

Comparison of Processing Conditions for Plasticized PVC and PVB

Michael Tupý, Jaroslav Císař, Pavel Mokrejš, Dagmar Měřinská, Alice Tesaříková-Svobodová

Abstract—It is the worldwide problem that the recycled PVB is not recycled and it is wildly stored in landfills. However, PVB has similar chemical properties such as PVC. Moreover, both of these polymers are plasticized. Therefore, the study of thermal properties of plasticized PVC and the recycled PVB obtained by recycling of windshields is carried out. This work has done in order to find non-degradable processing conditions applicable for both polymers. Tested PVC contained 38% of plasticizer diisononyl phthalate (DINP) and PVB was plasticized with 28% of triethylene glycol, bis(2-ethylhexanoate) (3GO). The thermal and thermo-oxidative decomposition of both vinyl polymers are compared by calorimetric analysis and by tensile strength analysis.

Keywords—Poly(vinyl chloride), Poly(vinyl butyral), Recycling, Reprocessing, Thermal analysis, Decomposition.

I. INTRODUCTION

A. Poly(Vinyl Chloride)

THE poly(vinyl chloride) (PVC) is mostly used for flooring applications [1], [2]. As it was previously published, the blends of PVB and PVC can be also applied in next applications of sheathing of wires, production of carpets, drainage, window profiles, waterproofing membrane and sheets, sewer pipes, various automotive applications, adhesives and synthetic leather [3], [4]. It is given that PVC and PVB are polymers which are used in plasticized form in order to achieve toughness as well. Both systems of are very similar in case of polarity of macromolecules such as used plasticizers [5]. Therefore, this theory is assumption to the miscibility of all blended compounds and also keeps good mechanical properties of used blends. Any possible contribution is reduction of the price of plasticized PVC.

B. Poly(Vinyl Butyral)

The poly(vinyl butyral) (PVB) is mostly used in the form of plasticized PVB sheet for production of laminated safety glass used as windshield and safety glass in civil engineering. The

PVB is a polymer which can connect two sheets of float glass resulting in a laminate with excellent optical and mechanical properties [6]-[9]. The most significant properties of plasticized PVB are elasticity, strength, toughness, high light transmission and adhesion to siliceous substances [6]. 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 [7]. 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) [12]. Nevertheless, this polymer has to be plasticized to become softer in order to achieve required mechanical and optical properties, mostly by branched ethylene glycol esters in amount 25 to 30% [8], [10].

The total amount of manufactured cars was 87 million cars in worldwide [11]. Thus, total amount of PVB sheet produced by automotive industry and civil engineering is estimated around 150 million kg per year. The current windshield recycling process is based on mechanical peeling. This type of recycling technology provides the PVB which contains high degree of residual glass dust (1-5%, w/w) and other contaminants: water, parts of color PVB sheets, mixed of various PVBs, sludge, paper and foreign plastic matters [1], [10]. This PVB is a waste material and it cannot be reprocessed again into PVB sheet suitable for glass lamination. Furthermore, this PVB scrap is incinerated or land-filled [13], [14]. The possible application of recycled PVB can helps to solve a major environmental problem. However, the separated PVB waste is not degraded and it is still fully recyclable [15]. This is very important because the PVB is not essentially exposed to UV radiation (up to 320 nm), mechanical stress, elevated temperature, oxygen and any corrosive damaging substances [15]. Due to this knowledge, the PVB has still excellent physical properties and this material can be used again, for example in application of blend with PVC.

The aim of the present work is to characterize the thermal and thermo-degradable properties of plasticized PVB and plasticized PVC and find if both polymers can be processable as blend in similar processing conditions.

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II. EXPERIMENTAL

A. Materials

The suspension type of PVC with K value 70 was fluidly mixed with DINP plasticizer in ratio 3:2 (w/w). Organic thermal stabilizer was also added (2.0 % w/w to PVC).

