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PVB Sheet Recycling and Degradation

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1. 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, poly(ethylene terephtalate) and poly(styrene). Though extensively used for the glass lamination, poly(vinyl butyral) (PVB) does not belong to this group. It is generally known that during the glass lamination process, large volume of PVB trim is formed.

The PVB polymer is mostly used in the form of plasticized PVB sheet for preparation of laminated safety glass (LSG). At present time, Solutia, DuPont, Seki sui and Kuraray are worldwide PVB manufacturers. The PVB is the material which can stick together float glasses with holding excellent optical and mechanical properties of the glass laminate (Ivanov, 2006; v. Elasticity, mechanical strength, toughness, high light transmission and the adhesion to glass are the most significant PVB properties (Tupý, Měřínská, et al, 2010). Toughness of PVB sheet is based on high molecular weight of PVB chain. Certainly, the PVB has to be plasticized for achieving high material elasticity (Iwasaki, et al, 2006; Keller, Mortelmans, 1999; Svoboda, Balazs., et al, 1988). Admittedly, the plasticizer must not reduce light transmittance through the sheet, PVB adhesion to glass, generate haze and yellowness, and migrate out of the polymer matrix (Wade, D'Errico, et al, 2004). In addition, plasticizer must have perfect compatibility with the polymer and low evaporability during processing conditions.

2. Sources for recycling of PVB sheet

Worldwide, 65% of all PVB sheets are used in automotive applications (Dhaliwal, Hay, 2002). According to data from (OCIA, 2007), the worldwide car's production is estimated around 60 millions cars per a year. Assuming that one windshield contains approx. 1 kg of PVB sheet, total amount gives between 60-70 million kg of PVB sheets per year. In addition, by-products from PVB sheets manufacturing (5%) and trimmings (< 10%) from windshield production must be added (Goroghovski, Escapante-Garcia, et al, 2005). It represents total amount of 80 million kg of automotive PVB sheet waste annually. Total worldwide amount of produced PVB sheets for automotive and architectural industry is estimated around 120 million kg per year.

2.1 By-product from sheet manufacturing process

This kind of PVB sheet has the best quality for following recycling process. By-product sheets are not contaminated by powder fragments but there may be present some un-homogeneous parts like plasticizer, light and heat stabilizers, adhesion modifiers, pigments and other elements of the system. The reasons why the sheet has to be re-processed are some specified defects in manufacturing technology (thickness, sheet roughness, edges). In every case, sheet edges must be cut approx. 10-20 cm from the edge beginning. The PVB sheet with a width around 2-3 meters has very high material shrinkage in this place. The edges can be replaced back to the extrusion process for re-extruding (Zvoníček, 1999).

2.2 Trim

The first step in LSG manufacturing is the lamination of PVB sheet between two glasses. It this part, probable defects on laminate edges must be reduced. It is performed by layering of PVB sheet between glasses with a larger sheet surface than the glass sizes are. Prepared "sandwich" is fixed by nipp-roll pre-lamination process and consequently it is possible to trim off oversized PVB sheet. While the sheet oversize would not be used, the laminate would be produced with visible defects (it does not meet the quality specifications) (Svoboda, Balazs., et al, 1988; Zvoníček, 1999).

The quantity of a trim generation depends on the geometry of produced windshield and the geometry of used PVB sheet surface. The width of trim obtained from the pre-laminating process is around 1–20 cm, based on glass geometry. Therefore, the trim quantity is between 5-10% from total amount of processed PVB sheet and the worldwide PVB trim capacity obtained from the windshield laminating process is approx. 4-6 million kg (Svoboda, Balazs., et al, 1988; Zvoníček, 1999).

The trim is created also at manufacturing of architectural LSG. Nevertheless, the ratio of a collected architectural trim is lower than amount of automotive trim. It is influenced by a higher glass powder contamination of this trim (different trimming technology) (Zvoníček, 1999).

2.3 PVB sheet from windshield

Some specialized companies deal with the re-application possibility of PVB sheet obtained from recycled windshield. All present recycling processes produce a good quality of glass scrap which is fully re-used in the glass batch. However, the separated PVB waste is not recyclable due to high amount of glass, water content in the sheet, parts of color PVB sheets, mixed of various PVBs (after blending a haze is created) and foreign plastic matters (Zvoníček, 1999; Plaček, 2006; Recycling .., 2007; Tupý, Měřínská, 2011). Nevertheless, if somebody would develop the recycling technology ensures high-grade of glass separation, obtained PVB sheet may be re-processable to new PVB sheet without optical defects (Tupý, Měřínská, 2011).

Moreover, it is necessary to remain that the laminated (interglassed) PVB is not essentially exposed to UV radiation (up to 320 nm), mechanical stress, elevated temperature, oxygen and any various substances. Thus, the interglassed PVB sheets should keep very similar

physical properties as extruded material before the lamination process and it can be re-extruded and re-laminated to new PVB sheet again.

3. PVB sheet composition

3.1 Poly(vinyl butyral)

The way assigned for PVB production is not easy. Firstly, it is necessary to produce poly(vinyl acetate) (PVAc) by the radical vinyl acetate polymerization. Consecutive hydrolysis at acidic or basic ambient creates poly(vinyl alcohol) (PVAl) which provides poly(vinyl butyral) by acetalization with butyraldehyde at acidic environment. The final structure of high-molecular PVB is used for LSG manufacturing and it is compounded from atactic copolymers 80% of vinyl butyral, 18-23% of vinyl alcohol and up to 1% of vinyl acetate [Wade, D'Errico, et al, 2004; Dhaliwal, Hay, 2002; D'Errico, Jemmott, et al, 1996; Nghuen, Berg, 2004; Svoboda, et al., 1970). This chemical structure, viewed in Fig.1, is the same for every manufacturer today. Nevertheless, exact consequence and properties of every PVB sheet depends on every PVB type, manufacturer and PVB sheet composition. The sheet is mostly stabilized by antioxidants and thermal stabilizers in many times (Saflex, 1993).

