

## Research Article

# New Evidences on the Process Sensitivity of Some Renewable Blends Based on Starch considering Their Melt Rheological Properties

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Received 26 September 2014; Accepted 21 January 2015

Academic Editor: Jean-Marc Saiter

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The degradability and processability of new renewable materials based on starch and PVOH were studied using the melt flow index (MFI) method by measuring the melt rheological properties which depend not only on the extrusion conditions and material formulation but also on the macromolecule characteristics which can be modified by chemical degradation. These results were correlated with other material properties like color and cross-linking degree. The obtained results show that flowing in the melted state of the studied materials is accompanied by a second process of chains chemical degradation. It was observed that, at the same level of additivation, under identical extrusion conditions, the melted blends with corn starch as main component are highly mechanically sensitive and degrade mostly by chains scission and those with PVOH as major component are highly temperature sensitive and degrade mainly by cross-linking. The obtained results show also that each PVOH-starch blend requires particular formulation and individual windows of melt processing conditions. These results are a good proof that the MFI method is a good path to study the degradability and moldability of process sensitive polymeric materials like those based on starch and PVOH.

## 1. Introduction

In our time, the interest in developing of new degradable materials compatible with the environment is still important not only because of societal concerns about the accumulation of environmental plastic wastes [1–3] but also for a better adjustment of material properties to the increasingly demands of various applications. Nowadays a particular interest for the implementation of new biodegradable material sources developed based on transgenic technologies is also registered [4].

Starch is a renewable polymer which can be converted into goods with high biodegradability, but poor mechanical

properties and high hygroscopicity [5, 6]. Compounding with other polymers and additives at melt processing is a practical method to overcome these limitations and to achieve new materials, moldable by various techniques into goods for several applications [7–11].

Even the blends of starch with polyvinyl alcohol (PVOH) have been extensively studied [12–15]; their importance is however alive, mainly because they can be designed for applications which require particular properties. The degradability of starch [16–22] and PVOH [23–28] has been also broadly studied. The starch can be degraded by thermal or/and shear stress influences through intra- and intermolecular reactions of chains scission, dehydration, fracture of the glycosidic

rings with water elimination and double bonds formation, cross-linking, and so forth [21, 22, 26]. Shear and thermal stress degrade both polymers from starch composition, more the branched amylopectin and less the linear amylose [16, 21, 22]. Partially hydrolyzed PVOH is less resistant to degradation than fully hydrolyzed grades, because the residual vinyl acetate groups liberate acetic acid which catalyses the degradation [25]. At temperatures of about 150°C, because of inter- and intramolecular chemical reactions, the macromolecules of partially hydrolyzed PVOH degrade by double bonds formation (responsible for polymer color), cross-linking, releasing of water, acetic acid, or other small molecules (chain fragments) [17, 25]. Details on the degradability of blends based on starch and PVOH, its dependence on formulation, and/or melt processing conditions or details about the possibilities both to control their degradation and to obtain, in practical conditions, colorless blends with smooth surfaces however cannot be found.

The authors have observed that, during melt processing, the starch-PVOH blends degrade by visually changing of color, from natural to yellow, beige, or brown shades [12–15]. The degradation can occur in the first 2–4 min after the solid and liquid components, premixed in advance, are added into the mixing chamber of Brabender plastograph or almost immediately after the polymers plasticizing, even if additional plasticizers were used [12–14].

The authors intend to study the degradability of these blends based on melt rheological properties estimated with melt flow index (MFI) method which has as base principle finding the quantity of melted material extruded through a die in a given time, by working in specified conditions [29–39]. The polymer degradation is a chemical process which affects the macromolecules considering their length, shape, polydispersity, ramification, cross-linking degree, and so forth [28]. In the melted state, the quantity of material which will flow through a die, in given time and given conditions will depend on both the material fluidity and the degradation scale and therefore the MFI method can be used for degradability studies [25, 37, 38].

The aim of this study was to add knowledge on the degradability of some new blends based on starch and PVOH and on its dependence on formulation and melt processing conditions by highlighting possible destructive processes under mechanical stress and temperature influence in order to achieve, by melt processing techniques, new colorless renewable materials based on starch.

## 2. Materials and Methods

The new compounds were obtained considering Brabender-roller procedure according to which corn starch with 27–29% amylose was blended with polyvinyl alcohol (PVOH) with 85% hydrolysis degree and with usual melt processing additives. The blending ratio of starch related to PVOH was of 70/30, 50/50, and 20/80 and the plasticizer level of the three compounds was the same, respectively, of 50% considering 100% blend of starch with PVOH.