Recycled PVB sheet was supplied from windshield recycling process with very low amount of residual glass slivers. Particles of recycled PVB sheets were in size 3-10 μm^2 and it contained less than 0.03% (w/w) of impurities such as glass, sand, etc. Tested PVB contained approx. 28 % (w/w) of plasticizer triethylene glycol, bis(2-ethylhexanoate) (labeled 3GO) [14], [16].

B. Sample Preparation

Recycled PVB was obtained from windshield recycling process as mentioned before. Plasticized PVC was prepared in total material amount 2 kg in continual BUSS continual kneader with two kneading chambers and friction. The whole processing time is estimated for 6-8 minutes. Process conditions for 1st (blending) chamber were: temperature 130 / 140 / 150 / 160 / 160 / 160°C and rotation speed 250 rpm. Process conditions for 2nd (transport) chamber were: temperature 160°C and rotation speed 55 rpm. Extruded string was cut and pelleted as well.

Specimens for tensile strength measurement were prepared by molding injection process in equipment ERGOTECH 50-200 SYSTEM. Polymers in form of pellets were added in the equipment and molded in process conditions: temperature of 30 / 125 / 135 / 145 / 155°C, injection pressure of 1500 bars, additional pressure of 400 bars for 200 s. Molded specimens were cooled into the forms to temperature 40°C.

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.

The glass transition temperature and melting behavior of the composites were investigated by the differential scanning calorimetry (DSC) using a device 200PC Phox NETZSCH, operating under nitrogen flow. Samples of approximately 10 mg were weighed and sealed in aluminum sample pans. Before the heating and cooling scans, composites were melted at 150°C and maintained at this temperature for 5 min in order to erase the thermal history of tested material. Subsequently they were cooled from 150 to -80°C at a rate of 10°C/min, and then heated from -80 to 160°C at 10°C/min. The transition temperatures were taken as the inflection point in the calorimetric curves.

The determination of onset oxidative temperature (OOT) was also determined by DSC 200PC Phox NETZSCH device. The measurement was carried out under nitrogen atmosphere, from room temperature to 70°C with nitrogen flow of 50 mL/min. In the temperature of 70°C, the oxygen purge was

added in a flow of 50 mL/min and the measurement continued till the sample was not fully degraded.

The thermal and thermo-oxidative stability (decomposition) of PVB and PVC polymers and its blends in amount of 10 mg was analyzed by thermogravimetric analysis (TGA). The measurements were carried out using a TG 209 F1 Libra NETZSCH, at heating rate of 10°C/min. The thermal decomposition was carried out under nitrogen atmosphere with dynamic conditions, from 15°C to 1000°C, with a gas purge of 50 mL/min. The thermo-oxidative decomposition was carried out under pure oxygen environment, from 15°C to 600°C. The oxygen flow was 40 mL/min.

III. RESULTS AND DISCUSSION

A. Thermo-Mechanical Properties

The first step of the work was focused on describing of the thermo-mechanical properties of tested plasticized PVC/PVB samples. The DSC analysis determined that a glass transition temperature (T_g) of commercially used plasticized PVC was -38.4°C. The changing of glass phase started at -55.9°C and completely converted in rubbery phase at -21.0°C.

The (T_g) of recycled PVB, was determined to value 16.2°C. Changing of the glass transition phase started at 2.6°C and completely converted at 29.7°C. Obtained curves from differential scanning calorimetry are shown in Fig. 1.

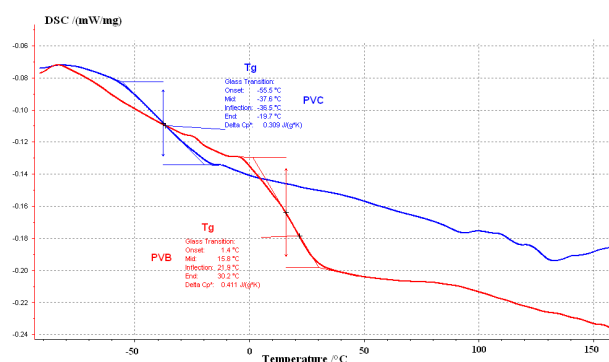


Fig. 1 Glass transition temperature of pure PVC and PVB polymers, determined by DSC analysis

For the comparison, the (T_g) of un-plasticized PVC was determined at 78°C and for PVB at 49°C, respectively. Thus, it is observable that plasticizing process reduced the (T_g) of PVC about 116°C and about 65°C in case of PVB. Mentioned difference can be explained by lower plasticized degree of PVB (28 %, w/w) while PVC contained 38 % (w/w).