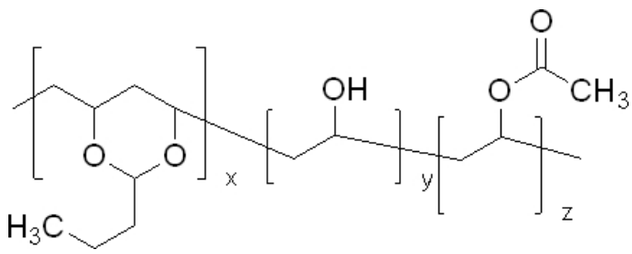


Fig. 1. PVB chain structure with composition of functional groups: vinyl butyral 81%, vinyl alcohol 18-23%; vinyl acetate <1%.

Final PVB properties are assigned by polymerization degree of input PVAc, distribution curve of molecular weight, PVAl hydrolysis degree, catalyst acid strength, reaction temperature and PVAl conversion degree to PVB. The last one is crucial for final polarity of produced PVB. The PVB polymer is white powder, dissolvable in ethanol, THF, ketones and other semi-polar dissolvent (Mrkvičková, Daňhelka, 1984). The PVB solubility depends on –OH group content in the polymer chain and PVB molecular weight (Physical prop.SekiSui, 2001).

3.2 PVB sheet

Certainly, achievement of high PVB toughness must be proved by polymer plasticizing. However, the plasticizer must not considerably reduce light transmittance through the sheet, increase haze and yellowness, reduce PVB adhesion to glass and migrate out of the polymer matrix (Svoboda, Balazs, et al, 1988; Zvoníček, 1999). The plasticizer also must have perfect compatibility with polymer matrix and its evaporability during the processing is prohibited (Zvoníček, 1999). Different plasticizers, used in beyond, were for example triethylenglycol-di-2-ethylbutyrate, dibuthylsebacate, tetraethylenglycol-di-heptanoate and

dihexyladipate (Dhaliwal, Hay, 2001; Zvoníček, 1999). Mentioned plasticizers have different molecular polarity. There through, due to this it was indispensable to produce PVBs with different amount of hydroxyl groups in PVB chain (Dhaliwal, Hay, 2001; D'Errico, Jemmott, et al, 1996; Phillips, 2005). The final polymer system has a different absorbability of the plasticizer and water (Mrkvičková, Daňhelka, 1984). At present time, produced PVB sheets assigned for the glass lamination are plasticized with 28% of applied plasticizer; mostly triethylenglycole-bis(2-ethylhexanoete), (labeled 3GO) (Wade, D'Erricco, 2004; Phillips, 2005; Mister, Bianchi, et al, 2007; Smith, Rymer, et al, 2008).

Due to mentioned sheet physical properties, the most important characteristics of windshield are high mechanical strength and absorbability of kinetic energy during car-crash (Keller, Mortelmans, 1999; Svoboda, Balazs, 1988). However, PVB interlayer must keep glass particles on its surface [2, 3]. All these described properties provide an exactly adjusted adhesion grade of PVB to glass. Because the PVB has exceedingly high adhesion degree it cannot be used for automotive glass lamination. Thus, high adhesion degree it is necessary to reduce to ½ of the original adhesion value (Keller, Mortelmans, 1999; Wade, D'Erricco, 2004; Dhaliwal, Hay, 2004; Smith, Rymer, et al, 2008). The virgin adhesion is reduced by an addition of organic salts of alkali metals or alkaline-earth metals during an extrusion process of plasticized PVB sheet. This is described in several patents (Smith, Rymer, et al, 2008; Aoshima, Shohi, 2000; D'Errico, 1995; D'Erroco., 1997; Fowkes, 1987 Herman, Fabian, et al, 1984; Shichiri, Miyai, et al, 2002). The mostly used substances modifying the adhesion are organic salts of Na^+, K^+ and Mg^{2+}. Ion ratio and its total amount are strictly specified (Smith, Rymer, et al, 2008; Aoshima, Shohi, 2000; D'Errico, 1995; D'Errico., 1997; Fowkes, 1987 Herman, Fabian, et al, 1984; Shichiri, Miyai, et al, 2002). Moreover, the water content in PVB sheet must be in range 0.3-0.5% which is necessary for a maintaining the required adhesion grade (Keller, Mortelmans, 1999; Wade, D'Errico, 2004; D'Errico, Jemmot, 1995; Shichiri, Miyai, 2002).

4. Extrusion of PVB sheet

The formation of the PVB trim is the consequence of the production technology, in which laminated glass without defects having irregular shape are manufactured. The PVB assigned for re-processing is usually recycled together with the waste sheets originating from the PVB manufacturing (Tupý, Zvoníček, et al, 2008). However, to find the ideal PVB re-processing conditions is not easy.

Due to its composition, PVB is very sensitive to the degradation and the migration of plasticizer. It was found, that at the atmospheric pressure, plasticizer migrates at the temperature of 260 °C (Dhaliwal, Hay, 2002). 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 (Svoboda, Balazs, 1998).

Based on several authors (Keler, Mortelmans, 1999, Svoboda, Balazs, 1998; Nagai, 2001; Neher, 1936; Svoboda, 1987), all PVB sheet manufacturing technologies are based on similar principle. Melt plasticized PVB is extruded by sheet extrusion die at temperature 160-220°C into water. The screw placement is evacuated in order to adjust the water content in the

sheet. The PVB melt retains its shape, thickness and specific sheet surface which are necessary for de-aeration at pre-lamination process (Svoboda, Balazs, 1998; Zvoníček, 1999). Plasticizer and additives addition runs at mixing equipments before the extruder in many times.

