Mechanical Properties of Recycled Plasticized PVB/PVC Blends

Michael Tupý, Dagmar Měřínská, Alice Tesaříková-Svobodová, Christian Carrot, Caroline Pillon, Vít Petránek

Abstract—The mechanical properties of blends consisting of plasticized poly(vinyl butyral) (PVB) and plasticized poly(vinyl chloride) (PVC) are studied, in order to evaluate the possibility of using recycled PVB waste derived from windshields. PVC was plasticized with 38% of diisononyl phthalate (DINP), while PVB was plasticized with 28% of triethylene glycol, bis(2-ethylhexanoate) (3GO). The optimal process conditions for the PVB/PVC blend in 1:1 ratio were determined. Entropy was used in order to theoretically predict the blends miscibility. The PVB content of each blend composition used was ranging from zero to 100%. Tensile strength and strain were tested. In addition, a comparison between recycled and original PVB, used as constituents of the blend, was performed.

Keywords—Poly(vinyl butyral), poly(vinyl chloride), windshield, polymer waste, mechanical properties.

I. INTRODUCTION

THE *poly(vinyl butyral) (PVB)* polymer is mostly used in the form of plasticized PVB sheet for the production of laminated safety glass used as windshield, and safety glass in civil engineering applications. PVB is a polymer which can connect two sheets of float glass resulting in a laminate with excellent optical and mechanical properties [1]-[6]. The most significant properties of plasticized PVB are elasticity, strength, toughness, high light transmission and adhesion to siliceous substances. Toughness and excellent tensile properties of PVB sheet are achieved due to high molecular weight of PVB. PVB is a polyacetal produced by the condensation of polyvinyl alcohol with n-butyraldehyde in the presence of an acid catalyst [5]. The condensation reaction does not run to 100% conversion and the final structure can be considered to be a random atactic ter-polymer of vinyl butyral 79 to 81% (w/w), vinyl alcohol 18 to 19% (w/w) and vinyl

acetate < 2% (w/w) [14]. Nevertheless, this polymer has to be plasticized to become softer in order to achieve the required mechanical and optical properties, mostly by branched ethylene glycol esters in amount 25 to 30% [1], [2].

Worldwide, the total amount of PVB sheet produced for automotive industry and civil engineering is estimated around 120 million kg per year [7]. The current windshield recycling process is based on mechanical peeling. This type of recycling technology provides PVB, which contains high degree of residual glass dust (1-5%, w/w) and other contaminants, such as water, parts of colored PVB sheets, mixtures of various PVBs, sludge, paper and foreign plastic matters [8], [11]. This PVB is a by-product and it cannot be reprocessed again into PVB sheet suitable for glass lamination. Furthermore, this PVB scrap is incinerated or land-filled [9], [12]. Thus, the recycling processes used nowadays produce a good quality of glass scrap which could be partially re-used in the glass batch or in other technologies. Nevertheless, the separated PVB waste is not still fully recyclable [10]. Thus, investigating the possibility of new applications of recycled PVB may help to solve a major environmental problem. Anyway, the indisputable advantage of PVB is that the interglassed PVB is not degraded. This is very important because PVB is not essentially exposed to UV radiation (up to 320 nm), mechanical stress, elevated temperature, oxygen and any corrosive damaging substances [8], [10]. Therefore, the interglassed PVB sheets should possess physical properties very similar to those of the extruded material before the lamination process. Due to this knowledge, PVB may be used again, for example in blends with similar polymers. The obtained materials can be used in various applications such as flooring, production of glue, in civil engineering, as well as in automotive industry. This is also one of the assumptions for use of recycled PVB as protection of concrete structures against environmental effects which cause degradation.

The *poly(vinyl chloride) (PVC)* is mostly used for flooring applications [11]. Moreover, PVB/PVC blends can be also applied in applications like sheathing of wires, production of carpets, drainage, window profiles, waterproofing membrane and sheets, sewer pipes, automotive applications, adhesives and synthetic leather as well. Other important information is that PVC and PVB are typical polymers which are plasticized in order to achieve high toughness. The mentioned PVB and PVC systems have very similar macromolecules polarity, which is also the case for the plasticizers used. Due to the similar polarity, it is assumed that some blends of PVB and PVC could have good miscibility, resulting in blends with good mechanical properties. Concerning economical aspects,

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the price of original PVB is much higher than common plastics (such as PE, PS, PVC). On the contrary, the price of recycled PVB (having also very good mechanical properties) is lower than that of PVC. Thus, the use of recycled PVB as a partial substitution of PVC could contribute in lowering the cost of PVC products.

