Research Article

Controlling the Melt Resistance to Flow as a Possibility of Improving the Miscibility and the Time Behavior of Some Blends Based on Starch

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The paper proves that the miscibility of some blends based on starch can be improved by finding for each of them the melt resistance to flow at which the nonstationary flow and the melt degradation are avoided and the developed shear rate homogenizes optimally the material composition. The obtained results show that, for process sensitive materials like starches, the border between good and less miscibility is so narrow that the window of melt processing conditions and the best formulation must be found for each of them. The improving of miscibility by controlling the melt resistance to flow proves to be a good method to prevent retrogradation and plasticizer leaching and so to handle the new compounds behavior during usage.

1. Introduction

Physical modification of starch is a common practice to diminish its limitations such as poor processability, brittleness, hydrophilicity, and low compatibility [1] and involves also the obtaining of multicomponent, multiphase materials [2–4]. In this respect, the main concern is to reach high miscibility of the material components or, at least, to diminish the interface tensions [4–9] for reaching an advanced dispersion of minor components into the main polymer matrix [5].

The blends based on starch and polyvinyl alcohol (PVOH) present the advantage of being totally environmental destroyable materials and therefore were intensively studied [8–23]. PVOH is a water soluble vinyl polymer which, at first sight, seems to be not biodegradable [9]. However literature from PVOH manufacturers such as Kuraray Co. Ltd. indicated that PVOH can be biodegraded by activated sludge treatment [15]. Biodegradation of PVOH in soil is expected to be very slow and to take place only under selective microorganisms actions [8]. The PVOH-starch materials are still attractive for applications which require particular properties such as film and/or thermoforming capability, chemical resistance, and transparency [8–21]. The greatest difficulty in achieving of these materials is mainly the consequence of high interactions between the macromolecules of each polymer, both of them having well-defined semicrystalline morphology: granular with concentric crystalline-amorphous zones for starch and semicrystalline with high orthorhombic crystals for PVOH [9–12]. As a consequence, the free flow without degradation of the macromolecules of each polymer (destruction under shear) and the creation of new interactions, this time, between the chains of PVOH and those of starch are hard to be reached simultaneously [8, 12–14]. These difficulties lead to undesired blends behavior during usage as retrogradation and plasticizer leaching [14, 18], phenomena which diminish severely the quality of goods achieved from the new materials.

The paper aim was to study the possibility of improving the miscibility of some blends based on starch by controlling the melt dynamic viscosity to avoid the nonstationary flow of the melt and the retrogradation and the plasticizer leaching in the solid state and so to handle the time behavior during usage of new obtained amorphous materials designed for goods with short life.

2. Experimental

By blending of corn starch (27–32% amylose, T_g of 67°C) with PVOH (85% hydrolysis degree, T_g of 50°C) at the same ratio of 2.33 of PVOH related to starch (PVOH/starch), three new blends were obtained on both well-known Brabender roller and extrusion procedures. A partially soluble PVOH was selected to make certain the dissolution of new materials in cold water. The three new compounds contain glycerol (GLYC-2593-06) for three plasticizing levels: low (27%), medium (35%), and high (43%). These blends contain also common melt processing additives used in the same percentage for each of them. These plasticizing levels were chosen to ensure the obtaining of highly amorphous materials which can be melt processed, by various techniques, more easily [24, 25]. The obtaining of such materials based on starch is possible if the glycerol content is higher than 30% [20]. The blend miscibility was studied by FTIR [26–28] and X-ray diffraction (XRD) [27]. The obtained results were correlated with the blends melt flowability [23–25, 29–33] which was studied using the melt flow index (MFI) method [8, 25, 29, 30]. The MFI measurements were performed on a 4000 DYNISCO indexer, LMI type, which had provided the following melt properties: shear rate (ShR), melt flow index (MFI), dynamic viscosity (DV), and flow ratio (FR). The rheological measurements were done with a nozzle having 2.09 ratio between height and diameter (h/D), in the temperature range from 145°C to 175°C, at three loading levels, low (2.16 kg and 3.8 kg), medium (5 kg), and high (10 kg), and at cutting after 30 s. The FTIR spectra were recorded on a DIGILAB FTIR spectrometer, equipped with ZnSe crystal, via Attenuated Total Reflectance (ATR) method. The recording was made at 4 cm^{-1} resolution, using an average spectrum resulting from 5 other spectra. Each spectrum was processed with Grams/32 software and was analyzed in the following spectral range identified as representative for the miscibility of PVOH-starch multiphase materials: 3700 cm^{-1}–2500 cm^{-1}, 1800 cm^{-1}–1500 cm^{-1}, 1500 cm^{-1}–1170 cm^{-1}, and 1170 cm^{-1}–800 cm^{-1} [14]. The spectra were recorded on extrudates with smooth appearance melt processed from medium and highly plasticized blends at high load (10 kg) and four temperatures from the range of 145°C–175°C. The FTIR analyses were not made for low plasticized blend because of the numerous surface defects of the extrudates. A diffractometer Panalytical X'PERT MPD type with Bragg-Brentano geometry was used for XRD analysis. The heating enthalpy was measured by Differential Scanning Calorimetry (DSC) with Netzsch DSC 204 F1 Phoenix equipment by heating from −30°C to 100°C to remove thermal history, cooling again to −30°C, and heating to 200°C with 10°C/min under nitrogen (20 mL/min flow rate). Each blend was in addition analyzed in terms of extrudate surface quality, plasticizer leaching (assessed visually and according to [32]), and pellets quantities used to estimate, in the same conditions, the melt flowability and mechanical properties.

3. Results and Discussions

3.1. Melt Rheology

3.1.1. Shear Rate. The shear rate of the low (Figure 1(a)), medium (Figure 1(b)), and high (Figure 1(c)) plasticized blends at low load rises on the entire temperature range from 145°C to 175°C, from approximately 10 s^{-1} to about 20 s^{-1} and, respectively, to 50 s^{-1}. The increase of the shear rates is biggest at higher plasticizer content and great load almost on the entire temperature range, mainly from 155°C to 175°C. At 175°C and high load, the ShR of the low plasticized blend was of approx. 90 s^{-1}. In the same extrusion conditions, the ShR becomes 200 s^{-1} and approx. 500 s^{-1} for medium (Figure 1(b)) and highly (Figure 1(c)) plasticized blends. The shear rate-temperature dependence is almost linear both for the low plasticized blend, regardless of the extrusion conditions, and also for the highly plasticized blend extruded at high load. The nature of shear rate-temperature dependency characterizes the melt flow [31–33]. The melt flow can be unstable when this relationship is linear and the resulting extrudates, as a consequence, have sharkskin surface or are stable when this relationship is concave and the obtained extrudates present smooth appearance [31–33]. The magnitude of the surface defects depends on the extent of the material melt flow instability [33]. Accordingly, the extrudates obtained from the medium plasticized blend, extruded at medium and high loads, have smooth surfaces without any defect because the shear rate-temperature dependence is concave. The extrudates achieved both from the low plasticized blend and from highly plasticized ones, extruded at low load, have sharkskin surfaces because this dependency is linear.