The PVB sheet is mostly manufactured at the thickness 0.38 mm (LSG for architectonical industry) and 0.76 mm (LSG for automotive and architectonical use). Special applications require thicknesses 1.14 and 1.52 mm. The width of PVB sheet can be up to 3.5 meters. Manufactured PVB sheet is rolled and either separated by thin patterned polyethylene sheet or rolled under-cooled (Tg = 15°C) because the PVB sheet must not be stuck for following use (Svoboda, Balazs, 1998; Zvoníček, 1999; Saflex, 1973).

Shear and thermo oxidative degradation of polymer represents more serious problem observed during reprocessing. Both degradation types induce the cleavage of polymer chains, albeit the degradation mechanism is not the same. Generally, the shortening of polymer chains negatively influences mechanical properties of PVB, resulting in an undesirable lowering of safety characteristics of the produced sheet. The deterioration of mechanical properties of PVB consequently decreases its ability to absorb the mechanical energy (when it is used for the safety car glass) in the case of an accident (Tupý, Zvoníček, 2008; Tupý, Měřínská, 2010). On the other hand, a decreasing of molecular weight and a decreasing of viscosity caused by the degradation can favorably influence rheological properties of PVB melt during the extrusion on the flat die (Měřínská, Tupý, 2010; Grachev, Klimenko, et al, 1974).

In order to decrease power consumption during re-processing, PVB hygroscopicity can be utilized. Because water contained in PVB matrix can act as an additional plasticizer and lower the rigidity of the material, processing of "wet" PVB can be advantageous (Mrkvičková, Daňhelka, 1984). However, during the re-processing 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 re-processed PVB (Dhaliwal, Hay, 2002; Měřínská, Tupý, 2010).

The aim of the following test was to determine the degradation of PVB sheet at different kneading conditions and to estimate an influence of temperature, air oxygen content and mechanical stress on the course of degradation process. The work is also focused on the possibility to find optimal re-processing conditions of PVB whereat the mechanical and thermal degradation as well as yellowness of the re-processed polymer are minimal.

5. PVB sheet degradation by thermogravimetric analysis

First of all, the relative thermal stability of commercial PVB sample was measured by thermogravimetric analysis, from mass loss against temperature plots. As the Fig.2 shows, weight loss occurred in two distinct regions between 175–325 and 325–500 °C and corresponding to about 27-28 and 65-70% mass loss. No marked differences were observed between the various commercial grades. The first part of temperature range is the plasticizer evaporation. The final weight loss was the same for all the samples and a brown residue, approximately 5% of the original mass (Tupý, Měřínská, 2011). The evolved volatiles were analyzed by mass spectrometer as a function of time and temperature at fixed m/z ratios.

These corresponded to the top m/e ratio for acetic acid, butenal, butyraldehyde, benzene and toluene the expected products from the thermal decomposition of PVB (Wade, D'Errico, 2004).

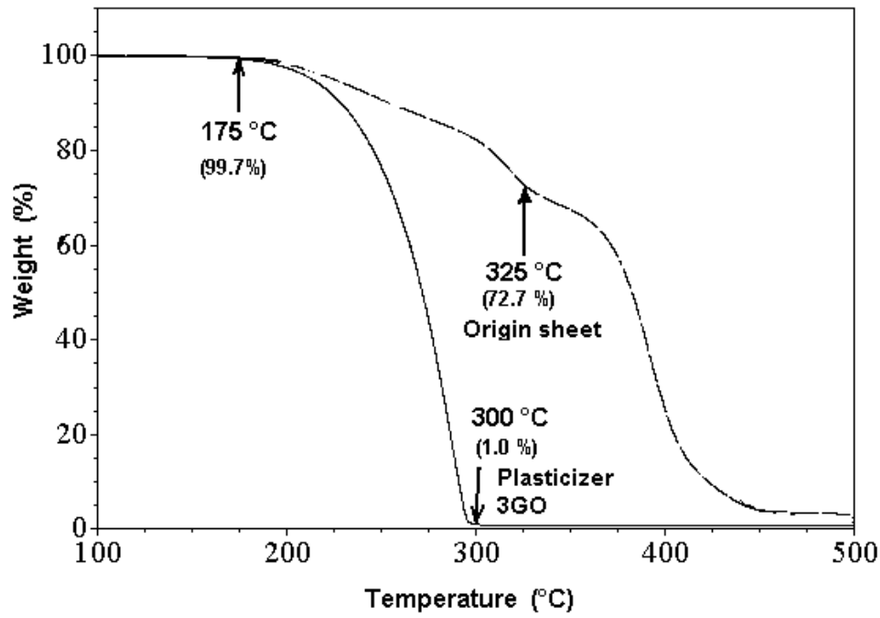


Fig. 2. TGA evaluation of plasticized Butacite PVB sheet.

Little or no degradation products were observed below 250 °C although the PVB samples had lost about 10–12% of mass under these experimental conditions were initially. The major products of the decomposition were observed above 260 °C. Acetic acid was a minor component of the volatile degradation products. Aromatic species, such as benzene and toluene, were also observed. These have been attributed to the break down of the polyene products produced by the elimination reactions.

From the relative % mass loss and the absence of volatiles detected by the mass spectrometer it was deduced that the PVB was primarily losing plasticizer in the temperature volatilization process between 200 and 260 °C. The loss of additives from a polymer is a complex process involving diffusion, transport and evaporation from the surface of the polymer.

6. Degradation by kneading

6.1 Samples preparation

By the reason of finding degradation mechanism of plasticized PVB, this material was reprocessed by kneading, rolling and pressing. Both dry (0.5 % water) and wet (8% water) sheets were tested. Increasing moisture content was reached by the soaking of "dry" PVB sheet in water for 14 days (Grachev, Klimenko, 1974).