The aim of the present work was to characterize the mechanical properties of blends consisting of plasticized PVB and plasticized PVC at various concentrations. In addition, a comparison between recycled and original PVB, used as constituents of the blend, was performed.

II. EXPERIMENTAL

A. Materials

Original PVB sheets were supplied by DuPont *(USA)* and under the trade name Butacite B5. The PVB sheets contained approx. 28% (w/w) of plasticizer triethylene glycol, bis(2-ethylhexanoate) (labeled 3GO) [12], [13]. The average molecular weight (M_w) of PVB was assessed by GPC analysis at 410 kg/mol; the PVB polydispersity was 4.0 [14].

Recycled PVB particles, derived from windshields, were supplied from Praktik group *(Czech Republic)*. The particles of PVB had a size of 1-5 cm^2 and it contained less than 0.03% (w/w) of impurities such as glass, sand etc.

A suspension type of PVC polymer, Ongrovil S 5070 with K value 70, was fluidly mixed with DINP plasticizer in a ratio of 3:2 (w/w). Thermal stabilizer was also added (0.5% w/w to PVC) in the mixture. The material obtained was PVC powder with adsorbed additives. The molecular weight of PVC was estimated according to K value to be 75 kg/mol [15].

B. Sample Preparation

Blends of recycled PVB and PVC were prepared. Samples (blends) were prepared in a Brabender kneader device to determine the optimal process conditions. The device contained two blungers W50, and used a friction of 2:3. The volume of the heated chamber was of 55 cm^3. A constant amount of 40 g input material (PVB plus PVC) was placed in the chamber and processed for 10 minutes at different temperatures (130, 140, 150, 160, 170°C), at rotation speed of 20 rpm.

The blends of each PVB/PVC ratio were prepared in total material amount of 2 kg in continual BUSS extruder with two kneading chambers with friction. The whole processing time was estimated to 6-8 minutes. The process conditions for 1st (blending) chamber were: temperature of 130 / 140 / 150 / 160 / 160 / 160°C; rotation speed of 250 rpm. The process conditions for 2nd (transport) chamber were: temperature of 160°C; rotation speed of 55 rpm. The extruded string was cut in the form of pellets and mixed in a bag. This process was performed once more as previously, in order to achieve polymers homogenization as well.

The specimens for tensile strength measurement were prepared by sintering. The blends, in form of pellets, were placed between two PET sheets preventing the contact with air and thus oxidative degradation. The mould's dimensions were 125 × 125 × 2 mm. The sintering conditions were: pressure

1.5 MPa; temperature 170°C; process duration 7 minutes. After sintering, the mould was allowed to cool at room temperature, being under steady pressure.

C. Tests

The mechanical properties of the samples obtained were determined using a T 2000 Tensile tester *(Alpha Technologies)* with a 2 stages displacement rate. The 1st stage had speed configuration of 1 mm/min up to strain 2.00 %, while the 2nd stage had a speed configuration of 500 mm/min till the sample was broken. The measurement was carried out at room temperature. Tensile strengths and strain were determined according to the norm EN ISO 527-3.

III. RESULTS AND DISCUSSION

A. Optimal Process Conditions

As it was previously mentioned, the optimal process conditions were determined through testing, using a Brabender kneader device, which had two blungers W50, and used friction. The importance of testing lies in the fact that the optimal temperature was determined, which ensures optimal polymer homogenization, thus not allowing the thermo-oxidative degradation of both vinyl polymers. The starting kneading temperature was 130°C and was raised until 170°C. In this case, pure plasticized polymers (not recycled) were used. The reference PVB/PVC ratio was suggested to be 1:1, in order to avoid the influence of any of the polymers used.