3.1.2. Melt Flow Index. If the extrusion was made at low load, then, regardless of the plasticizing level, the blend fluidity reflected by MFI values is almost the same on the entire temperature range from 145°C to 175°C (Figure 2).

At medium and high loads, on the same temperature range, the melt fluidity increases more as the plasticizing level is high. At high load, the fluidity of the low plasticized blend is more than double as its values at small load. The melt fluidity is almost similar for the low plasticized blend extruded at high load, for the blend with medium plasticizer content extruded at medium load, and for the highly plasticized compound extruded at low load. If the temperature exceeds 165°C and the load is below medium level (3.8 kg) then the fluidity of the low plasticized blend increases sharply with about 150% considering its fluidity at the other temperatures. A similar sharp increase of the MFI because of the temperature increasing, under the same loading, was not observed for the blends with medium or high plasticizer contents.

The dependence of the blend fluidity on the plasticizing level and on the extrusion conditions can be explained
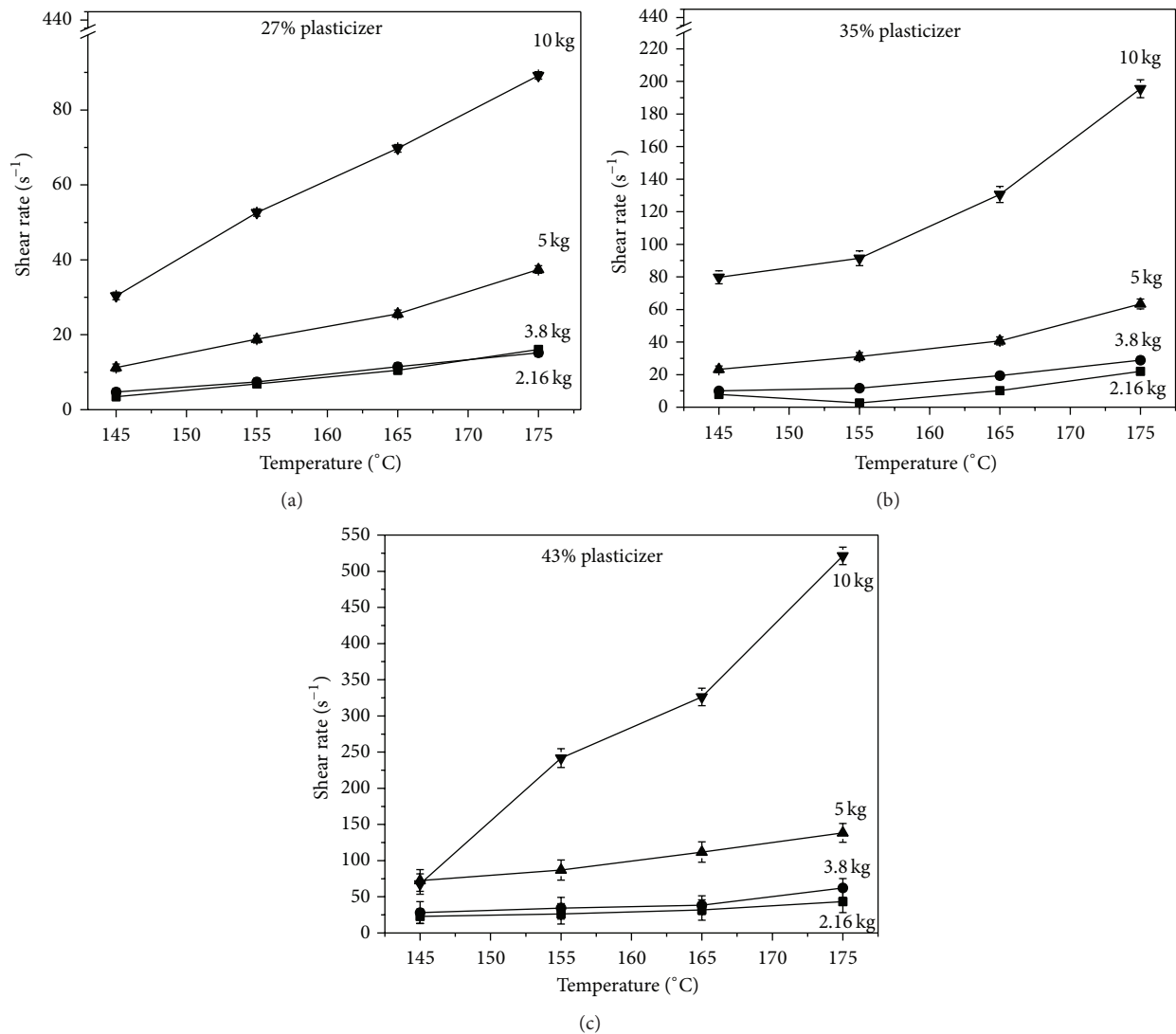
(a)

(b)

(c)

Figure 1: The dependence of the shear rate on the extrusion conditions and the plasticizing level ((a) 27%; (b) 35%; (c) 43%).

considering the macromolecules mobility and their entanglement and alignment in the flow direction. The mobility of the macromolecules is low and almost the same at loads under 5 kg, on the entire studied temperature range, regardless of the plasticizing level, probably because, in these conditions, the macromolecules are extremely entangled. At high plasticizer content and low load, in the same temperature range, the mobility remains small, probably because the macromolecules entanglement is still enhanced. At high load the fluidity has the same magnitude if the plasticizer content is low or medium and it becomes double for highly plasticized blend. At high plasticizer amount and high load, the macromolecules entanglement probably begins to decrease causing the increase of their mobility and possibly the chains alignment in the flow direction. These results show that the macromolecules mobility is dependent normally both on the plasticizing level and on the melt flow conditions. The large increase of fluidity of the low plasticized blend, extruded at high temperature, under high load, can be the consequence

of the macromolecule degradation during extrusion by chain breaking [13, 34].

3.1.3. Dynamic Viscosity. As compared with its values for the low plasticized blends (Figure 3(a)), the DV decreases with up to 40%–50% for the medium (Figure 3(b)) and with about 80%–84% for the high (Figure 3(c)) plasticizer blends. At medium and high loads, regardless of plasticizing level, the DV does not show significant variations at the temperature increasing. The temperature influence on this property is more obvious at small plasticizing level and low load.