Samples stressed by kneading were prepared in the Brabender kneader with two blunders W50 at the friction of 2:3. Volume of the heated chamber was of 55 cm^3. Constant amount of

40 g PVB was placed in the chamber and processed for 10 minutes at different temperatures (100, 130, 160, 190, 220 °C) and rotation speeds (40, 60, 80 rpm). The chamber of kneader was filled only to the ¾ of the volume in order to have the sufficient amount of oxygen in order to study thermo-oxidative degradation. During kneading, both thermo-oxidative and shear degradation are assumed to take place.

In order to simulate solely shear degradation with absence of thermal stress, PVB sheets were re-processed by rolling at the temperature of 78°C in the presence of air. Laboratory double-roller was used. Rollers were preheated to 60-70°C in order to allow the PVB calendaring corresponding to processing of the rubber. 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 temperature of 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 with 60 rpm.

6.2 Analysis and methods

Mechanical properties of the stressed samples were determined using a T 2000 Tensile tester *(Alpha Technologies)* with the displacement rate of 500 mm/min at room temperature. For testing, material was pressed onto the plates with the thickness of 1.0 mm at the temperature of 130°C and the standard testing specimens were prepared. Tensile strengths and strain were determined.

Rheological properties of re-processed samples were tested in terms of MFI measurements using the extruding plastometer M201 (Haake) according to EN ISO 1133. 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 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 $\underline{Y}_{\underline{ID}}$, was calculated from the measurements of spectroscopic values $\underline{L}$, $\underline{a}$ and $\underline{b}$. The 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.

Thermo-gravimetric analysis (TGA) was determined by thermogravimetric analyzer TGA Q500 *(TA Instruments, New Castle, USA)* in open platinum crucibles and weighed-in. Amount of PVB sample for thermal analysis was approx. 8 mg and measurements were

taken in temperature interval 20-500 °C, dT/dt = 10 °C min^{-1} in protective nitrogen atmosphere (150 mL min^{-1}).

GPC analyses were conducted 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 x 300 mm; Polymer Laboratories)* at 30 °C with the mobile phase flow rate of 1 mL/min. Tetrahydrofurane was used as the mobile phase. The column was calibrated using narrow molecular weight polystyrene standards *(Polymer Laboratories Ltd, Church Stretton, UK*) with molecular weights ranging from 580 to 451 000 $g.mol^{-1}$ (given by supplier). A 100 µL injection loop was used for all measurements. For the determination of molecular weight, universal calibration was applied. 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 to exactly determine molecular weight as well as detect the PVB aggregation.

6.3 The influence of kneading conditions on the change of plasticized PVB sheet 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 brought the lowering of melt rigidity (measured as MFI), lowering of tensile strength and strain. These changes are visualized in Figs. 3-4.

The MFI values are shown in Fig.3. To sum up, the MFI increases with the increasing of re-processing temperature and the increasing of rotation speed systematically up to 60 rpm.

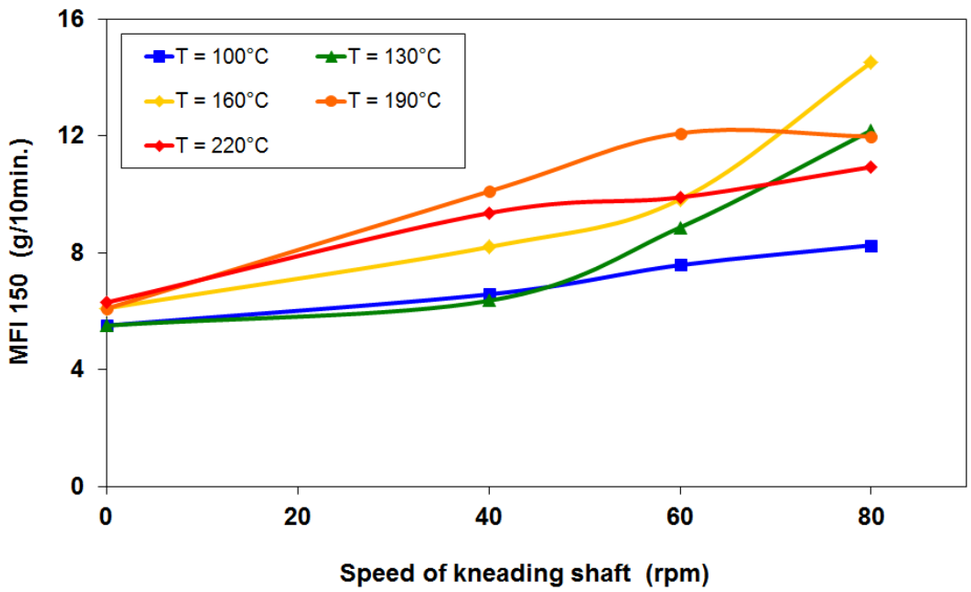


Fig. 3. The change of MFI at the different conditions of the kneading of PVB sheet with water content 0.5%.

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 rising or even slight drop of MFI (see Fig.3). The lowering of the degradation at the higher rotation speed (above 80 rpm) is possible to explain by the sliding of polymer chains in the stressed melt resulting in the lower effect of kneading.

The results obtained from the measurement of tensile strength of the "dry" PVB samples (0.5 % moisture content) in dependence on speed of the kneading shaft are shown in Figure 4. 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 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 curving. Minima on the curves observed at rotation speed of 60 rpm and temperatures 190 and 220 °C indicate, hence, the highest degradation of PVB. Samples re-processed by pressing were used as a background for the kneaded samples at the same temperatures. Slight increase of tensile strength, strain at break, MFI and yellowness were observed for the samples pressed for 10 minutes at the all tested temperatures.