The following step was a measurement of mechanical properties at room temperature. Both tested polymers were in rubbery phases at 23°C. The analysis was carried out as a dependence of tensile strength on elongation at break. Obtained curves are viewed in Fig. 2. It describes the tensile properties of plasticized PVC and PVB obtained from recycled windshield.

This dependence shows that tensile curve of the PVC had character of typical amorphous thermoplastic polymer while

the behavior of PVB curve was close to rubbery characteristic. The shape of the tensile curves caused final affect to the ultimate tensile strength and also elongation of the material before breakage occurred. The tensile curve of PVB significantly increased until the value 19.3 MPa which caused at break at 265%. However, the PVC properties provided tensile strength only of 15.8 MPa but elongation of 353%. The strength of PVC was lower about 18% than strength of PVB and the elongation of PVC was higher about 33% than in case of PVB. It was also achieved by a slightly higher ratio of PVC plasticizer.

TABLE I
THERMAL DEGRADATION IN NITROGEN ATMOSPHERE

decomposition stages	PVC	PVB
1.stage		
start – finish (°C)	185 - 345	45 - 303
degradation onset (°C)	292.9	266.4
mass loss in stage (%)	-72.47	-22.06
mass flow (%/min)	-17.63	-3.22
2.stage		
start – finish (°C)	380 – 500	303 – 460
degradation onset (°C)	459.3	378.1
mass loss in stage (%)	-83.9	-89.2
mass flow (%/min)	-1.66	-9.65
3.stage		
start – finish (°C)	500 – 610	460 – 550
degradation onset (°C)	551,6	505,3
mass loss in stage (%)	-98.63	-99.57
mass flow (%/min)	-2,42	-2,24

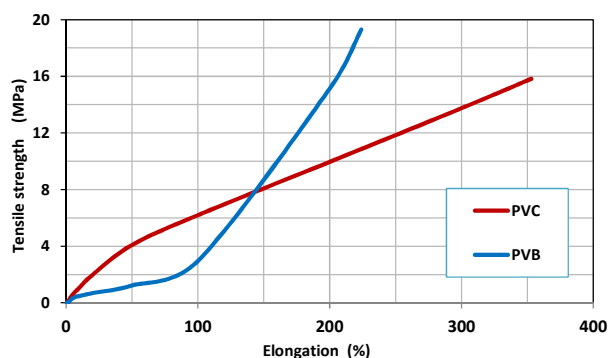


Fig. 2 Dependence of tensile strength on elongation at brake of plasticized PVC and PVB polymers

The result of tensile strength measurement found that PVC can be blended with plasticized PVB; mechanical properties are similar in room temperature. Final blend composition should have material properties directly proportional to the PVB content in the mixture.

B. Thermal Degradation

Following test imitated the decomposition behavior of tested vinyl polymers when they are reprocessed. It tried to point out what can happen if the processing temperature suddenly increased. Therefore, the degradation was tested in an atmosphere of nitrogen, in order to avoid influencing results by oxidizing reaction.

The results show the PVB was more susceptible polymer near to common processing conditions (160-200°C) than PVC is. The thermal degradation of PVB has obtained to be started at 45°C while the PVC began to decompose thermally at 185°C. When PVB is decomposed, it loose only 2% till 200°C, however, the decomposition is particularly accelerated when the temperature is increased. It is given by plasticized elimination (vaporization). The following decomposition process was almost similar until the temperature attained 280°C. However, the reversion occurred at this moment. The PVB degradation and the plasticizer evaporation have stopped in mass loss of approx. 20% (w/w). On the other hand, the decomposition of PVC was wildly spread until 345°C. The mass loss in mentioned first degradation stage was 72% (w/w).

