C to 260 °C. The surface tension of PVB decreased linearly with increasing temperature. However, the dependence of surface tension with temperature was much larger than for other molten polymers due to a chemical degradation suffered by the polymer during the measurement.

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