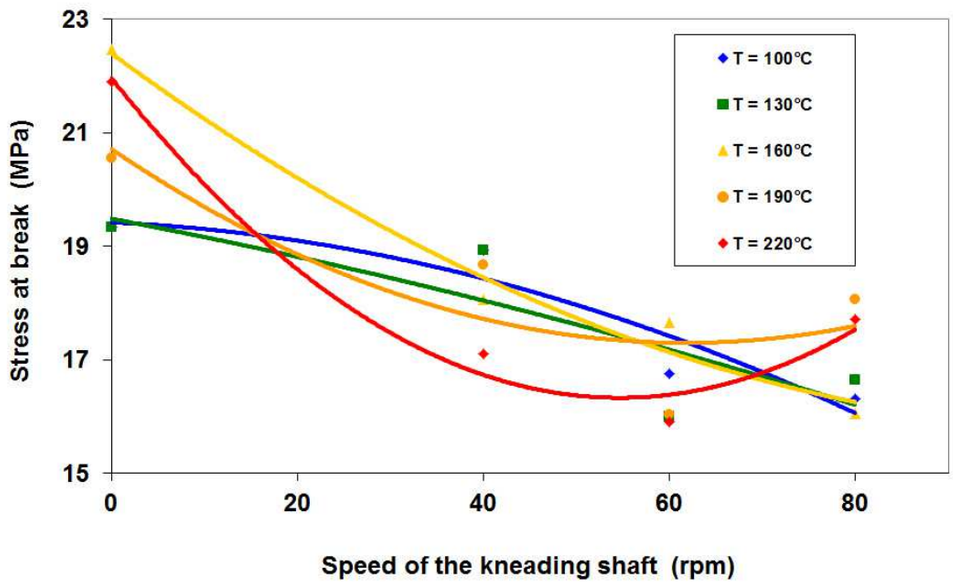


Fig. 4. Tensile strength of the re-processed PVB sheet at the different conditions of the kneading of PVB sheet with water content 0.5%.

6.4 The transformation of the process energy into heat

During the PVB re-processing on the Brabender kneader the temperature of the kneading chamber was measured. The chamber was tempered on the required temperature, but with on-going process of kneading, the temperature slightly increased. The course of temperature

changes is summarized in Figure 5. The more noticeable energy transformation was observed at the lower processing temperatures (100 and 130 °C). This effect is clearly correlated to the higher rigidity of the processed material. It is also demonstrated that the evolution of dissipation heat depends on the rotation speed and kneading time. With the higher rotation speed, the amount of dissipated heat rises significantly. Above 130 °C the heat was formed only at the beginning of the kneading, when the material was still rigid enough. At 220 °C, due to the low material rigidity, the evolution of the transformation heat is minimal.

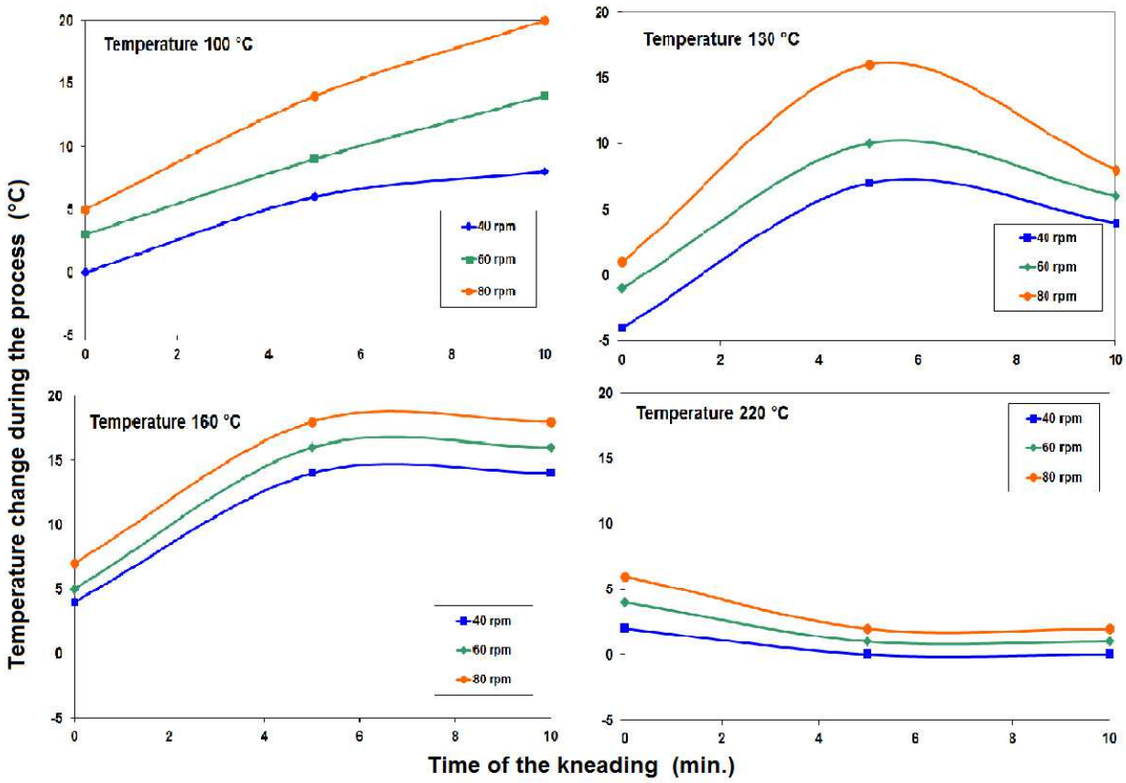


Fig. 5. Temperature change during the kneading process at different temperatures.

7. The influence of water on the change of mechanical properties

In order to lower the energy consumption during the PVB re-processing, its hygroscopicity was employed. As water presented in the PVB matrix can act as an additional plasticizer, it can decrease PVB rigidity (Tupý, Měřínská, 2010). It is supposed that lower material rigidity can decrease the energetic intensity of the re-processing. The comparison of MFI values measured for dry (0.5 % water) a wet samples (8 % water) shows that MFI increases proportionally to the water content (see Fig. 6). On the contrary, the tensile strength decreased. The change of the mechanical properties of "wet" PVB was caused by higher polymer plasticity and the reduction of intermolecular forces.