The second degradation stage for PVB was recorded between 303-460°C and the material lost next 67% of the mass. The degradation stage for PVC was between 380-500°C and the material lost 11 % in the stage.

The last stage obtained complete carbonization of both vinyl polymers. It happened between 460-550°C for PVC and between 500-610°C for PVC, respectively. The thermal decomposition curves are recorded in Fig. 3 and the summary of results is shown in Table I.

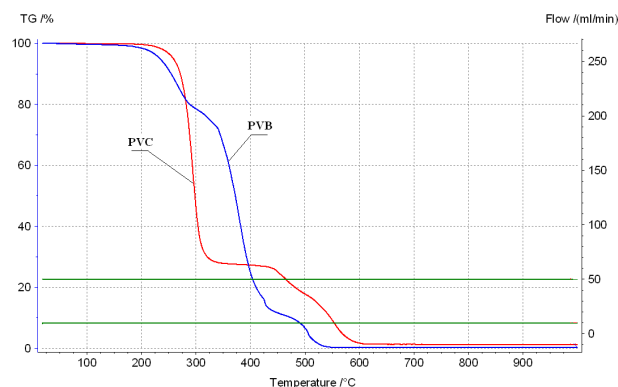


Fig. 3 Thermal degradation of recycled PVB and PVC in nitrogen environment

Above results may describe technologies (processes) such as sintering, extruding and injection molding. In general, processes where the polymer melt is not exposed by air (oxygen) environment. Nevertheless, according observations and results [12], the PVB is wildly processable by extrusion process until 200°C and by sintering until 250°C without recordable PVB thermal degradation.

C. Thermo-Oxidative Degradation of Vinyl Polymers

This test was as similar as the previous in chapter "B". However, the test imitated the decomposition during reprocessing in presence of environment oxygen. It was carried out in order to of describe the influence of polymer oxidizing reaction. The same samples were used as in the previous case. The behavior TG curves were very similar as the analysis in nitrogen environment. Significant changes were

mostly evident at the beginning of oxidative disruption of polymeric material, such as in the end of the decomposition process when the carbonized residual mass was burned as well. The values of each stages of the thermo-oxidative decomposition are shown Table II. The behavior of this process is recorded in in Fig. 4. The detail behavior is shown in Fig. 5.

TABLE II
THERMAL DEGRADATION IN OXYGEN ATMOSPHERE

decomposition stages	PVC	PVB
1.stage		
start – finish (°C)	170 - 390	45 - 310
degradation onset (°C)	250	260
mass loss in stage (%)	-72.47	-30
2.stage		
start – finish (°C)	390 – 490	310 – 450
degradation onset (°C)	460	378
mass loss in stage (%)	-83.15	-89.20
3.stage		
start – finish (°C)	490 – 590	440 – 485
degradation onset (°C)	520	470
mass loss in stage (%)	-98.52	-99.33