Dynamic viscosity represents the tangential force per unit area required to move, at unit rate, one horizontal plane with respect to the other (Newton's law of friction) [34]. In a simple expression, viscosity characterizes the melt flow resistance and signifies the internal friction resulting in a melt when one layer of fluid is moving in relationship to another one [34, 35]. Accordingly, the melt flow resistance of highly plasticized blend decreases more if the extrusion load is greater than
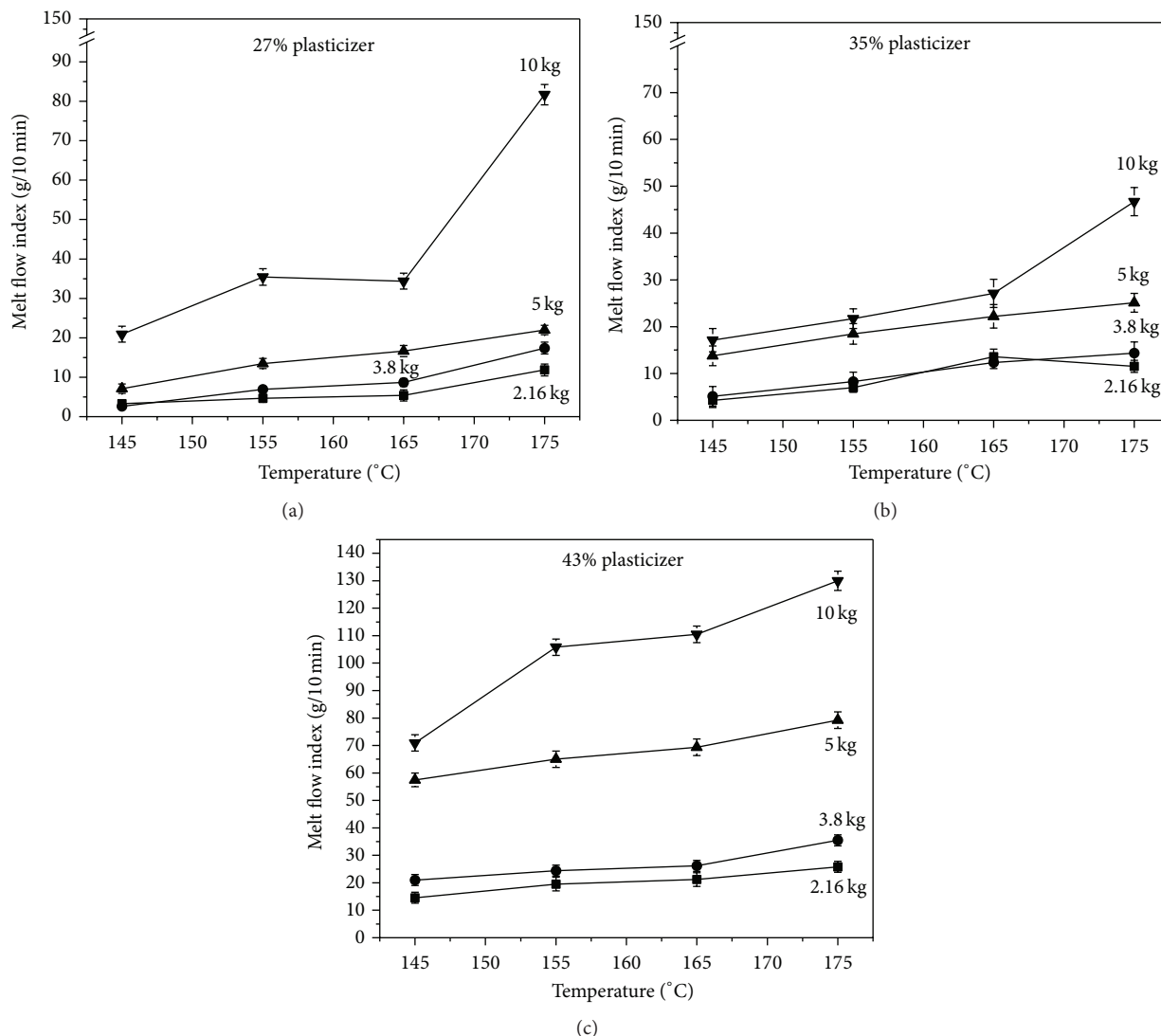
(a)

(b)

(c)

Figure 2: The dependence of the MFI on the extrusion conditions and the plasticizing level ((a) 27%; (b) 35%; (c) 43%).

3.8 kg, most likely because the chains are more disentangled and their mobility increases significantly. At low load, the melt resistance to flow decreases more at higher temperatures probably because, in these conditions, the macromolecules have greater mobility only due to the bigger kinetic energy generated by the temperature increase. The lowering of the DV with the increasing of the shear rate is in all probability the result of the alignment of disentangled macromolecules in the flow direction, aligned macromolecules having greater mobility than clew, unaligned ones. The obtained results prove that the melt flow resistance of the studied blends is more dependent on load than temperature.

3.1.4. Flow Ratio. At low load, the flow ratio practically does not depend on either the temperature value or the blend plasticizing level (Figure 4). The FR dependency on the temperature is more significant if the indexer load and plasticizer amount are higher. As compared with its values for the low plasticized blend (Figure 4(a)), the FR increases

with almost 50% and, respectively, with 200% for medium (Figure 4(b)) and highly (Figure 4(c)) plasticized blends.

The flow ratio represents the ratio between two flow rates at two different loads and characterizes the melt sensitivity to the changing of the melt processing conditions [25, 29]. The increase of the flow ratio with the plasticizing degree raise is the consequence of the diminishing of the melt flow resistance due to the interposing of the plasticizer molecules between the macromolecules of the two polymers. Higher temperatures favor the FR only at high load because the melt amount which flows through the same nozzle, in the same time, under the same temperature, is higher than the quantity which flows under low load.

3.2. Blends Miscibility

3.2.1. FTIR Analysis. The perturbations of the IR spectrum are qualitative criterion of component miscibility, grounds which make from FTIR a good tool to control the material
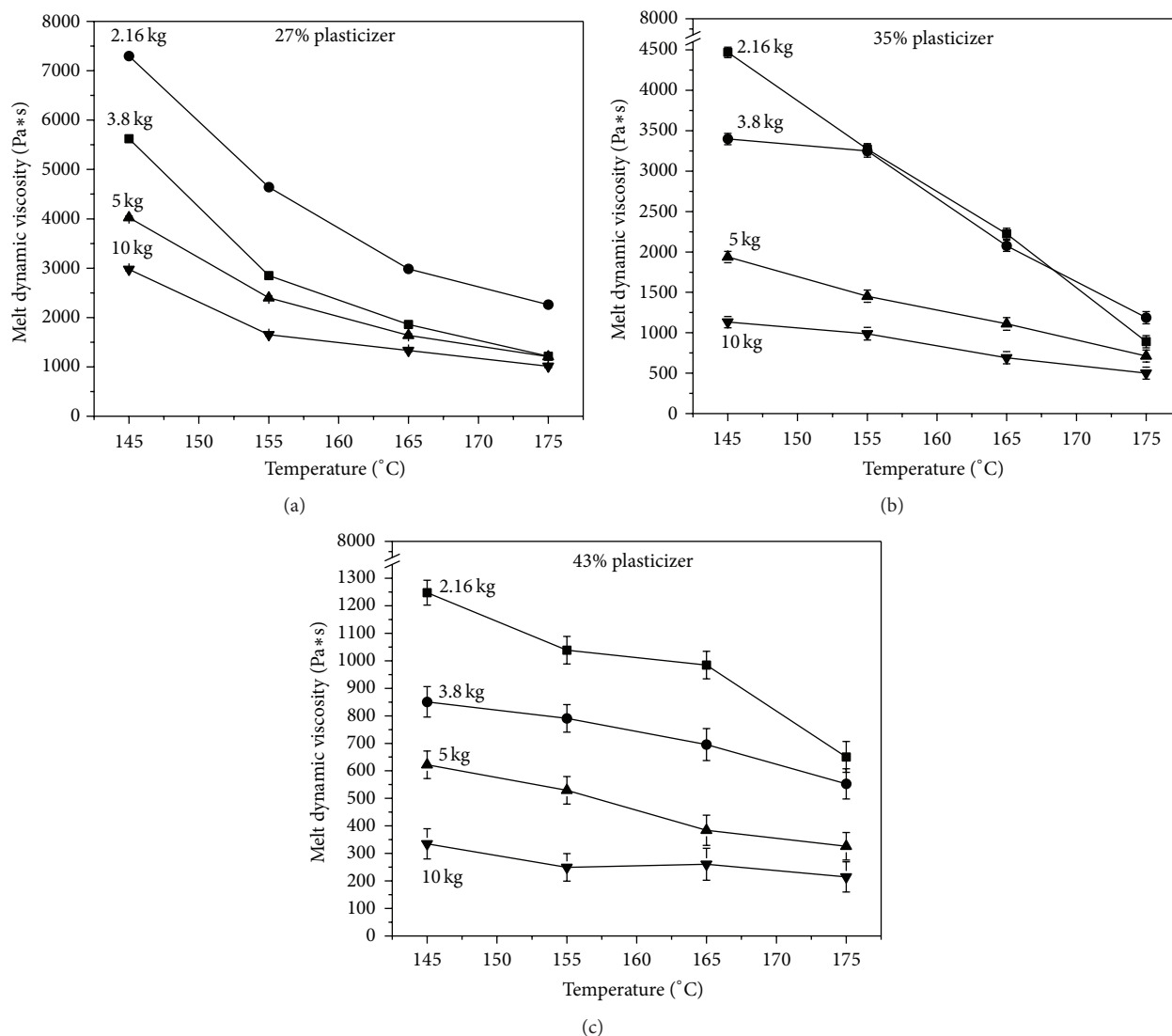
(a)