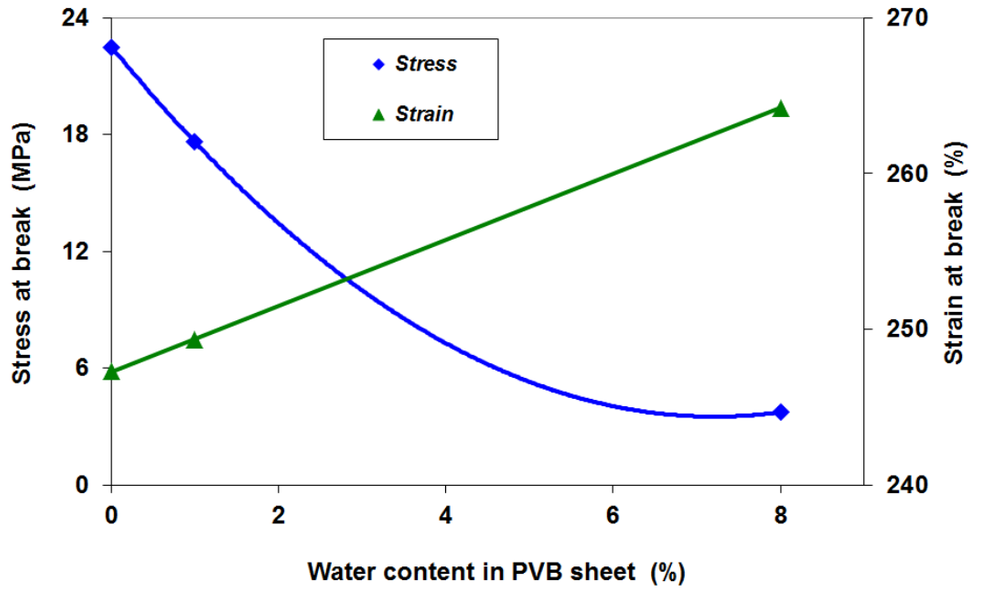


Fig. 6. The influence of water content on the change of mechanical properties of no re-processed PVB sheet.

During the re-processing of wet PVB material at the higher temperature, hydrolysis and elimination of butyric group can occur. This process results in the formation of hydroxyl groups and consequently conjugated double bond, which brings the change of PVB chain structure (Wade, D'Errico, 2004; Remsen, 1991). Thus, the hydrolysis causes considerable changes of the final properties of re-processed PVB. Due to this fact, an effort was done to find the optimal conditions for PVB re-processing with as low hydrolysis as possible. Hydrolysis was qualitatively estimated from the changes of molecular weight and increasing of the sheet yellowness.

Although water present in PVB evaporates very quickly at the beginning of the process, it influences the results of all the tests. The values of MFI for re-processed "wet" PVB show the significant increase in the dependence on temperature in the comparison with the "dry" PVB (see Fig. 7). A notable increasing of MFI values observed for wet PVB is caused by the degradation, which is induced by thermo oxidative reactions and better diffusion of gases into the PVB melt.

The comparison of mechanical properties of "dry" and "wet" PVB presents Fig. 8. The figure shows tensile strength and strain of both PVB types kneaded at different temperatures at the 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 150 °C as the maximum of the curve. This maximum, with the highest values of tensile strength, corresponds to the minimum degradation of PVB. Below and above 150 °C tensile strength decrease; this can be caused by the lowering of the molecular weight induced by the degradation. Regarding the degradation mechanism, the scission of the "dry" PVB chains less than 150 °C is prevailingly caused by shear stress, whilst at higher temperatures thermo-oxidative degradation takes place.

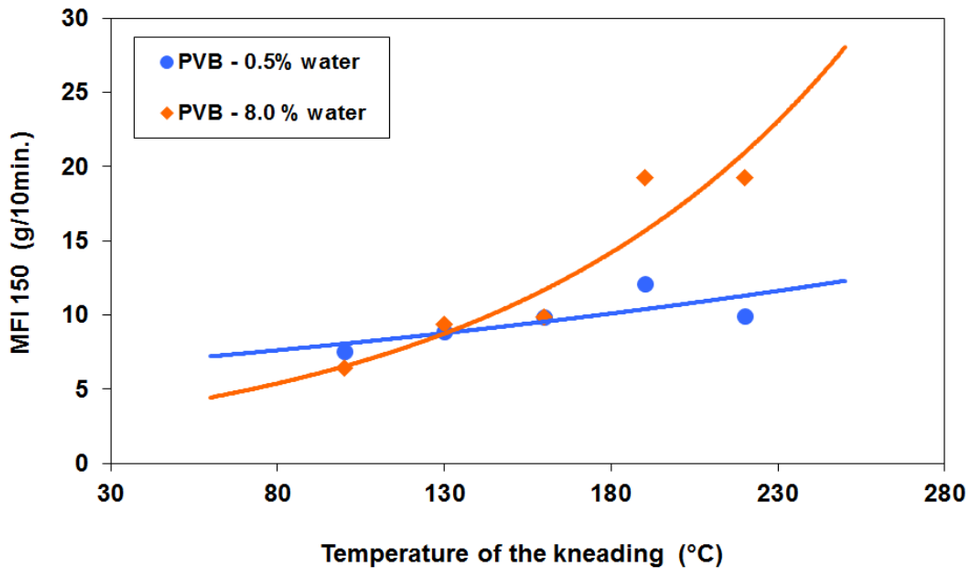


Fig. 7. MFI of kneaded PVB samples with different water content (0.5 % and 8 %) at 60 rpm during ten minutes.