The specimens supposed to be used for the tensile strength test were sintered. It was experimentally found, that the sintering temperature had to be at least 170°C (or higher) and the process time 7 minutes. The specimen thickness was 2 mm. When the temperature was lower than 170°C, sintering was not effective. According to the observations, this negative phenomenon was caused by an infelicitous sintering of polymer particles, which resulted in shortening of the tensile curves. The dependence of tensile properties on the applied sintering temperature is shown in Figs. 1, 2.

It was observed, that the stirring of the processed polymers was considerably complicated at lower temperatures, such as 130 to 140°C. At these temperatures, it was necessary to feed PVB sheet as a first and PVC powder in a second step. Moreover, PVC was not still melted after 10 minutes of kneading. On the other hand, the kneading of PVC powder was very easy at temperatures above 160°C. However, when the process temperature was higher than 170°C, thermo-oxidative degradation of PVC and PVB was observed, which resulted in slight polymer yellowing. The degradation was more probable in the case of PVB; PVC contained a thermal stabilizer. All these statements were also reflected on the tensile strength and elongation measurements (Figs. 1, 2).

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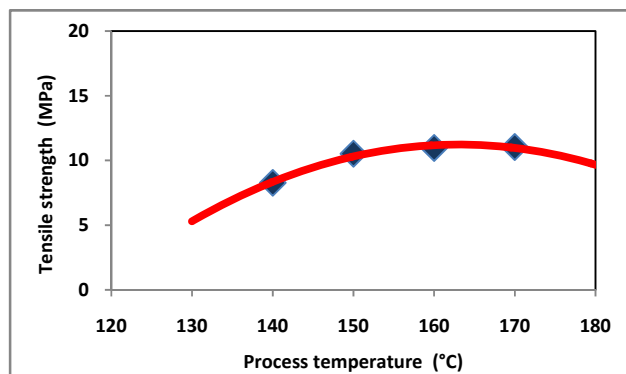Vol:8, No:9, 2014

Fig. 1 Strength at break of blend: PVB/PVC (in ratio 1:1), after various process conditions
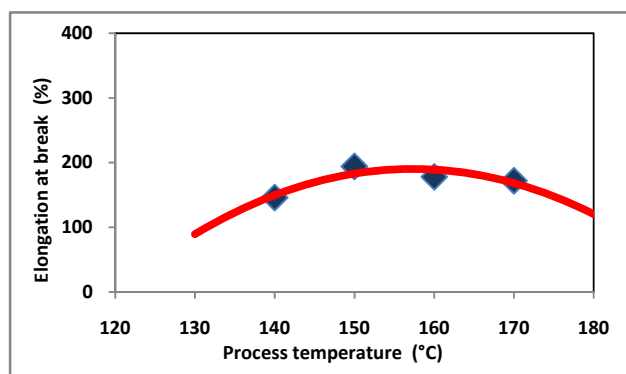

Fig. 2 Elongation at break of blend: PVB/PVC (in ratio 1:1), after various process conditions

B. Various PVB and PVC ratio in Blends

As it was mentioned before, blends with various PVB/PVC composition were prepared in continual BUSS extruder with two kneading chambers with intensive friction. Due to a double-thread worm with high rotation speed, the blending efficiency was very high. The amount of each processed blend was 2 kg.

Two existing plasticized systems with similar plasticizing degree of both polymers were used. In case of PVB, the system has an amount of 28% (w/w) of 3GO. The mixture is applied for the manufacturing of laminated safety glass. In case of PVC, it was the system with 38% (w/w) DINP which is typical for flooring.

The miscible theory of the tested polymers was estimated by the Gibbs energy of blending. The entropy part of blending depended on polymer's morphology. It was given by the size of the molecular weight of the blended polymers. The enthalpy part of Gibbs law was given by interaction between PVB and PVC. Thermo-mechanical considerations can be used to determine the approximate position of the critical blending point. Lowering of temperature results in a bimodal decomposition and co-continuous morphology can be expected. The bimodal curve is strongly influenced by the used mechanical energy. This estimation should positively contribute to the blending. Another point, which positively contributes to the blending process, is the similarity of the density of cohesive energies (polymer polarity) between PVB

and PVC polymers. The difference between them determines enthalpy *ΔH*. The values for PVC and PVB are very similar [16]. In the case of PVB, the density of cohesive energy value was adjusted by an amount of residual vinyl alcohol units.