The melt rheological properties were measured according to [28–34, 40, 41], on a DYNISCO 4000 LMI indexer which displayed the following properties: melt flow index (MFI), dynamic viscosity (DV), flow ratio (FR), shear rate (ShR), and shear stress (ShS). Additionally, the activation energy of the viscous flow ( $E_a$ ) was calculated with (1) [41]. The indexer was equipped with a nozzle having 2.09 ration between height and diameter (h/D) The measurements were done at four temperatures (from the range of 125°C–170°C) and four loads (between 2.16 kg and 10 kg) because, in accordance with the experimental statistic, this is the minimum number of experimental points which ensure the relevance of the conclusions on a process or a phenomenon [42]. Each extrudate was cut after 120 s. In (1)  $T_1$ ,  $T_2$  represent the temperature limits for which  $E_a$  is computed, MFI ( $T_1$ ,  $G$ ) is the MFI at temperature  $T_1$  and load  $G$ , and MFI ( $T_2$ ,  $G$ ) represents the MFI at temperature  $T_2$  and load  $G$ :

$$E_a = R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \left| \ln \left( \frac{\text{MFI}(T_1, G)}{\text{MFI}(T_2, G)} \right) \right|. \quad (1)$$

The melt rheological properties were correlated with other extrudate properties as color, voids content, and cross-linking degree (measured according to [43]).

## 3. Results and Discussions

**3.1. Melt Flow Index.** When the plastograph's load is of 2.16 kg or of 3.8 kg then on the entire temperature range from 125°C to 155°C the MFI of the 70% starch blend is almost constant (Figure 1(a)). At greater load of 5 kg or 10 kg, up to 145°C, the material's fluidity increases 3–8 times and, then, till 170°C decreases about 25%. At 2.16 kg or 5 kg load and temperatures between 130°C and 140°C, the fluidity of the 50% starch blend slightly increases, remaining approximately constant up to 150°C, and then between 150°C and 160°C slightly decreases (Figure 1(b)). If the indexer's load is 10 kg then the MFI increases approximately 50% up to 155°C and between 155°C and 170°C decreases almost 55% (Figure 1(b)). If the blend contains 20% starch, then, at small (2.16 kg, 3.8 kg) and medium (5 kg) loads, the fluidity starts to decrease at 135°C (Figure 1(c)). At high load of 10 kg the MFI is 7–8 times higher than those recorded at 2.16 kg–5 kg. Between 125°C and 170°C, the main parameters which control the blend's MFI are starch content and indexer's weight. In the studied temperature ranges, the highest fluidity was obtained for the blend with highest starch content (70%) at the highest load of 10 kg. The increasing of fluidity at high load is much more pronounced than its decrease in the same conditions of flow.

**3.2. Shear Stress and Shear Rate.** If the highest ShS is developed at the high load of 10 kg and is of 0.1 MPa, the lowest stress appears at the low load of 2.16 kg or 3.6 kg and is of 0.02 MPa–0.038 MPa (Figure 2). The ShS depends only on the load and does not present variation with the blend's composition and/or the temperature.

At 10 kg load, the shear rate of the 70% starch blend increases from approx. 55 s<sup>-1</sup> at 135°C to 105 s<sup>-1</sup> at 155°C (Figure 3(a)). If the blend contains 50% starch then the shear