(b)

(c)

FIGURE 3: Dynamic viscosity dependence on the extrusion conditions and the plasticizing level ((a) 27%; (b) 35%; (c) 43%).

structure-properties relationship. The component miscibility can be revealed by *gross and/or appreciable changes* of the FTIR spectrum and/or by *small shifts* of the characteristic peaks of each component [8, 9, 14, 17, 22, 23, 26]. The *gross modifications* of the FTIR spectra refer to the new appearing spectral features and/or to the changes in intensities higher than 50% of the material peaks as compared with the component absorption. The *appreciable spectral changes* are those changes in which the component absorption is presented in the material spectrum but shifted with more than one width at the half height of the peak of components. The *small spectral shifts* refer to the shifting of the material absorption at wavenumber smaller than 10 Å considering the absorption of each component [14, 23, 26].

All the above described spectral changes are presented in the FTIR spectra of the studied blends (Figures 5–8) but with individual characteristics reliant on the plasticizing degree and the obtaining conditions of each of them.

The *main spectral change is a gross* one since it is about the appearance *of a new large peak* ranged from $1170\,\mathrm{cm^{-1}}$ to $955\,\mathrm{cm^{-1}}$, with maximum at $1035\,\mathrm{cm^{-1}}$ and intensity of 1.4 ATR units (Figures 8(a) and 8(b)). This peak *was* observed in all situations with the exception of the medium plasticized blend extruded at 155°C which is smaller with about 60% as in the other cases (Figure 8(b)). With the exception of the medium plasticized blend extruded at 155°C, the intensity of this new band for all the other studied blends is *the same* with the absorption of starch at $997\,\mathrm{cm^{-1}}$ and nearly the same with the one of PVOH at $1087\,\mathrm{cm^{-1}}$ (Figure 8(a)). This new peak most likely results from the large starch saccharide band by 1.5 ATR units which lies between $1180\,\mathrm{cm^{-1}}$ and $960\,\mathrm{cm^{-1}}$ and has maximum at $970\,\mathrm{cm^{-1}}$ and from those of PVOH generated both by the skeletal vibrations and by stretching of the C-C-O group and is ranged between $1170\,\mathrm{cm^{-1}}$ and $950\,\mathrm{cm^{-1}}$ [26, 36]. This new appearing peak has also features of *appreciable spectral change* because its maximum *is shifted*
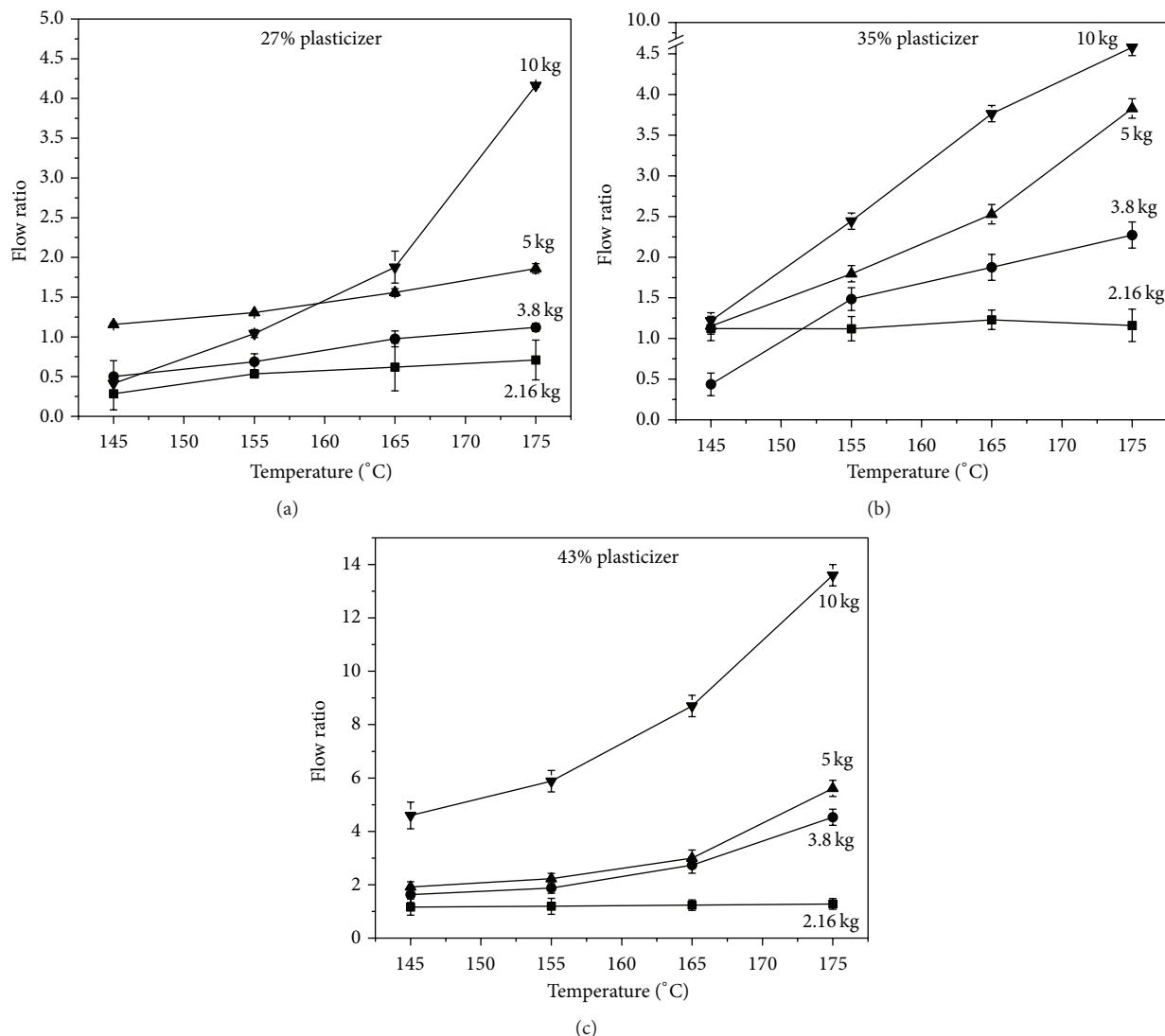
(a)

