Degradation of Plasticized PVB During Reprocessing by Kneading

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Summary: Possibility and conditions for optimal re-processing of plasticized polyvinylbutyral (PVB) were tested. The aim of this work was to investigate degradation of PVB sheet at various kneading conditions and to estimate the influence of temperature, air oxygen and mechanical stress on the progress of degradation process. In order to confirm the influence of humidity on the PVB properties during reprocessing, the sheets with the humidity content of 0.5 and 8.0% were tested. The PVB degradation was determined from the changes of melt flow index, mechanical properties in terms of stress and elongation at break, yellowness and molecular weight distribution. The optimal recycling conditions for PVB were estimated from the evaluation of all measured properties and their changes.

Keywords: degradation; kneading; polyvinyl butyral; recycling; thermo-oxidation process

Introduction

Increasing growth of raw material prices, environmental aspects and still growing landfill fees bring about the increasing interest encountered with the plastics waste recycling. Globally, the problem has been solved for the common plastics such as polyolefins, polyethylene-terephtalat and polystyrene. Though extensively used for the glass lamination, polyvinyl butyral (PVB) does not belong to this group. It is generally known that during the glass lamination process, large volume of trim is formed. The formation of the trim is the consequence of the production technology, where the PVB sheet is used larger than the glass so that the edge is perfect. This extra material after pre-pressing is cut. The trim is usually recycled together with the waste sheets originating from the PVB manufacturing.[1] However, to find an ideal PVB recycling conditions is not easy. Due to its composition, PVB is very sensitive to degradation and migration of plasticizer. It was found, that at the atmospheric pressure, plasticizer migrates at the temperature of 260 °C.[2] During repeated processing of plasticized PVB, both water and plasticizer were reported to be extracted from polymer by vacuum. However, the loss of plasticizer at the common processing temperatures (up to 200 °C) is minimal.[3]

More serious problem observed during reprocessing represents shear and thermo oxidative degradation of the polymer. Both degradation types induce the breakdown of polymer chains, even though the degradation mechanism is not the same. Generally, the shortening of polymer chains negatively influences mechanical properties of PVB, resulting in undesirable lowering of safety characteristics of the produced sheet. Deterioration of mechanical properties of PVB consequently decreases its ability to absorb the mechanical energy (when it is used for the safety glass in the car) in the case of an accident.[1,4] On the other hand, decreasing of molecular weight and decreasing of viscosity caused by degradation can favorably influence rheological properties of PVB melt during extrusion in the flat die.

In order to decrease power consumption during re-processing, it is possible to take

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advantage of PVB hygroscopicity. As water contained in PVB matrix can act as an additional plasticizer and lower rigidity of the material, processing of "wet" PVB can be advantageous.[4] However, during reprocessing of material containing high moisture content (8%), water can react with butyric groups, which induces the change of the polymer structure. As the consequence, hydrolysis occurs significantly changing the final properties of the reworked PVB.[2,5]

The aim of this work was to determine degradation of PVB sheet at different kneading conditions and to estimate an influence of temperature, air oxygen and mechanical stress on the progress of degradation process. The work is also focused on the possibility to find the optimal re-working conditions of PVB when the mechanical and thermal degradation as well as yellowness of the reprocessed polymer are minimal.

Experimental Part

Samples

Plasticized polyvinylbutyral sheet (moisture content of 0.5 wt%) from RETRIM (part of DuPont *Czech Republic)* was used in the study. The sheet was of the Butacite B5 type, containing butyric (80%), hydroxyl (18–19%) and acetate (less than 2%) units.[1,2,4] Tested PVB film was highly plasticized with 28 wt% of triethyleneglycol bis (2-ethylhexanoate) (3GO).[6].

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Sample Preparation

PVB was reprocessed by kneading, callendering and pressing. Both dry (0.5 wt% water) and wet (8 wt% water) sheets were tested. Increasing moisture content was reached by the soaking of "dry" PVB sheet in distilled water for 14 days.