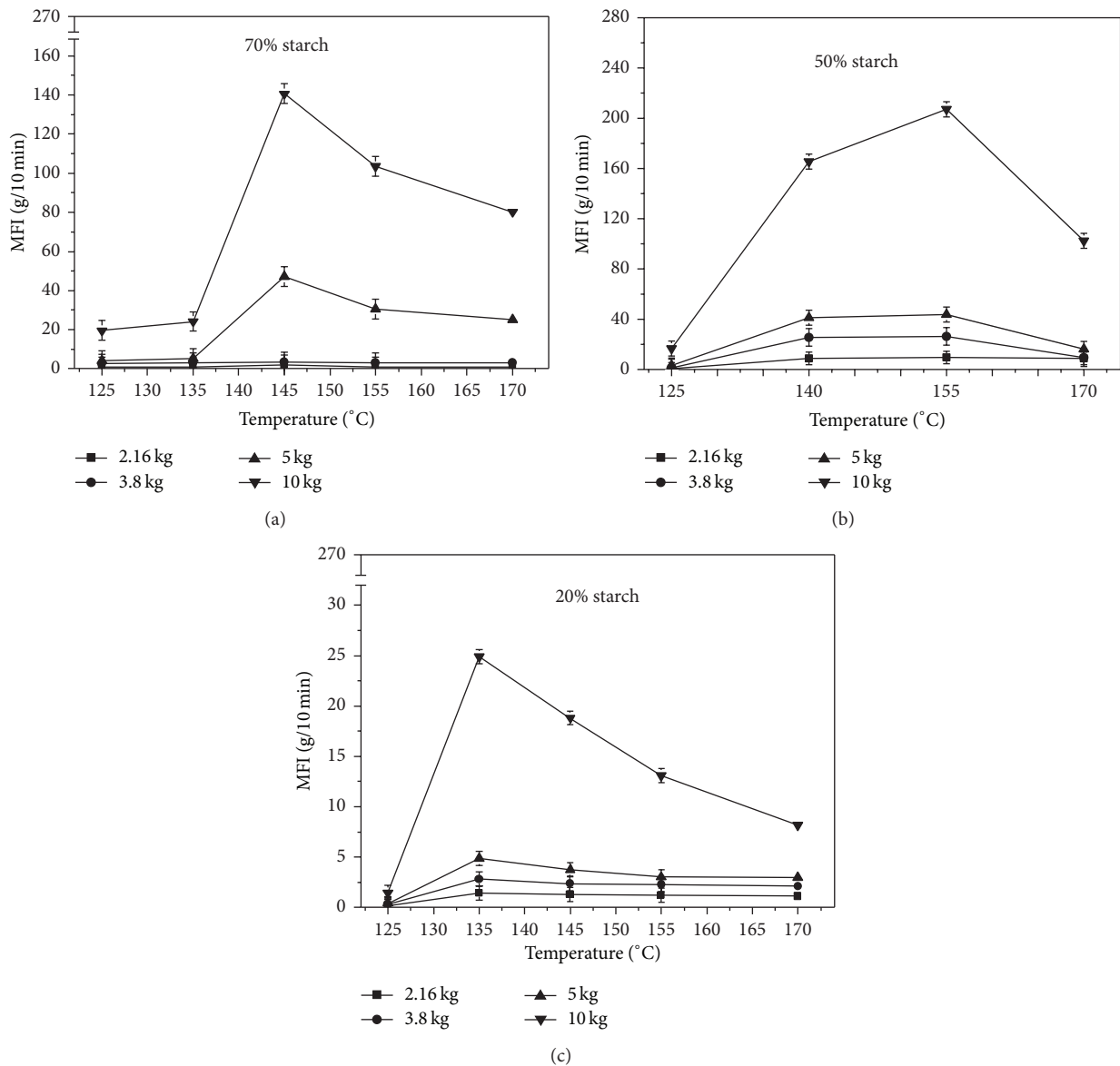


FIGURE 1: The MFI's dependency on temperature, load, and starch content for the blends with 70% (a), 50% (b), and 20% (c) starch (line only for eliminating the confusions regarding the symbols' affiliation to a certain dependence).

rate rises from approx.  $80 \text{ s}^{-1}$  at  $135^\circ\text{C}$  to  $350 \text{ s}^{-1}$  at  $160^\circ\text{C}$  and reaches  $450 \text{ s}^{-1}$  at  $170^\circ\text{C}$  (Figure 3(b)). The shear rate of the blend with 20% starch, on the entire studied temperature range, at low or medium loads from 2.16 kg to 5 kg, is relatively small, of about  $2\text{--}10 \text{ s}^{-1}$ . The ShR reaches high values at 10 kg if the starch content is greater than 50% (Figure 3(c)).

**3.3. Dynamic Viscosity.** Between  $125^\circ\text{C}$  and  $135^\circ\text{C}$ , regardless of the indexer's load, the DV of the 70% starch blend is almost constant (Figure 4(a)). At low loads of 2.16 kg or 3.8 kg, if the temperature increases from  $135^\circ\text{C}$  to  $170^\circ\text{C}$  then DV decreases with about 80–85%. If the load is of 5 kg or of 10 kg, then DV decreases about 45–50%. For loads of 10 kg or 5 kg and temperatures varying between  $145^\circ\text{C}$  and  $170^\circ\text{C}$ , the DV increases by only 2–3% considering its values at  $125^\circ\text{C}$

(Figure 4(a)). For the blend with 50% starch, regardless of the load's level, the DV decreases up to  $140^\circ\text{C}$  with high rate. Between  $140^\circ\text{C}$  and  $155^\circ\text{C}$  the DV of this blend is almost constant and from  $155^\circ\text{C}$  to  $170^\circ\text{C}$  it continues to decrease (Figure 4(b)). Regardless of the load's level, between  $125^\circ\text{C}$  and  $135^\circ\text{C}$  the DV of the blend with 20% starch decreases drastically by almost 60–80% and increases less by almost 5–10% in the following temperature range of  $135^\circ\text{C}$ – $170^\circ\text{C}$  (Figure 4(c)). The DV of the blends with starch as major component is 3–5 times smaller than the DV of the blend in which the starch is the minor component.

**3.4. Flow Ratio.** The flow ratio of the 70% starch blend has the lower values at 2.16 kg varying from 1.5% to 2.9% on the entire temperature range from  $125^\circ\text{C}$  to  $170^\circ\text{C}$  (Figure 5(a)).

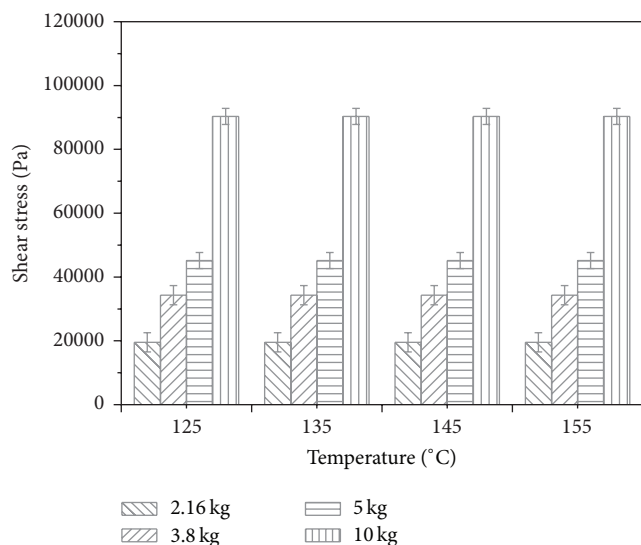


FIGURE 2: Shear stress versus temperature and indexer's load and for the blends with 20%, 50%, and 70% starch.