(b)

(c)

FIGURE 4: The dependence of flow ratio on the extrusion conditions and the plasticizing level ((a) 27%; (b) 35%; (c) 43%).

with almost $45\,\mathrm{cm^{-1}}$ as the maximum of the starch peak at $997\,\mathrm{cm^{-1}}$.

Another *gross spectral change* registered only for the medium plasticized blend extruded at 155°C is the *disappearance of the absorption* generated by stretching and bending of the -CH$_2$ from PVOH with maximum at $1373\,\mathrm{cm^{-1}}$, $1326\,\mathrm{cm^{-1}}$, $1259\,\mathrm{cm^{-1}}$, and $1246\,\mathrm{cm^{-1}}$ or those caused by bending and wagging of the -CH$_2$ and -C-H from starch with maximum at $1462\,\mathrm{cm^{-1}}$, $1325\,\mathrm{cm^{-1}}$, or $1243\,\mathrm{cm^{-1}}$ (Figure 7(b)). These spectral changes do not appear in all the other analyzed situations (Figures 7(a) and 7(b): 145°C, 165°C, and 175°C).

Another *gross spectral change* occurring only for the medium plasticized blend extruded at 155°C is the diminishing with more than 70% of the bands intensities from the PVOH at $2917\,\mathrm{cm^{-1}}$ and $2849\,\mathrm{cm^{-1}}$ generated by the -CH and the -CH$_2$ stretching (Figure 5(b)). For all the other cases the blends absorption is almost overlapped with the mentioned PVOH peaks (Figures 5(a) and 5(b): 145°C, 165°C, and 175°C).

A further *gross spectral change* visible only for the medium plasticized blend extruded at 155°C is represented both by the residual acetate vibration at $1715.84\,\mathrm{cm^{-1}}$ with shoulder at $1713.80\,\mathrm{cm^{-1}}$ which is smaller with about 83–89% as for PVOH (Figure 6(b)) and by the vibration of adsorbed water which is absorbed in a wide range with maximum at $1652.56\,\mathrm{cm^{-1}}$ and which is smaller with about 75% as for the PVOH (Figure 6(b)). The similar spectral modifications registered for all the other analyzed situations do not qualify for any changes showing the components miscibility (Figures 6(a) and 6(b): 145°C, 165°C, and 175°C).

Another *gross spectral change* appearing for the medium plasticized blend extruded at 155°C is the band generated by the stretching and bending of the -CH$_2$ with absorption in the range of $1418\,\mathrm{cm^{-1}}$–$1246\,\mathrm{cm^{-1}}$. This absorption is smaller with almost 60%–80% as the similar peak from PVOH (Figure 7(b)).

A further gross spectral change visible also only for the medium plasticized blend extruded at 155°C is the absorption
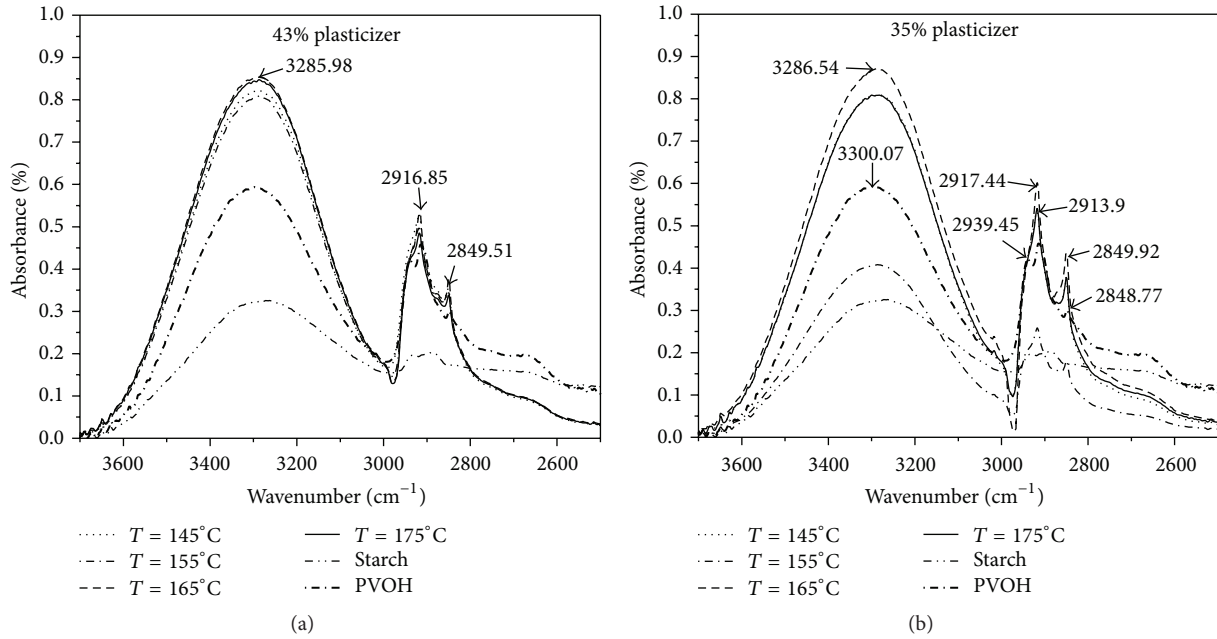
FIGURE 5: The dependence of ATR absorption in the absorption range of 3700 cm^{-1} to 2500 cm^{-1} on the plasticizing level ((a) 43%; (b) 35%) and the extrusion temperature (10 kg load).
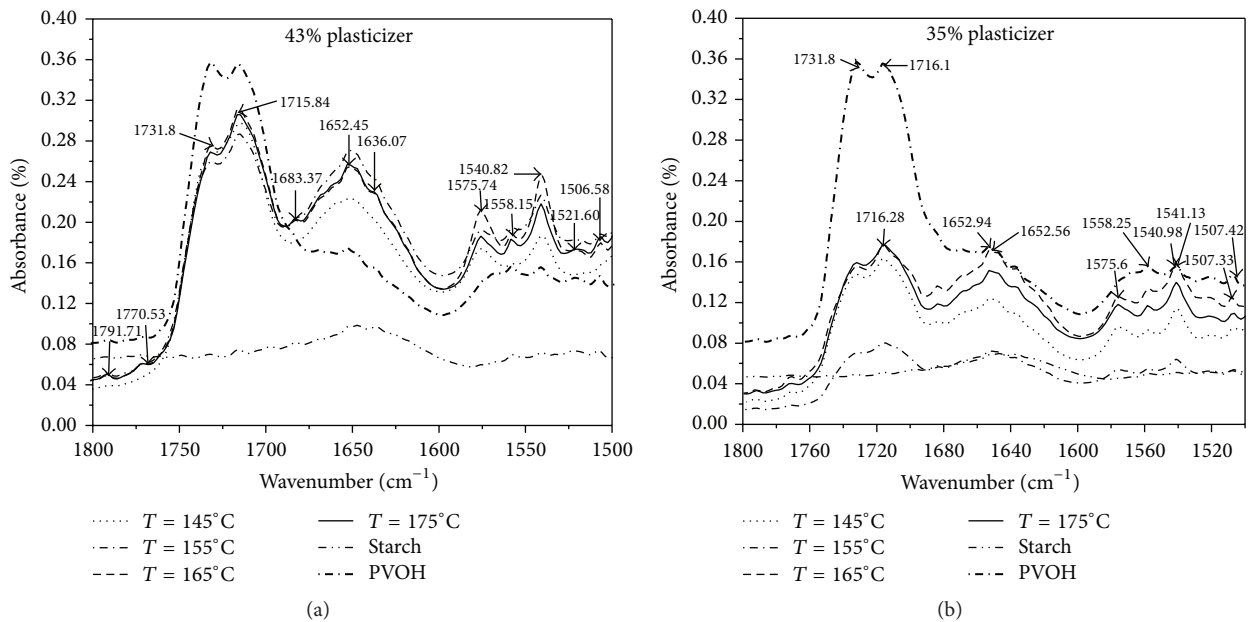