Samples processed by kneading were prepared in the Brabender kneader with two rotors W50, and the friction of 2:3. Volume of the heated chamber was of 55 cm^3. Always the same amount of 40 g PVB was placed in the chamber and processed for 10 minutes at various temperatures (100, 130, 160, 190, 220 °C) and at various rotation speeds (40, 60, 80 rpm). The chamber of internal mixer was filled only to the ¾ of the volume so that there is sufficient amount of oxygen for thermo-oxidative degradation study. During kneading, both thermo-oxidative and shear degradation are supposed to take place.

In order to simulate solely shear degradation with absence of thermal stress, PVB sheets were re-processed by calendering at the temperature of 78 °C in the presence of air. Laboratory callender was used. Rollers were preheated to 60–70 °C. After the initial preheating, the roller temperature was kept only by the energy dissipation. After 10 minutes the temperature reached 78 °C and this value remained almost unchanged.

Pure thermal degradation with low shear stress was simulated by pressing. PVB was placed between two PET sheets preventing the contact with air and thus oxidative degradation. Then, the material was pressed at 1 MPa at various temperatures 160, 190 a 220 °C for 10 minutes.

Dry PVB was tested at all the above presented conditions; wet one was tested at all temperatures but only at 60 rpm.

Methods

Mechanical properties were measured using a T 2000 Tensile tester (Alpha Technologies) with the displacement rate of 500 mm/min at room temperature. For testing, material was pressed into a sheet 1.0 mm thick at the temperature of 130 °C and the standard testing specimens were prepared. Tensile strength and elongation at break were evaluated.

Rheological properties of re-processed samples were tested in terms of MFI measurements using the extruding plastometer M201 (Haake) according to EN ISO 1133.[7] Samples were conditioned at 25% relative humidity and then extruded at 150 °C through the 2 mm capillary using the load of 100 N. The MFI correlates to the polymer mass passing through a standard

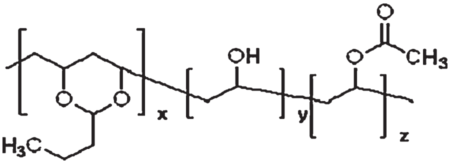

Figure 1.
Polyvinyl butyral chain structure.

capillary in an interval of 10 minutes, at a given load.

Quantification of water content was carried out by the Karl Fischer method *(Metrohm AG)*. The method is based on the conductometric determination of water evaporated from the sheet into the iodine solution and sulphur dioxide in methanol.

Yellowness was evaluated using the CIE Lab. colour scale. Handy Color *(BYK Gardner)* instrument was applied and calibrated with the white and black standards. Measurement was carried out against the white background at the angle of 10°. Illumination type of D65 corresponding to daylight was applied. Yellowness $\underline{Y_{ID}}$, was calculated from the measurements of spectroscopic values $\underline{L}$, $\underline{a}$ and $\underline{b}$. Obtained value was converted to the value corresponding to the PVB sheet with the standard thickness of 0.76 mm, which is typical for applications in automotive industry and in architecture.

GPC analyses were performed using a PLGPC-50 (Polymer Laboratories,) equipped with a PL differential refractometer (DRI) and on-line viscometer detectors (VIS). Analyses were performed with a PL gel Mixed-C column *(7.8 × 300 mm; Polymer Laboratories)* at 30 °C with the mobile phase flow rate of 1 mL/min. Tetrahydrofurane was used as a mobile phase. The column was calibrated using narrow molecular weight polystyrene standards (Polymer Laboratories Ltd, Church Stretton, United Kingdom) with molecular weights ranging from 580 to 451 000 $g \cdot mol^{-1}$ (given by supplier). A 100 μL injection loop was used for all measurements. Universal calibration was applied for the determination of molecular weight from the DRI and the VIS signals. Data processing was performed with Cirrus GPC, Multi Detector Software. The concentration was of about 0.2 g/100 ml and samples were dissolved at room temperature for 20 hours under stirring. The combination of both types of detectors enabled exact determination of molecular weight as well as detect the PVB aggregation.