However, for the load range from 3.16 kg to 10 kg, if the temperature increases from 125°C to 145°C, then the flow ratio rises 1 to 3 times. Over 145°C, the flow ratio decreases by approx. 30–40% for all the 4 loads. The flow ratio of the blends with 50% (Figure 5(b)) and 20% (Figure 5(c)) starch has almost the same behavior, with the difference that the decrease of FR begins at 145°C if the blend has 50% or 70% starch (Figures 5(a) and 5(b)) and at 135°C if the blend has 20% starch (Figure 5(c)). The FR has the highest values for the blend with 50% starch at 10 kg load and temperature variation from 125°C to 145°C (Figure 5(b)) and for the blend with 20% starch also at 10 kg load, in the temperature range of 125°C–135°C (Figure 5(c)).

It must be underlined that the temperatures at which the biggest value of FR was registered are the same as those registered for the other measured rheological properties (MFI, Figure 1, DV, Figure 4). In all cases these temperatures represent points in which the variation of each property is changed which means that, around these temperatures, modification of the characteristics of the same phenomenon takes place.

**3.5. Activation Energy of Viscous Flow.** The  $E_a$  required by the melted blends to flow depends on their starch content and the temperature at which the flow takes place. The smaller the starch content the highest the required energy to flow. At 70% starch, between 145°C and 155°C the  $E_a$  is two times higher than the  $E_a$  required between 125°C and 135°C (Figure 6(a)). For the blend with 50% starch (Figure 6(b)), the highest  $E_a$  of 250–275 kJ/mol is required at 140°C and loads of 2.16–10 kg. The  $E_a$  decreases up to 10–25 kJ/mol if the load is 5 kg or 10 kg and the temperature increases to 150°C. When the temperature reaches 160°C the  $E_a$  rises again till 75–100 kJ/mol (Figure 6(b)). In case of the blend with 20% starch (Figure 6(c)), at 130°C and 2.16 kg–10 kg, the  $E_a$  has the highest values of 250–375 kJ/mol (Figure 6(c)).

If the processing of the blend runs at 140°C–170°C, then the melt requires only 10–30 kJ/mol to flow, which means values of 12 to 25 times smaller.

**3.6. Color, Cross-Linking, and Voids Content.** All extrudates were colored in beige, even yellow, and contain 2–10% cross-linked macromolecules and approx. 5 small voids at 2 cm length if they were obtained at temperatures over 135°C–145°C in case of the blends with 50–70% starch and over 125°C–135°C for the blend with 20% starch.

The flow behavior of the two polymers in the melted state depends on many parameters including the macromolecule shape, polydispersity, ramification, and cross-linking degree, parameters which are affected also on the chemical degradation [28]. The variation of studied melt rheological properties is a consequence of both the material fluidity and the material degradation. The increasing of MFI and FR and the decreasing of DV and the  $E_a$  can be the effect both of the increase of the melt fluidity because of extrusion conditions and of the chain cleavage during flowing in the indexer. On the contrary, the decrease of MFI and FR and the increase of DV and the  $E_a$  is determined by the decrease of melt fluidity because of the extrusion conditions or by the chains cross-linking because of degradation during extrusion at indexer. The voids content is the consequence of the appearance of volatiles as a result of both water and/or acetic acid elimination because of degradation. The blend coloring at indexer extrusion accompanies the conjugated double bonds formation because of degradation of the two. The obtained results cannot be explained without considering the degradation that occurs during melt flowing through the indexer.

The biggest ShS appears at 10 kg load, regardless of the temperature values or blend's composition because this parameter represents the ratio between force applied tangentially to the flow direction and the flowing area [34]. The higher the force acting on the melt, the elevated the appeared shear stress. Therefore the ShS depends only on the indexer load and not on the indexer temperature. In other words ShS depends on the characteristics of the used rheometer and the values of the mechanical parameters under which the flowing is occurring. The ShR represents the ratio between the rates with which the melt flows into a capillary divided by the gap size through the flow occurs [34]. The melt will flow with different rate depending both on the blend's composition and the extrusion conditions (temperature and load). Therefore the ShR has high values if the indexer's load is 10 kg, the temperature is greater than 145°C, and the blend contains at least 50% starch, which has greater fluidity comparatively with PVOH. The ShR depends also on the melt degradability because the flowing rate of small chains resulting after chemical degradation is greater than the flowing rate through the same capillary and the same conditions of big cross-linked macromolecules. The sensibility of the used rheometers plays a major role in revealing of these aspects.

The MFI is an expression of *material fluidity*. The temperature at which, at high loads, the *fluidity* begins to decrease is around 145°C–155°C for the blends with 70%–50% starch and 135°C for those with 20% starch. These results can be explained only accepting that, for some compositions and