FIGURE 6: The dependence of ATR absorption in the range of 1800 cm^{-1} to 1520 cm^{-1} on the plasticizing level ((a) 43%; (b) 35%) and the extrusion temperature (10 kg load).

generated by the stretching vibration of the C-O-C linkage from starch at 859 cm^{-1} and by the bending vibration of -OH from PVOH at 841 cm^{-1} (Figure 8(b)). Both these blend peaks are smaller with more than 50% as the similar bands from each polymer (Figure 8(b)). The similar spectral changes which appear at these wavenumbers for the other blend and extrusion temperatures do not qualify for any spectral changes proving the component miscibility (Figures 8(a) and 8(b): 145°C, 165°C, and 175°C).

The FTIR spectra of medium plasticized blend extruded at 155°C show also *appreciable spectral changes* as larger shifting of the bands generated by the stretching vibration of the -OH at 3286 cm^{-1} which is shifted with 42 cm^{-1} as the PVOH band at 3328 cm^{-1} or with about 26 cm^{-1} as the starch peak at 3302 cm^{-1} (Figure 5(b)).

The FTIR spectra of medium plasticized blend extruded at 155°C present modifications which represent *combinations of gross with small spectral changes* as those characterizing
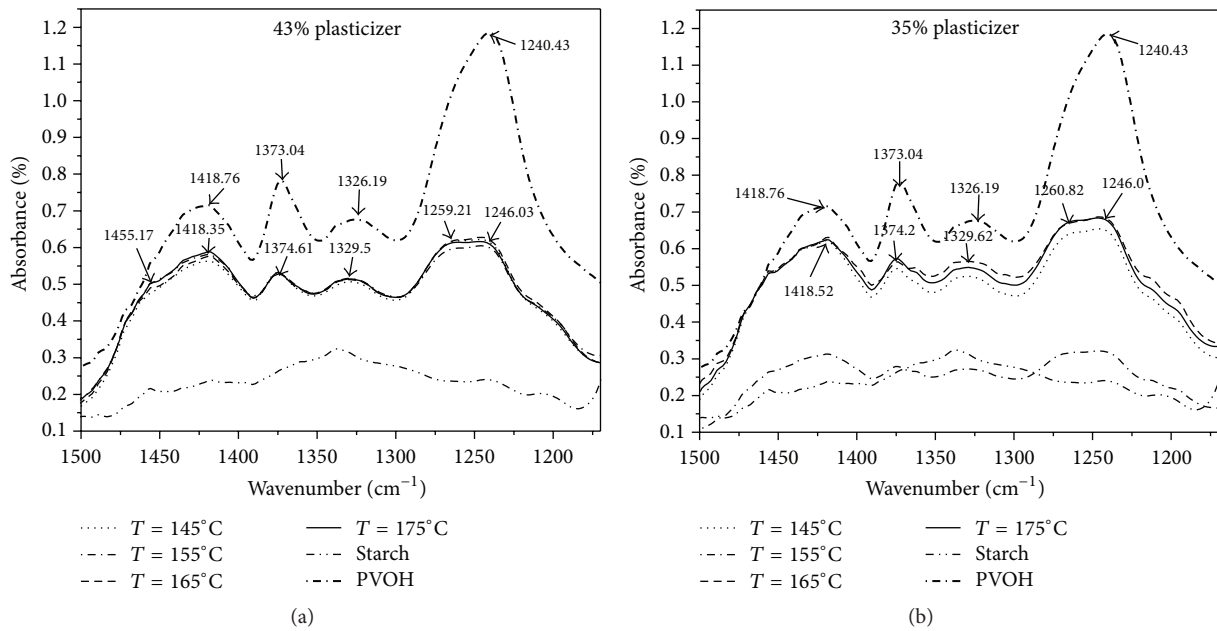
FIGURE 7: The dependence of the ATR absorption in the range of 1500 cm^{-1} to 1120 cm^{-1} on the plasticizing level ((a) 43%; (b) 35%) and the extrusion temperature (10 kg load).
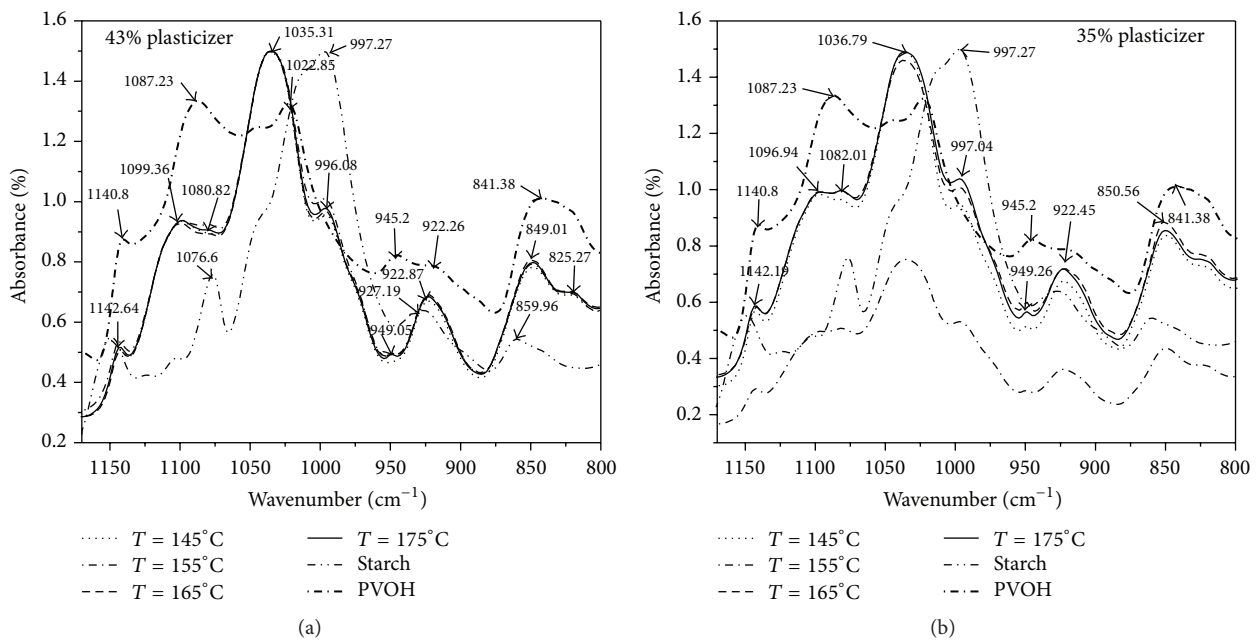