Results and Discussion

The Influence of the Kneading Conditions on the Change of Mechanical and Rheological PVB Properties

From the theory and practice it is confirmed that the PVB re-processing brings about the shortening of macromolecular chains, which induces the change of its mechanical properties. The results show that increasing of the re-processing temperature causes lowering of melt viscosity (measured as MFI), lowering of tensile strength and also lowering elongation at break. These changes are presented in Figure 2–3.

The MFI values are shown in Figure 2. To sum up, the MFI increases with increasing re-working temperature and increasing rotation speed systematically up to 60 rpm. It is consequence of thermo-oxidative degradation, which causes reduction of polymer molecular weight. However, at the rotation speed of 80 rpm, the MFI values behave differently. Degradation of PVB macromolecular chains (expressed as increasing of MFI) is reduced at the temperatures above 190 °C, which is indicated by no increase or even slight drop of MFI (see Figure 2). The lower degradation at the higher rotation speed (above 80 rpm) is possible to explain by polymer chain slipping in the stressed melt that results in the lower kneading effect.

The results obtained from the measurement of tensile strength of the ‘‘dry’’ PVB samples (0.5% moisture content) in dependence on speed of rotors are shown in Figure 3. At lower temperatures, degradation of ‘‘dry’’ PVB is proportional to increase of the rotation speed. For example, during processing at 100 °C degradation increased, which can be concluded from the

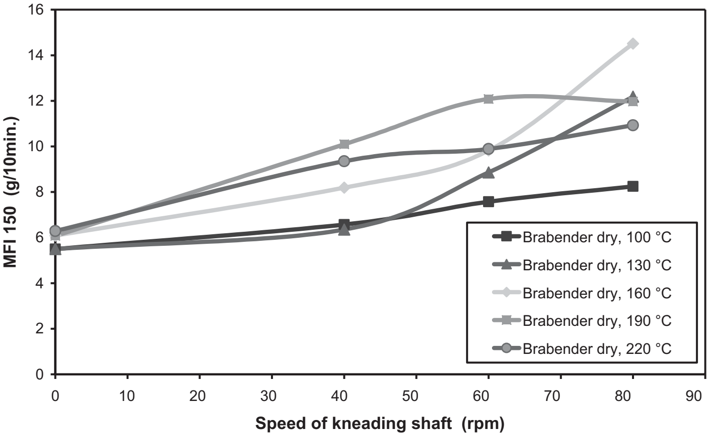

Figure 2.
The change of MFI at the various conditions of the kneading.

lowering of stress at break values (shape of the curve in concave). On the other hand, increasing of temperature caused straightening of this dependence and for the samples processed above 160 °C the curves exhibit the convex curve. Minima in the curves observed at rotation speed of 60 rpm and temperatures 190 and 220 °C indicate, hence, the highest degradation of PVB. Samples re-worked by pressing were used as a background for the kneaded samples at the same temperatures. Slight increase of tensile strength, elongation at break, MFI and yellowness were observed for the samples pressed for 10 minutes at all tested temperatures.

Transformation of the Process Energy into Heat

During the PVB re-processing on the Brabender internal mixer the temperature of the kneading chamber was measured. The chamber was kept at required temperature, but with on-going process of kneading, the temperature slightly increased. The progress of temperature changes is

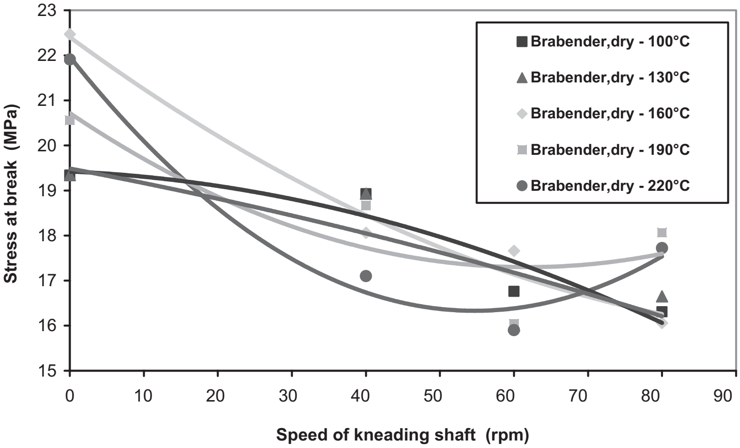

Figure 3.
Tensile strength of the re-processed PVB sheet at the various conditions of the kneading.