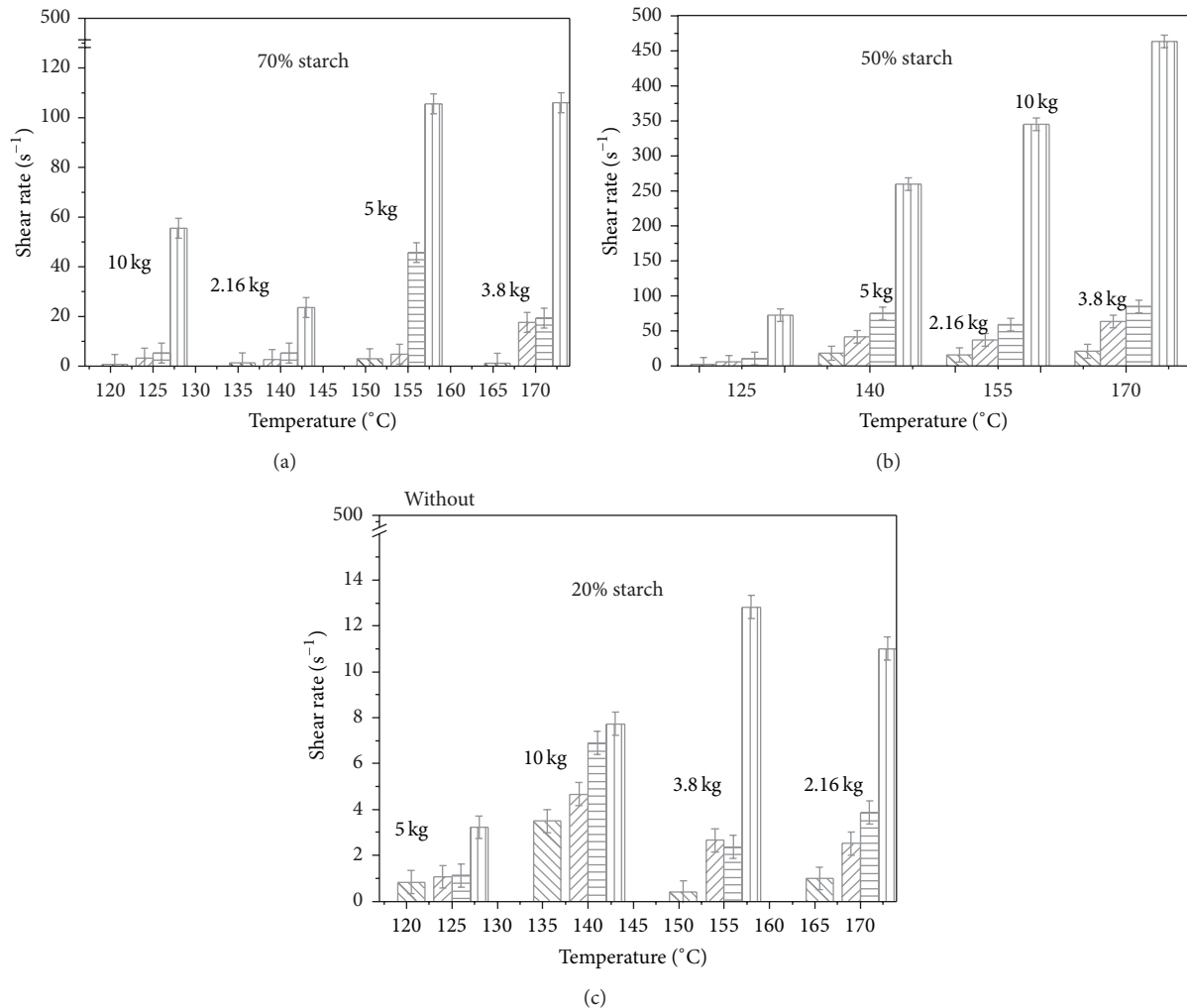


FIGURE 3: Shear rates versus blend composition and indexer's measurement conditions.

extrusion conditions, a cross-linking takes place and this process does not occur if the starch content is 70% and the load is small (2.16 kg, 3.8 kg). At small loads, the fluidity begins to decrease at 155  $^{\circ}C$  for the blends with high content of starch (minimum 50%) and at 135  $^{\circ}C$  for those with less content of starch (maximum 50%, i.e., 20%).

This dependency indicates that, besides the blend's fluidizing due to the extrusion conditions, during flowing in capillary occurs a parallel chemical process of degradation, dependent also on the extrusion parameters. Knowing that strong MFI growth illustrates the polymer degradation by chains scission [35], it seems that, in the temperature range in which the MFI increasing is 700%–1300% or greater, an intense degradation by chains scissions takes place, especially due to amylopectin content of the blends with high percentage of starch (73%–81%). The MFI decrease, after a temperature range in which it has continuously grown, is the evidence for the chain cross-linking which is responsible for the fluidity decreasing. This process occurs at larger scale in case of extrusion at high load, on the entire studied temperature range. The obtained results show that at 5 kg

or 10 kg load and temperatures between 130  $^{\circ}C$  and 135  $^{\circ}C$  the blends with higher than or equal to 50% starch endure a chain scission process and at increased temperatures of 145  $^{\circ}C$ –170  $^{\circ}C$  a cross-linking one. It appears that, in the indexer extrusion conditions, the blends with starch as major component are much more susceptible to chains scissions ( $T = 135^{\circ}C$ –145  $^{\circ}C$ , 5 kg–10 kg), while those with PVOH greater than or equal to 50% degrade much easier by chain cross-linking, even at low temperature (135  $^{\circ}C$ ) and moderate loads (3.8 kg, 5 kg). The lower temperature at which the blend with 20% starch begins to degrade shows probably that PVOH is more thermal sensitive than starch.