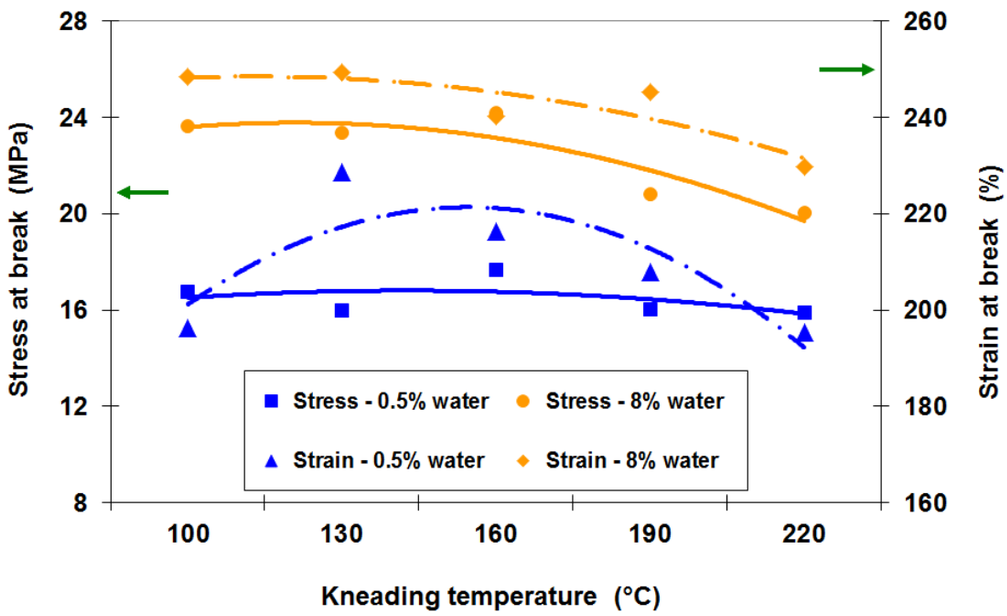


Fig. 8. Tensile strength of kneaded PVB samples with different water content (0.5 % and 8 %) at 60 rpm; arrows point out to values of virgin PVB sheet.

For the wet PVB, the values of stress at break and strain are systematically higher compared to those measured for dry samples. Moreover, dependence stress and strain *vs* temperature is monotonously decreasing not showing maxima or minima. The increase can be explained by the intramolecular crosslinking formed by the hydrogen bonds.

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

7.1 The influence of water on the yellowness

The PVB degradation was the most markedly reflected through the changes of PVB yellowness. Visually and also instrumentally, the yellowness (sometimes even brownness) of re–processed PVB samples was noticeable. Yellowness increased significantly with increasing 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 (Fig. 9). Measurements demonstrated that during kneading at the temperatures below 160 °C yellowness was almost unchanged. This can be explained by the stabilizing function of higher moisture content and consequently higher grade of PVB plasticization. At temperatures lower than 130 °C, the change of the yellowness is insignificantly irrespective of water content. With the increasing temperature, the yellowness grew markedly. 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 [35]. These are more reactive and bring more intensive lowering of molecular weight. The results from the yellowness measurements corresponds the results from determination of MFI (see Fig. 7).

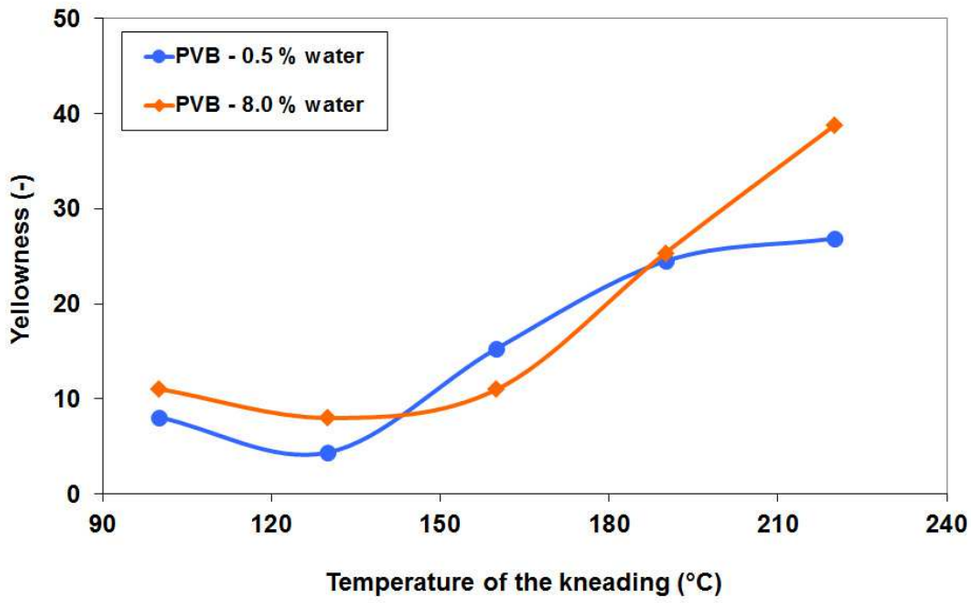


Fig. 9. Yellowness of kneaded PVB samples with different water content (0.5 % and 8 %) at 60 rpm during ten minutes.

8. The change of solution properties influenced by the degradation

Changes in molecular weight and molecular weight distribution of virgin and processed material were followed by gel permeation chromatography. Differential distribution curves of virgin and processed samples (kneading, 100°C, dry) are compared in Fig. 10. From figure it is obvious that the entire distribution of the processed sample compared to 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 $2x10^6$ $g.mol^{-1}$ (labeled with arrow). This peak was observed for all the processed samples irrespective 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 (Měřínská, Tupý, 2009; Remsen, 1991).