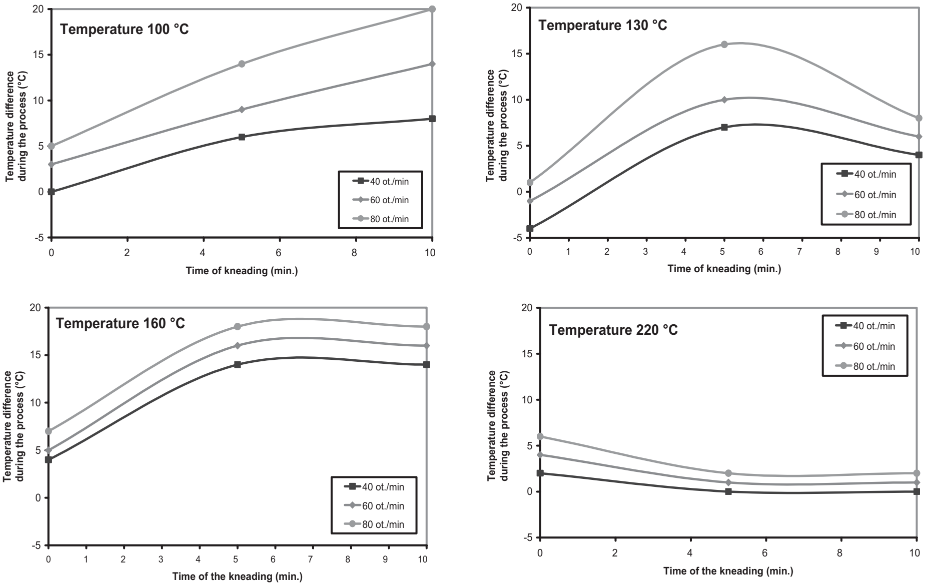

Figure 4.
The temperature procedure during the kneading process.

summarized in Figure 4. More remarkable energy transformation was observed at lower processing temperatures (100 and 130 °C). This effect is clearly correlated to higher viscosity of processed material. It is also demonstrated that evolution of dissipation heat depends on the rotation speed and kneading time. With the higher rotation speed, the amount of dissipated heat increases significantly. Above 130 °C the heat was formed only at the beginning of the kneading, when the material was still with high viscosity. At 220 °C, due to the low material viscosity, the development of the transformation heat is minimal.

The Influence of Water on the Mechanical Property Change

In order to lower the energy consumption during the PVB re-processing, its hydroscopicity was employed. As water contained in the PVB matrix can act as an additional plasticizer, it can decrease PVB viscosity.[3] It is supposed that lower material viscosity can decrease the energetic intensity of the reprocessing. Comparison of MFI values measured for dry (0.5% water) a wet sample (8% water) shows that MFI increased proportionally to the water content (see Figure 5). On the contrary, the tensile strength decreased. The change of the mechanical properties of ''wet'' PVB was caused by higher polymer plasticity and reduction of intermolecular forces.

During the re-processing of wet PVB material at the increased temperature, hydrolysis and elimination of butyric groups can occur. This process results is the formation of hydroxyl groups and consequently conjugated double bonds, which brings the change of PVB chain structure.[2,5] Thus, the hydrolysis causes considerable changes of the final properties of re-processed PVB. Due to this information, effort was made to find the optimal conditions for PVB re-processing with the lowest possible hydrolysis. Hydrolysis was qualitatively estimated from the changes of molecular weight and from the increase of the sheet yellowness.