Low enthalpy (*ΔH*) was assumed for low Gibbs energy (*ΔG*). It is generally known, that the negative value of Gibbs energy positively influences the polymers blending. Gibbs energy (*ΔG*) [J/mol] can be determined according to (1):

$$\Delta G_{blend} = \Delta H_{blend} - T\Delta S_{blend} \qquad (1)$$

where ΔG is the Gibbs energy of blending process; ΔH is the enthalpy of the polymers used in blending process; T is the temperature of blending process; ΔS is the entropy (degree of system disorderliness).

The entropy part was supported by the system of amorphous PVB and PVC macromolecules and the presence of both plasticizers. These rolled out a packet of both polymers. However, as it was mentioned before, the values of entropy (*ΔS*) were primarily determined by the molecular weight of the blended polymers. When the average molecular weight (M_w) of PVC was 75 kg/mol, the molecular weight of PVB was 410 kg/mol. Thus, M_w (PVB) was about 5.5 times higher than the PVC molecular weight. Therefore, the amount of PVB macromolecules has to be 5.5 times smaller than the amount of PVC macromolecules in unit volume. The entropy was determined according to (2):

$$\Delta S_{blend} = -R(n_{PVB} \ln \varphi_{PVB} + n_{PVC} \ln \varphi_{PVC}) \qquad (2)$$

where ΔS is the entropy of blending process; R is the molar gas constant [R = 8.314 m^2.kg/s^2.K.mol]; n_{PVB} and n_{PVC} are the amount of moles, which were calculated by the molecular weight of PVB and PVC, respectively, in unit volume; φ_{PVB} and φ_{PVC} are mole fractions of each polymer. The reference amount of PVC macromolecules was suggested to be 100 in unit volume. Thus, the calculated amount of PVB macromolecules was 18.3. According to (2), the calculated entropy of each blend in dependence of PVB concentration is displayed in Fig. 3. The results point out that a mixture with PVB composition between 10 to 90 % (w/w) can be blended with problems. It can be an assumption for the reduction of material strength. However, the final properties can be elevated by increasing the process temperature and stirring rate.

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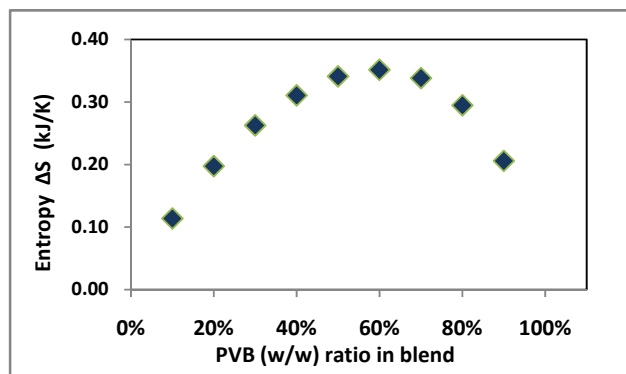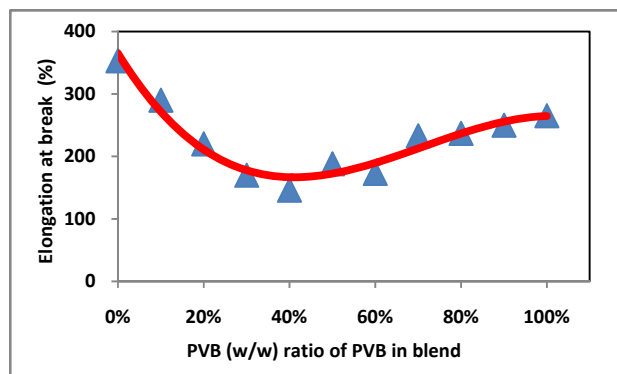Vol:8, No:9, 2014

Fig. 3 Entropy of each polymer blend

Fig. 5 Elongation at break of various PVB/PVC blends

One of the reasons of PVB application is the high molecular weight of this polymer, which provides interesting mechanical properties. On the other hand, high molecular weight also brings complications when the material is processed. As the results in Figs. 4, 5 show, the substitution from PVC to PVB reduced tensile strain and elongation dramatically. This can be clearly observed for PVB ratio 0 to 40% (w/w). The mechanical properties had the worst values when the PVB content was in the range between 30 and 50% (w/w). However, when PVB started to be the major component, the mechanical properties started to be stable. This effect was visible in PVB ratio above 60% (w/w). This could be due to the longer macromolecules of PVB, as previously mentioned. Nevertheless, it would be interesting to compare the results of mechanical properties with those obtained from differential scanning calorimetry (DSC) and the changes in the glass transition temperatures (T_g) for each blend. This will be the subject of a further research.