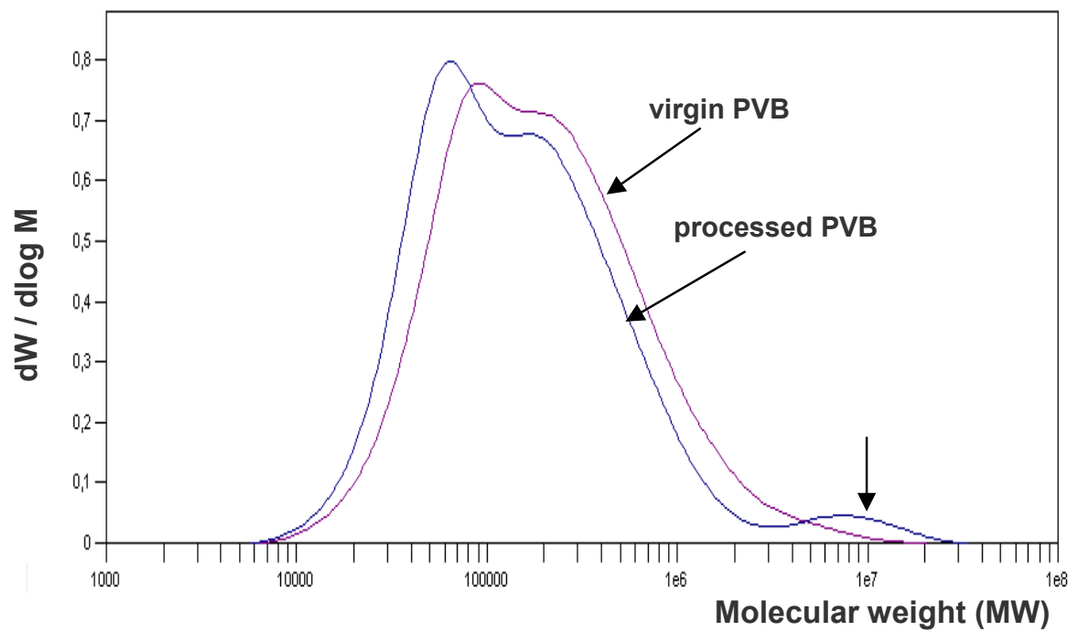


Fig. 10. Comparison of molecular weight distribution curves of virgin and processed PVB (100 °C, dry).

Changes of molecular weight in terms of M_w as a function of increased kneading temperature are for wet and dry samples depicted in Fig. 11. For dry sample, the lowest M_w values (weight average of molecular weight) 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 weights stay almost unchanged. For wet PVB, which posses 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. Hence, it can be assumed that degradation mechanism in this temperature region is similar. From Fig.11 it is also obvious that molecular weights of the wet PVB samples, with the exception of the sample processed at 220 °C, were systematically higher compared to dry ones.

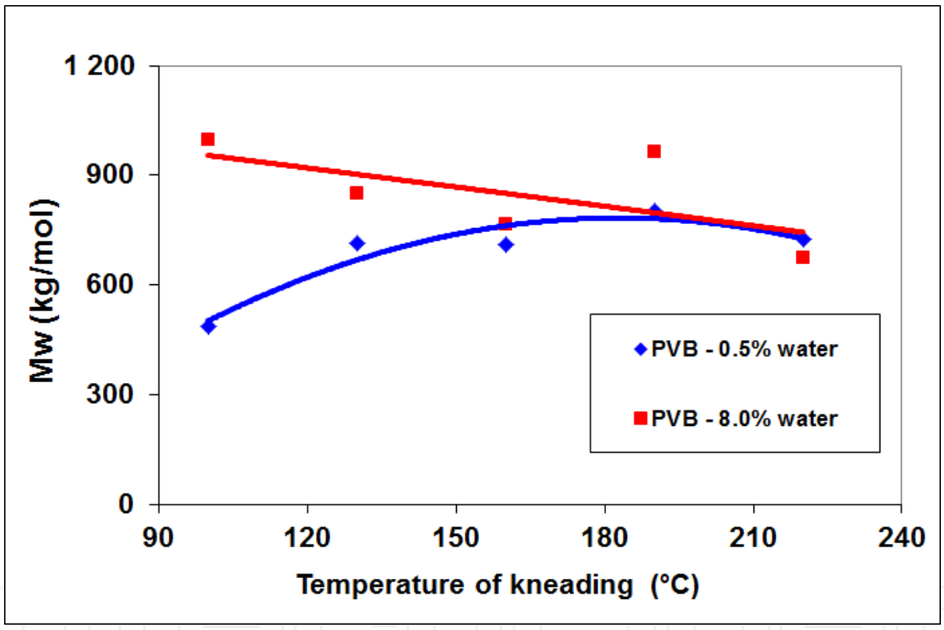


Fig. 11. Influence of kneading temperature on changes of weight average of molecular weight (M_w) recorded for (0.5% of water) dry and wet (8.0 % of water) PVB sheet.

9. Conclusions

In the presented work, conditions for re-processing of plasticized PVB sheets were investigated and influence of temperature, air oxygen content and mechanical stress on the course 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-processing by kneading occur at the temperature of about 150°C and rotation speed of kneader 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 corroborate the above conclusions showing minimal changes of PVB molecular weigh for this temperature. Increased amount of water in PVB sheet can act as and additional plasticizer improving workability of polymer melt and decreasing this energy consumption. However the "wet" samples are more susceptible to hydrolytic degradation and compromise decision has to be taken to find the balance between these two effects.

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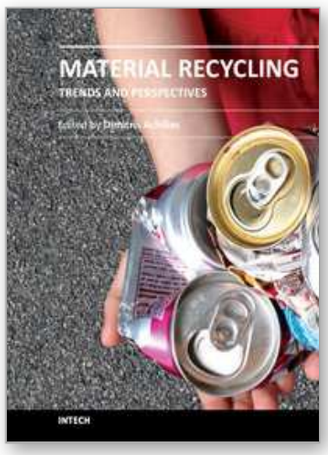
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The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

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