Although water that was present in PVB evaporated very quickly at the beginning of the process, it influenced the results of all the tests. The values of MFI for re-processed ''wet'' PVB show in the

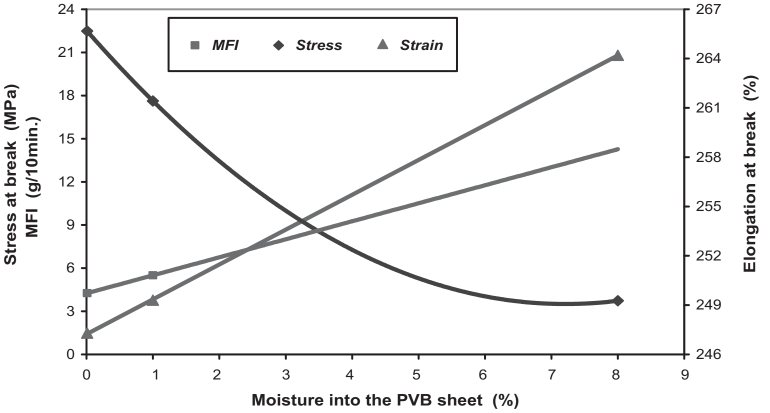

Figure 5.
The influence of water content on the change of mechanical properties of no re-processed PVB sheet.

comparison with the "dry" PVB a significant increasing in the dependence on temperature (see Figure 6) Notable increasing of MFI values observed for wet PVB is caused by degradation, which is induced by the thermo oxidative reactions and better diffusion of gases into the PVB melt.

The comparison of mechanical properties of "dry" and "wet" PVB is presented in Figure 7. The figure shows tensile strength and elongation at break of both PVB types kneaded at various temperatures at constant rotation speed of 60 rpm. Arrows denote the values measured for the original "dry" PVB. Optimal processing temperature for "dry" PVB, where the degradation was the lowest, is determined at the temperature of 150 °C as the maximum of the curve. This maximum, with the highest values of tensile strength, corresponds to minimum degradation of PVB. Below and above 150 °C tensile strength is decreasing, which can be caused by the lowering of the molecular weight induced by degradation. Regarding the degradation mechanism, the scission of the "dry" PVB chains at temperature lower than 150 °C is prevailingly caused by shear

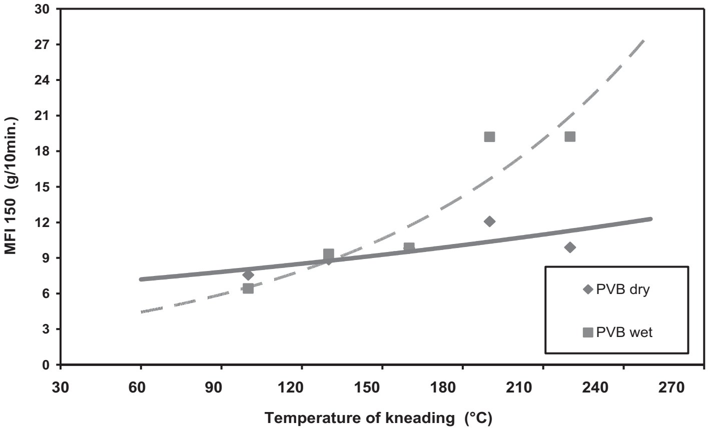

Figure 6.
MFI of kneaded PVB samples ("dry" and "wet") at 60 rpm after ten minutes.

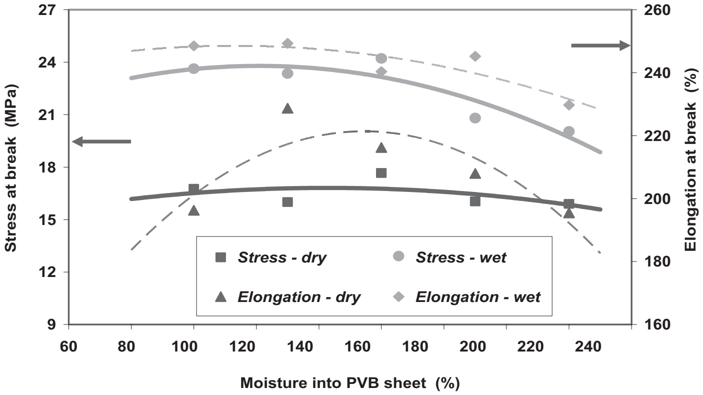

Figure 7.
Tensile strength of kneaded PVB samples ("dry" and "wet") at 60 rpm.

stress, while at higher temperatures thermo-oxidative degradation takes place.