As Fig. 6 shows, the tensile curve of PVC had concave form. When the elongation was 50%, the curve was very arduous. The tensile curve of PVB had the opposite form. When the elongation was 120 %, the tensile curve had a typical rubbery characteristic; the strength increased very slowly. Further, the PVB tensile curve significantly increased until the value of 19.3 MPa, which resulted in breaking at elongation of 265%. In the case of PVC, the break occurred for strain of 15.8 MPa which resulted in breaking at extension at break 350%. The strength of PVC was lower about 18% than that of PVB. However, the elongation of PVC was higher about 33% than in the case of PVB. It was also achieved by a slightly higher degree of PVC plasticizing. The worst mechanical properties were observed in the case of the blend with material composition 40% (w/w) PVB as Figs. 4, 5 show. The tensile strength was only 8.5 MPa, while the elongation at break was 146%. The obtained results describe that more practical is to use PVB/PVC blends when PVB is the matrix. However, this model is not so suitable for industrial use.
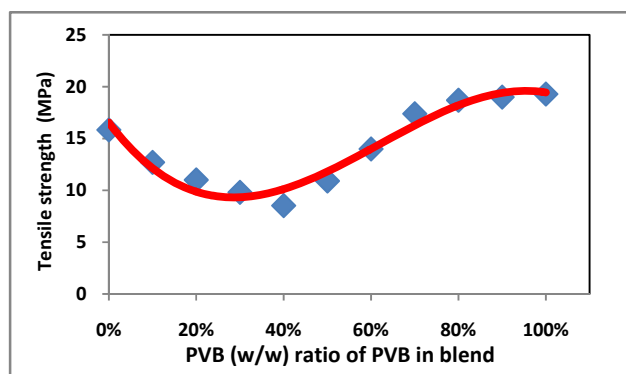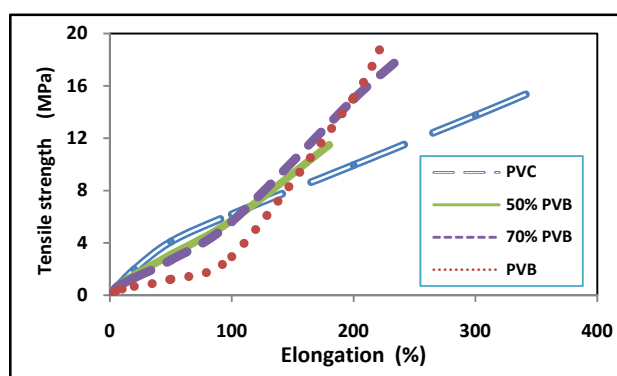

Fig. 4 Stress at break of various PVB/PVC blends

The calculated values of Young's modulus (*E*) depended on the ratio of PVB in the blend. The Young's modulus of plasticized PVC (without PVB) was 31.4 MPa, while the original plasticized PVB (without PVC) had a value of only 6.9 MPa. This big difference was determined by the behavior of tensile curves - Young's module is calculated by the curve in low elongation when the behavior is still linear.

Fig. 6 Strass/strain dependence of various PVB/PVC blends

However, when the plasticized PVB and PVC were immiscible, because the free energy is always positive and a two phase system was observed, the relation to mechanical properties was more dependent on the morphology than on the polymer miscibility. The partial mixing and miscibility at the interface can have a role but not in a great extent. When the high-molecular PVB is the matrix or for co-continuous morphologies (intermediate range), the elongation at break is limited by PVB, which is the weakest material from this point

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of view. Therefore, materials with low amounts of PVB give the best results. On the other hand, a similar case also exists when PVB is a co-continuous phase (PVB functions as matrix). It imposes better tensile strength, since pure PVB is better than pure PVC from this point of view. The overall improvement should be best viewed in terms of breaking energy. Therefore, the experimental observations on tensile data seem to be a trace of the morphology rather than of thermo-dynamical considerations. Thus, the morphology influence of high-molecular PVB needs to be explored in future research work.