FIGURE 8: The dependence of the ATR absorption in the range of 1170 cm^{-1} to 800 cm^{-1} on the plasticizing level ((a) 43%; (b) 35%) and the extrusion temperature (10 kg load).

the stretching of the -CH$_2$ at 2849 cm^{-1} which is smaller with 50% and is shifted with 6 cm^{-1} as the similar PVOH peak (Figure 5(b)). The similar spectral changes which appear at this wavenumber for the other blend and extrusion temperatures do not mean modifications revealing component miscibility (Figures 5(a) and 5(b): 145°C, 165°C, and 175°C).

The above presented results demonstrate that the main spectral changes illustrating the component miscibility occur

for medium plasticized blend extruded at 155°C. Even, in this situation, some peaks are absorbed at the same wavenumber with the two polymers; however their height is smaller with about 54%–83% as the similar peaks from the PVOH (ex. the absorption at 2918 cm^{-1}, 1541 cm^{-1}, 1142 cm^{-1}, 1036 cm^{-1}, and 850 cm^{-1}) or from the starch (at 1456 cm^{-1} or 997 cm^{-1} which in case of blends appear as shoulder at 922 cm^{-1}). These results prove that even for medium plasticized blend,
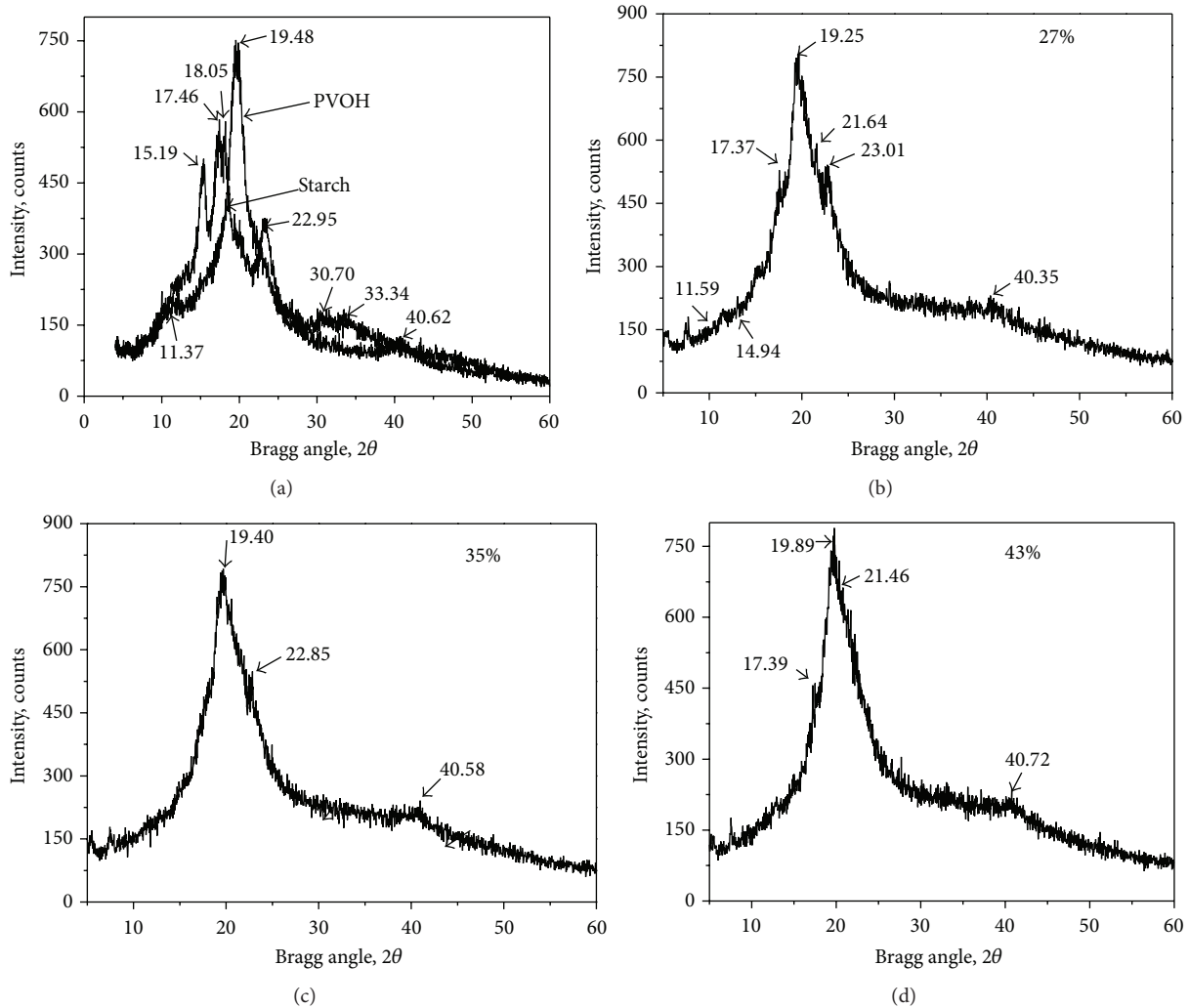
FIGURE 9: The diffractograms of studied blends (PVOH and starch (a); blends with plasticizing level of 27% (b); 35% (c); 43% (d)).

extruded at 155°C, the fingerprints of the two polymers are not entirely destroyed which means that the miscibility of the two polymers is not totally.