For wet PVB, the values of stress and elongation at break and strain are systematically higher compared to those measured for dry sample. Moreover, dependence of stress and strain *vs*. temperature is monotonously decreasing there is no maximum or minimum. The increase can be explained by the intramolecular crosslinking formed by the hydrogen bonding.

The comparison of "dry" and "wet" PVB indicates that water acted as a plasticizer and "wet" material was less stressed during reprocessing. Hence, the more plasticized "wet" PVB was not significantly stressed by shear and was mostly degraded by thermo-oxidative degradation.

The Influence of Water on the Yellowness

The PVB degradation was the most remarkably reflected through the changes of PVB yellowness. Visually and also instrumentally, the yellowness (sometimes even brownness) of re–worked PVB samples was noticeable. Yellowness increased significantly with increase of re-processing temperature. In the case of "dry" PVB, significant color change was observed above 130 °C. Color of "wet" PVB was significantly changed above 160 °C (Figure 8). Measurements demonstrated that during kneading at

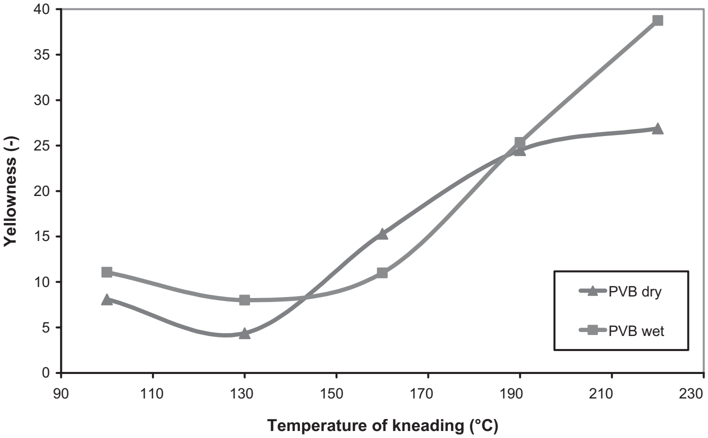

Figure 8.
Yellowness of kneaded PVB samples ("dry" and "wet") at 60 rpm after ten minutes.

the temperatures below 160 °C yellowness was almost unchanged. This can be explained by the stabilizing function of higher moisture content and consequently higher degree of PVB plasticization. At temperatures lower than 130 °C, the change of the yellowness is insignificant irrespective of water content. With the increasing temperature, the yellowness grows remarkably. This can be explained by thermo-oxidative reactions between oxygen and PVB accompanied by better gas diffusion as well as by water induced hydrolysis. It was reported that during hydrolysis, conjugated double bonds are formed.[5] These are more reactive and bring more intensive decrease of molecular weight. The results from the yellowness measurements relate to the results from determination of MFI (see Figure 6).

The Change of Solution Properties Influenced by the Degradation

Changes in molecular weight and molecular weight distribution of virgin and processed material were measured by gel permeation chromatography.

Differential distribution curves of virgin and processed samples (kneading, 100 °C, dry) are compared in Figure 9. From figure it is clear that the entire distribution of the processed sample compared to the virgin one is shifted to lower molecular weight region, which indicates degradation. Moreover the processed sample contains small but distinct peak with molecular weights higher that $2 \times 10^6 \, g \cdot mol^{-1}$ (indicated by arrow). This peak was observed for all of the processed samples irrespective to temperature and type of processing and its presence indicates that diluted solutions of processed samples contain structures with high molecular weight – aggregates. The aggregation of PVB solution and difficulties with polymer dissolution, even in thermodynamically good solvents, has been reported by several authors.[9,10]