In a simple expression, the melt viscosity is the reverse of its fluidity and represents internal friction which resulted in a melt when one layer of fluid is caused to move in relationship to another, which is similar to melt's resistance to flow [34]. So, the blend with high starch content (70% starch) has the same melt strength to flow if the temperature is kept between 125  $^{\circ}C$  and 135  $^{\circ}C$  because in this temperature range the DV remains almost unchanged and has greater values as the plastometer's load is smaller. The melt resistance

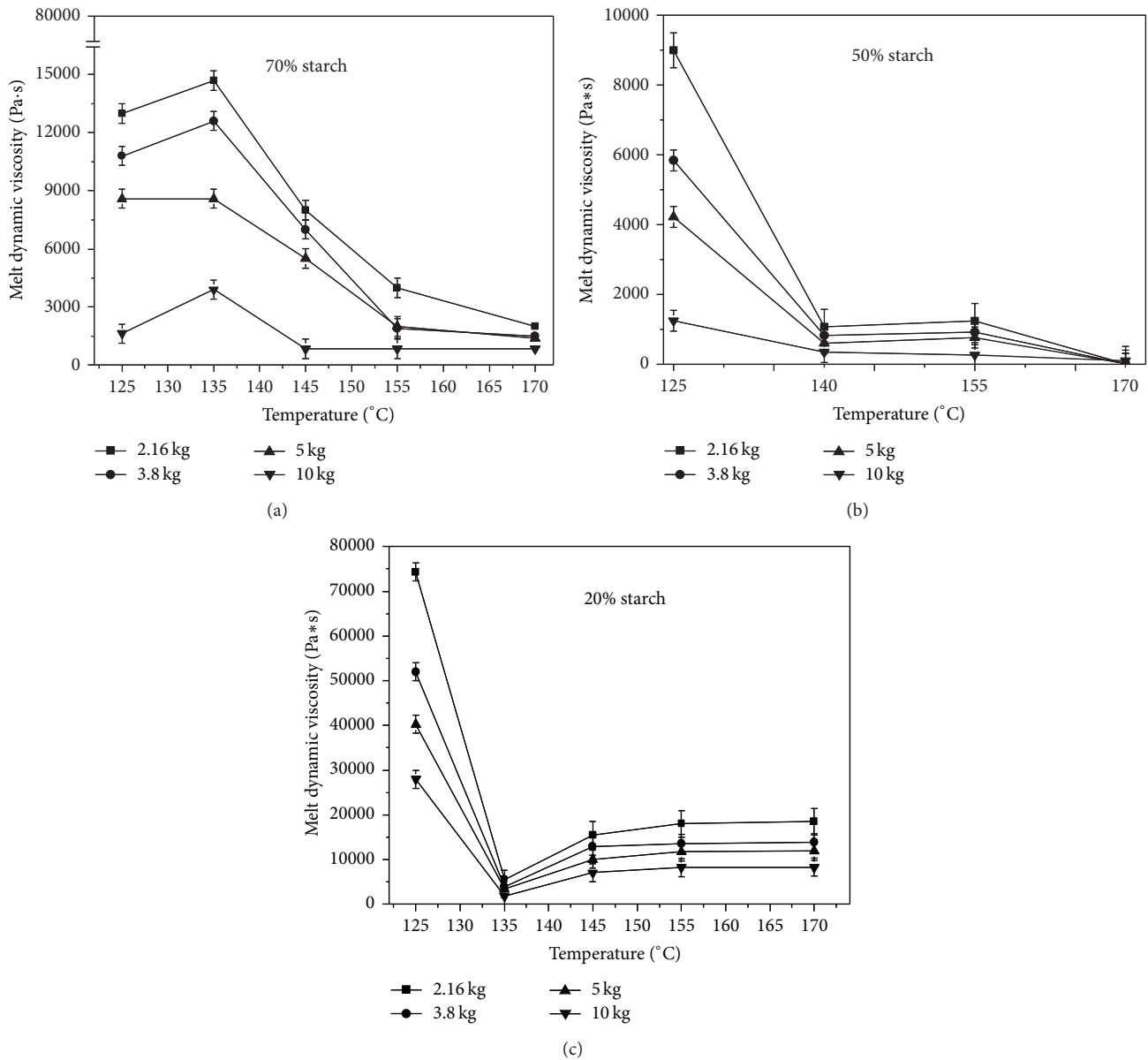


FIGURE 4: Dynamic viscosity versus temperature, load, and composition for the blends with (a) 70%, (b) 50%, (c), and 20% starch (line only for eliminating the confusions regarding the symbols' affiliation to a certain dependence).

to flow begins to decrease very much if the temperature increases from 135°C to 170°C, especially at 2.16 kg and 3.8 kg load. These results cannot be explained if the melt degradation is not considered. According to the DV values, in these conditions, both the material fluidization and the macromolecular chains scission take place. The breaking of the macromolecules can explain the smaller melt strength to flow because smaller chains can be moved easier and faster. The small increasing of the melt strength to flow between 145°C and 170°C and high loads (5 kg, 10 kg) can indicate the degradation by cross-linking, process which can increase the molecular weight of the melted macromolecules. The melted cross-linked macromolecules move heavier and need more

energy to flow because their resistance to flow is greater as compared with linear chains.