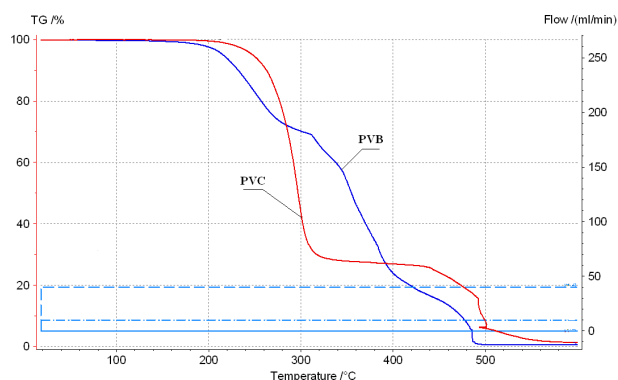


Fig. 4 Thermal degradation of PVC and PVB in oxygen environment

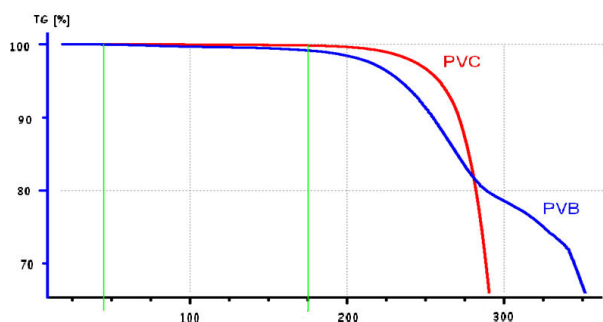


Fig. 5 Thermal degradation of PVC and PVB in oxygen environment – detail view

The generation of the oxidizing distortion of the polymer was determined by TG analysis and also by DSC analysis – by finding of Oxidative Onset Temperature (OOT). It was established that PVB already begins to oxidize at 45°C, while the PVC started at 170 °C. The OOT value for PVB was

determined at 203°C and for PVC it was 239°C. At this point, there has been intensive acceleration of oxidative degradation; the polymer began thermo-oxidative significant disintegration. The results of OTT analysis are placed in Fig. 6.

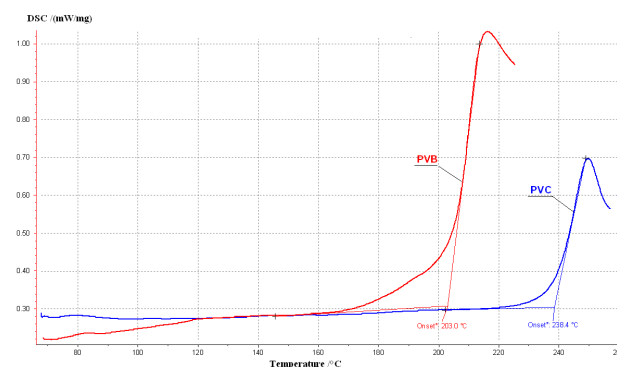


Fig. 6 Onset Oxidative Stability determining of pure PVB and PVC polymers by DSC analysis

In case of thermo-oxidative decomposition, the most important change was determined in case of PVC. This polymer was decomposition in three stages; last two stages carried out on in region between 390 and 590 °C. In this region, the carbonization of polymer chain happens and the PVC lost 25.9 % (w/w) of the polymer mass.

According the observations, when the PVB is reprocessed in room environment, the thermo-oxidative degradation starts around 155°C and the reaction wildly runs when the temperature is above 200°C approximately. When the PVC is stabilized, it can be processed in air environment until 210°C.

IV. CONCLUSIONS

- According to TG and OOT analysis, PVB starts to degrade in oxygen at 45°C, PVC at 170 °C
- When PVB is decomposed, it loose only 2% till 200°C, however, the decomposition is particularly accelerated when the temperature is increased. It is given by plasticized elimination (vaporization).
- Both vinyl polymers have different thermal stability, PVB is more sensitive that PVC, especially in typical processing temperatures in region 150 and 200°C. The PVB starts to degrade very easily, especially in oxygen environment.
- The reversion occurs between 290 and 330 °C when the PVC is losing more than 70% of mass, while PVB lost only 30% weight.
- PVB is more degradable by increased temperature. This polymer is completely thermally decomposed (in nitrogen) at 550°C while PVC is totally decomposed at 610°C.
- In summary, PVB and PVC can be processable in process conditions of 150 and 160 °C during several minutes. Obtained important values of thermal properties and the polymers decomposition are summarized in Table III.

TABLE III
RESULTS OF THERMAL ANALYSIS OF POLYMERS

method	PVC	PVB
DSC – T _g	16.2 °C	-38.4 °C
DSC – OOT	203.0 °C	238.9 °C
TG – N ₂	235.5 °C	275.1 °C
TG – O ₂	205.2 °C	254.7 °C

DSC = differential scanning calorimetry; T_g = transition glass temperature; OOT = onset oxidative temperature; TG = thermal gravimetric analysis; N₂ = nitrogen; O₂ = oxygen

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