Changes of molecular weigh in terms of M_w as a function of increasing kneading temperature are for wet and dry samples depicted in Figure 10. For dry sample, the lowest M_w values were measured on samples processed below 150 °C. Under these conditions, predominantly shear degradation takes place resulting in chain scission caused by mechanical stress. Temperature region between 150 °C and 180 °C seems to be favorable for reprocessing of dry PVB. Here, only minor changes in the sample are observed and molecular weight stays almost unchanged. For wet PVB which exhibits at lower temperatures low stiffness, molecular weight tends to decrease with increasing processing temperature. At temperatures above 190 °C, molecular weight of dry PVB is comparable to that measured for wet sample. Therefore, it can be assumed

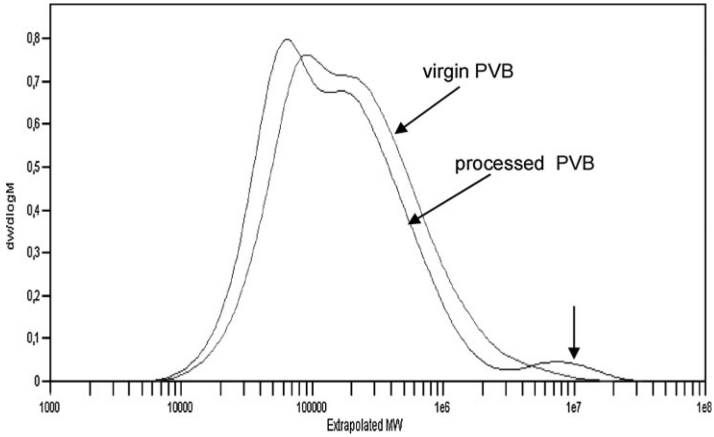

Figure 9.
Comparison of differential distribution curves of virgin and processed PVB (100 °C, dry).

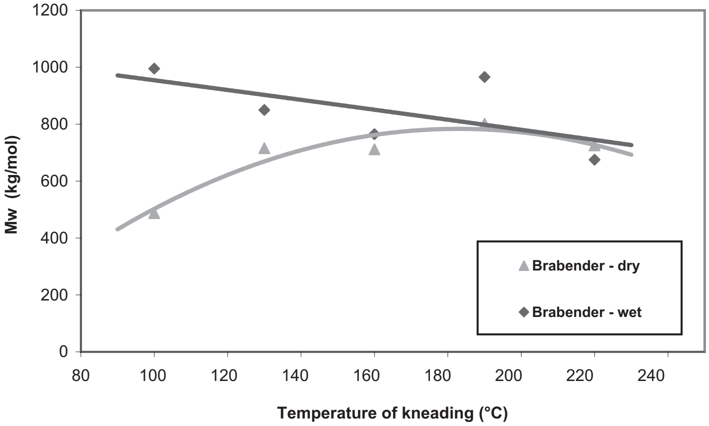

Figure 10.
Influence of kneading temperature on molecular weight changes (M_w) recorded for dry and wet PVB.

that degradation mechanism in this temperature range is similar. From Figure 10 it is also clear that molecular weight of the wet PVB samples, with the exception of the sample processed at 220 °C, was systematically higher compared to the dry ones.

Conclusion

In the presented work, conditions for reprocessing of plasticized PVB sheets were investigated and influence of temperature, air oxygen content and mechanical stress on the progress of degradation was studied. In order to find the possibility for reduction of energy consumption during re-processing, effect of moisture content in PVB sheets on processing parameters and degradation was examined. The obtained results show that, based on the evaluation of MFI and mechanical properties, the optimal conditions for PVB re-working by kneading occur at the temperature about 150 °C and rotation speed of rotors lower than 60 rpm. These conclusions are in the good agreement with the measurement of PVB yellowness. Below 150 °C yellowness remained almost unchanged and increased significantly above this temperature. GPC measurements support above mentioned conclusions showing minimal changes of PVB molecular weigh for this temperature. Increased amount of water in PVB sheet can act as additional plasticizer that improves processability of the polymer melt and decreases thus energy consumption. However the ‘‘wet’’ samples are more susceptible to hydrolytic degradation and compromise decision has to be done having in mind these two effects.

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