If the blend contains 50% starch, regardless of the load's value, the melt resistance to flow decreases with high rate up to 140°C and, after a plateau zone between 140°C and 170°C in which it has constant values, the decrease continues with very low rate, till 170°C. Regardless of the load, the melt strength to flow of the blend with 20% starch decreases strongly up to 60–80% till 135°C, and, then, between 135°C and 170°C, it grows by 5–10%. This behavior can be explained considering the same two parallel processes. Up to 135°C the increasing of the material's fluidity is probably due to both the increasing of melt fluidity and a parallel process

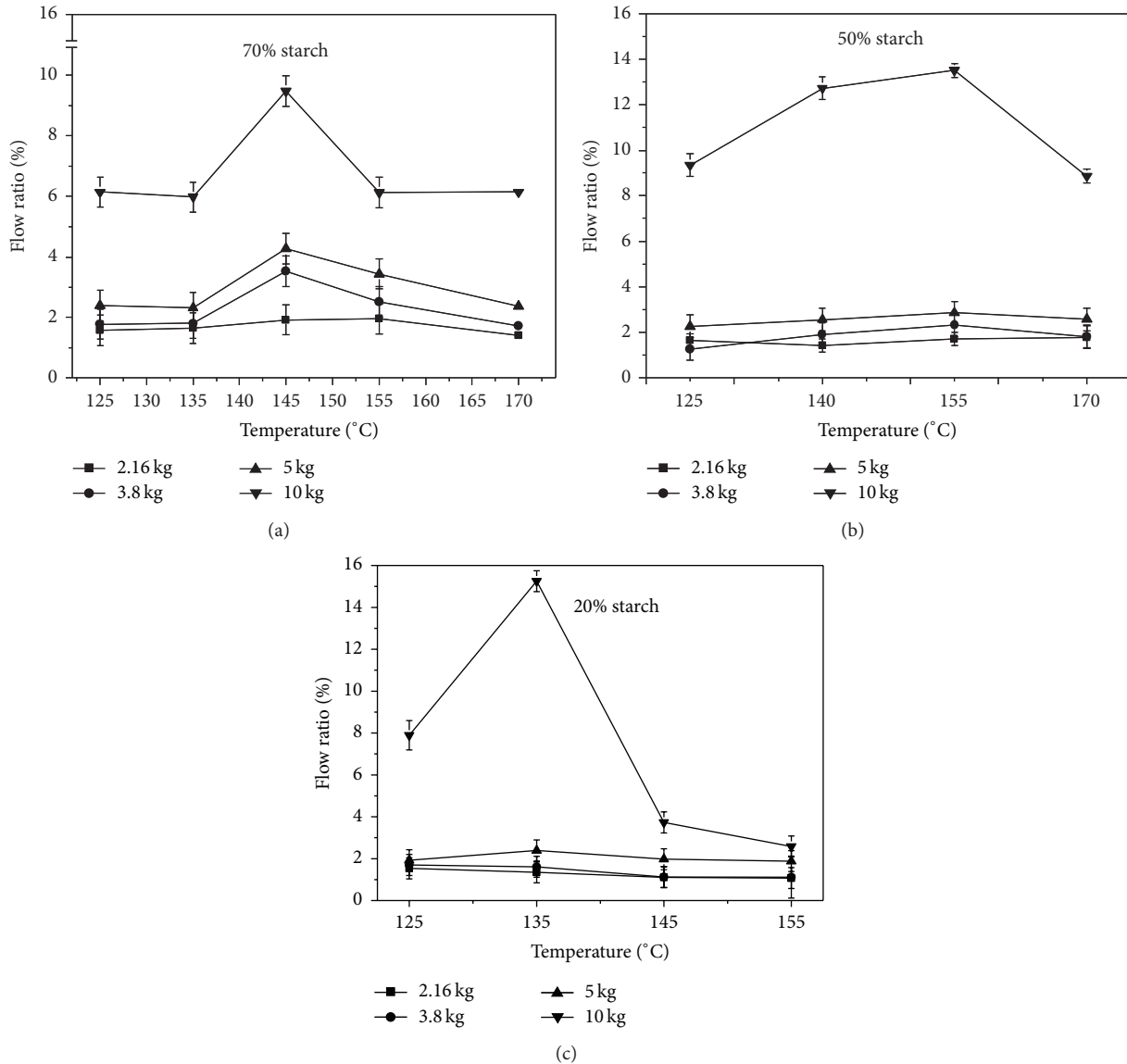


FIGURE 5: Flow ratio versus temperature, load, and composition for the blends with (a) 70%, (b) 50%, and (c) 20% starch (line only for eliminating the confusions regarding the symbols' affiliation to a certain dependence).

of strong degradation through chain scission. After 135°C the decreasing of the materials fluidity is generated by the macromolecules cross-linking. An increased PVOH content raises the melt strength to flow, probably because the chains cross-linking is more pronounced for the blend with higher PVOH content. The cross-linking is almost unnoticed if the blend's starch content is greater than 50%, when the melt strength to flow decreases 3–5 times, probably because of the diminishing of macromolecular weight as consequence of the intensity of the chains scission reactions. The information obtained considering the dependence of the melt resistance to flow with the blend's composition and the extrusion conditions is the same as that which has been proved by MFI. It seems that the DV reveals much better than MFI both processes of fluidization and degradation which take place at the extrusion in indexer of these blends.