C. Original vs. Recycled PVB

The last chapter is focused on the use of recycled PVB. The properties of recycled PVB were compared with the original PVB. Blends of original and recycled PVB with PVC in ratio 1:1 were also compared. The results of tensile tests are shown in Figs. 7, 8.
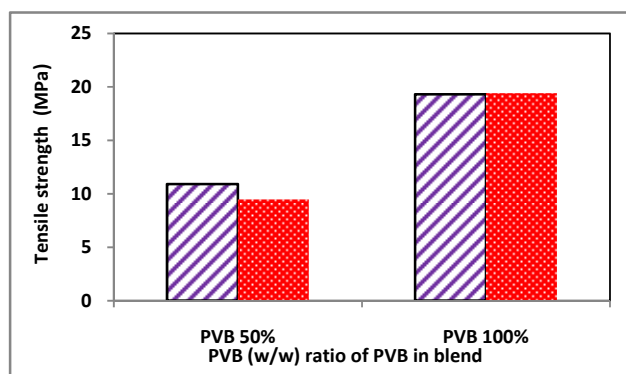

Fig. 7 Comparison of tensile strength of original PVB (dashed) and recycled PVB (filled), also in blend with PVC (1:1)
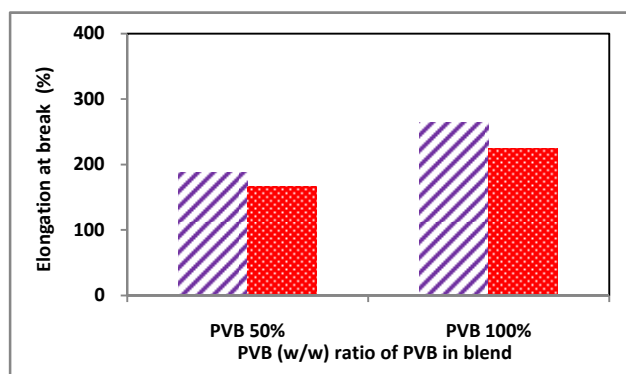

Fig. 8 Comparison of tensile strength of original PVB (dashed) and recycled PVB (filled), also in blend with PVC (1:1)

The results show that the tensile strength of the recycled and original 100% PVB does not differ. The elongation at break of recycled PVB was about 15% lower. The blend composition of recycled PVB/PVC (1:1) had tensile strength lower about 13% than the same blend with original PVB. The elongation was reduced by 11%. Although the recycled PVB was very clean, the lower mechanical properties were probably attributed to the presence of residual glass and other contaminants, which reduce the tensile curve of the material.

Some degree of mechanical properties reduction is certainly due to the PVB recycling process, which removes the plasticizer, while photo-oxidative aging of the material is also caused by PVB recycling and its transport.

IV. Conclusions

The tested polymers PVB and PVC had very similar polarity of their macromolecules and the plasticizers used. The work used PVB with high molecular weight, 5.5 times higher than that of the used PVC with K value 70. It was observed that the high-molecular PVC did not have a good compatibility in blends of PVC, even in PVB ratio from 30 to 50% (w/w). These polymers should be miscible; however, the measurement of mechanical properties confirmed considerably degreased strength and strain of blends, especially when the PVB ratio was between 10 to 0%. The stability of mechanical properties of various blends was detected for PVB ratios between 60 and 100% (w/w), which was probably caused by the mentioned high molecular weight of PVB. This assumption was confirmed by enthalpy, which was calculated for the used blends. Other comparison showed that the mechanical properties of recycled PVB and of the blend consisting of recycled PVB and PVC (1:1) are reduced about 10 to 15%, in comparison with the original PVB and its blends.

Anyway, the price of original PVB is much higher (as also the price of common plastics is, such as PE or PVC) than the price of recycled PVB, which is relatively low. In addition, recycled PVB has still very good mechanical properties, and thus it can be re-processed with PVC if the material requirements allow this substitution.

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