3.2.2. XRD-Retrogradation: Plasticizer Loss-Extrudates Appearance-Others.
The main diffraction peak of the studied blends presents small shoulders at angles very close to those characterizing the starch diffraction, in a number depending on the plasticizing level: many at low plasticizer amount (Figure 9(b)) and a few for medium (Figure 9(c)) and high (Figure 9(d)) plasticizing levels. The mentioned shoulders (at approx. $23.01°2\theta$, $22.85°2\theta$, $21.46°2\theta$, $17.39°2\theta$, and $11.79°2\theta$), depending on the plasticizing degree of each blend, can be found or not on the blends diffractograms. However the main diffraction peak of each blend was registered at the same diffraction angle of around $19°2\theta$ as for the PVOH alone. Another very small peak was registered at around $40°2\theta$ which can represent the PVOH peak from $40.97°2\theta$ but slightly shifted. The existence of these peaks on the blends diffractograms reminiscent from PVOH is understandable if it is considered that the PVOH represents

the main matrix of the new blends and accordingly to the FTIR results it was not entirely destroyed by blending, under shear, with starch. If the amylose content of the used starch were greater, probably peaks reminiscent from starch could not be found on the blends diffractograms. The tight arrangement of starch chains between those of the PVOH was not possible almost certainly because of the uncontrolled cluster structure of amylopectin. That is why the resulting PVOH-starch compounds are microstructured materials.

If, after 8 months in the laboratory conditions, the low plasticized blend shows immediately after the obtaining the phenomenon of plasticizer leaching, the medium plasticized blend extruded at 155°C does not behave in the same way. The increase of the heating enthalpy of the low plasticized blend with about 15% immediately after obtaining shows an increase of crystallinity most likely because of retrogradation, phenomenon which generates the plasticizer leaching.

The extrudates have sharkskin appearances, without gloss (Figure 10(a)) if they were obtained from the low plasticized blend regardless of the extrusion temperatures or from the highly plasticized one extruded at low load. The only

(a)   (b)
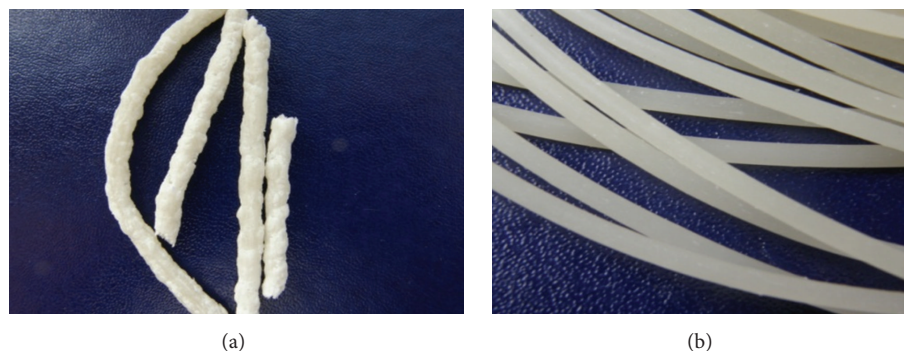
FIGURE 10: The dependence of the extrudate surface appearance (extrusion at 155°C and 10 kg load) on the plasticizing level ((a) 27%; (b) 35%).

extrudates with gloss and smooth surface were obtained from the medium plasticized blend, extruded at 155°C and high load (Figure 10(b)).

The pellets quantity used to measure, in identical conditions, all the flow properties depends also on the plasticizing level and the obtaining conditions of the studied blends. This quantity is 235 g for the blend with medium plasticizer content and 410 g and 400 g for low and highly plasticized ones. The mechanical properties depend also on these two parameters. With the increasing of the plasticizer content the tensile strength decreases in the range of 72–38 daN/cm^2 and the break elongation increases from 418% till 520%.

These results show that the improving of the blend miscibility by finding the proper plasticizer level and the window of melt processing conditions allowed the elimination of the melt flow instability, the blend retrogradation, and the plasticizer loss.

The dependence of the miscibility on the plasticizer content and on the extrusion conditions can be explained considering the flow properties [34] of the analyzed blends. At low plasticizing level the developed shear rates are much smaller and probably not enough to well homogenize the melt which, in this condition, is less fluid and opposes a greater resistance to flow. These remarks explain the practical observations according to which the starch-PVOH blends achieved by simply blending the two polymers using a common Brabender roller sequence loss of the plasticizer immediately after the obtaining. If the melt homogeneity is poor as in case of the low plasticized blend probably the plasticizer amount is too small to be well dispersed between the macromolecules of the two polymers and so to be adsorbed onto the H-bonding sites of starch and PVOH. Poor melt homogeneity favors the plasticizer leaching probably because its molecules were not absorbed onto the H-bonding sites of the two polymers and the suprasaturation level was not reached [10, 22]. Poor melt homogeneity probably favors also the nonstationary flow which generates the sharkskin appearance of the extrudates. For the medium and highly plasticized blends extruded at medium and high loads, the conditions of more intense homogenization are fulfilled because both the shear rate and the melt fluidity are higher. In this situation the glycerol acts as a plasticizer because the adsorbed glycerol

onto H-bonding sites of starch and PVOH had reached the suprasaturation level [10, 22]. Consequently the melt resistance to flow is lower and regardless of the extrusion temperature, the macromolecules of the two polymers behave similarly enough to ensure good miscibility. The medium plasticized blends have extrudates with smooth appearance because their melt flows in a stable manner. However the extrudates obtained from highly plasticized blend extruded at low load had no always very smooth appearance most likely because the homogenizing time was too short considering the greater plasticizer amount which must be dispersed between the other components. It should be recalled that the nonstationary flow of the poorly homogenized blend with high content of plasticizer was first revealed by the linearity of the shear rate-temperature dependency. The sudden increase of fluidity and of the flow ratio for the low plasticized blend at high thermal stress ($T = 165$°C–175°C) demonstrates that, in these conditions, beside the blend fluidization occurs a parallel process of macromolecules breaking which can be avoided if the extrusion temperature does not exceed 155°C.

The different melt flow properties of the studied blends explain the different pellets quantities used to measure for each blend, in the same conditions, the same melt flow properties. These quantities were twice greater for less miscible blends than the amount used for the high miscible blend represented by the medium plasticized blend extruded at high load and 155°C which proved to have the best flow properties in the melted state. The obtained results prove that the border between good and less miscibility of materials based on starch is so narrow that the best formulation and the window of melt processing must be found for each blend.

The best miscibility of the studied blends was reached for medium plasticized blend (37%) extruded at high load (10 kg) and 155°C almost certainly because only in these conditions does the melt resistance to flow have the smaller value. However, it should be noted that in case of the blend obtained using starch with great content of amylopectin the miscibility cannot be total, most likely because of the uncontrolled cluster structure of the amylopectin. The new materials were carried out with good results at various experimental levels into goods with short life which prove to have excellent application properties [35–41].

4. Conclusions

(1) The miscibility of some blends based on starch can be improved by finding for each of them the melt resistance to flow at which the nonstationary flow and the melt degradation are avoided and the developed shear rate can optimally homogenize the composition. The blends with improved miscibility do not show retrogradation and plasticizer leaching and flow in a molten state in a stable manner and because of this the resulting extrudates have smooth and glossy surface.

(2) The border between good and less miscibility for process sensitive materials like starch is so narrow that the best formulation and the window of melt processing must be found for each blend.

(3) The improving of miscibility by controlling the melt resistance to flow proves to be a good method to avoid the retrogradation and the plasticizer leaching and so to control the time behavior of materials based on starch during their usage.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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