The FR characterizes the melt sensitivity to the changing of flow conditions [30]. The increasing of the flow ratios with the load can be explained in that the melt amount which flows through a device is greater if the load acting on indexer is higher, because the ability of the macromolecules to be compacted is greater as the load is higher. These results cannot be explained also if the melt degradation is not considered. The increasing of the FR through a device in a certain time with growing temperature is a consequence of greater melt fluidity and/or because of smaller macromolecular weight consequence of degradation by chains scission. The decreasing of the flow ratio with the increasing of starch content is probably due to structural differences between the branched chains of amylopectin, the major component of the used starch, and the linear macromolecules of PVOH and amylose, the other two polymers from the blend.

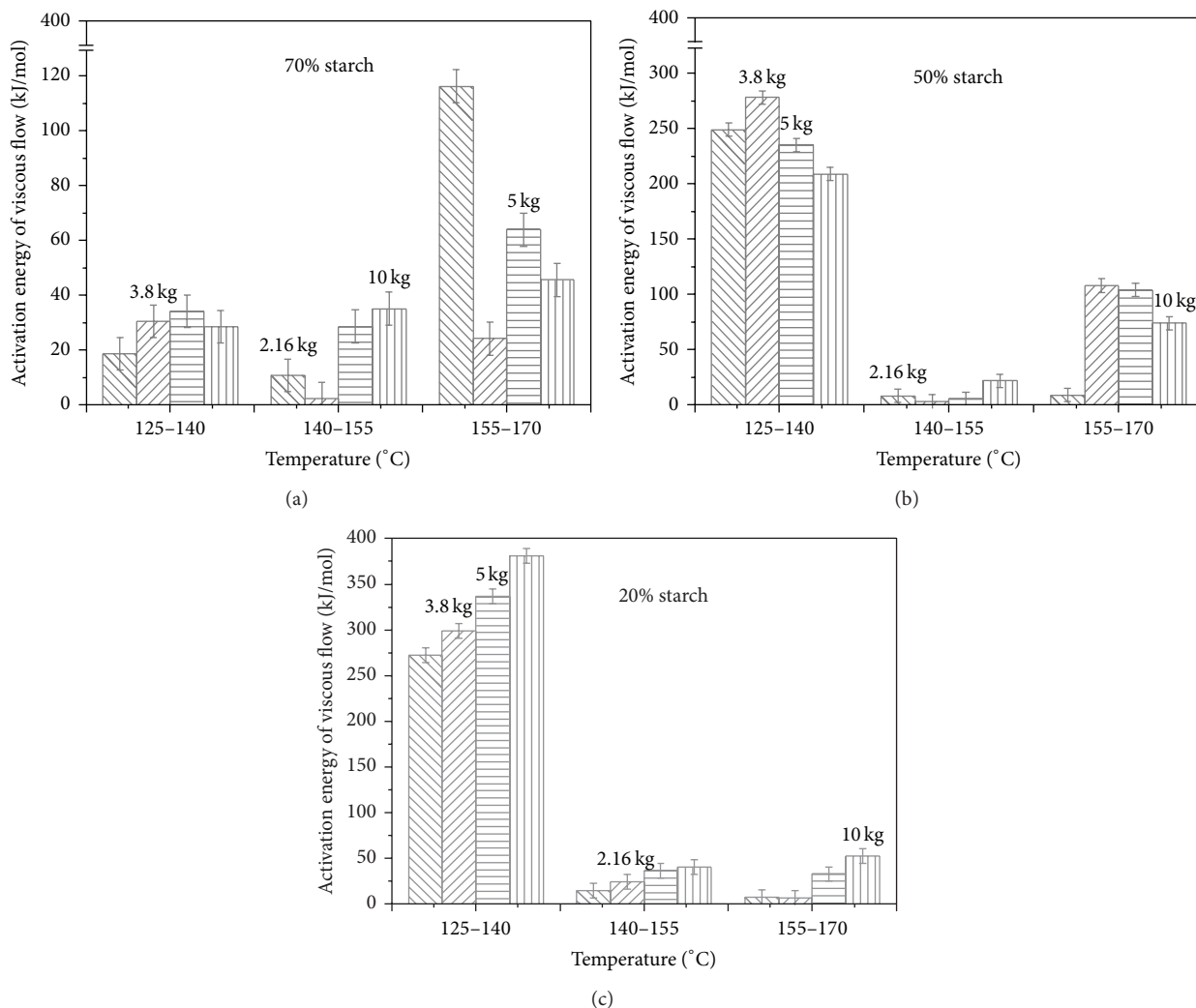


FIGURE 6: The activation energy for viscous flow versus blends' composition and indexer working conditions for blends with (a) 70%, (b) 50%, and (c) 20% starch.

In the same device and in the same flow conditions, a linear polymer flows more easily than a branched one. The flow ratio is also diminished in case of cross-linked macromolecules. The FR varies in the same way as MFI and DV and shows that near the change of the melt fluidity dependent on the extrusion conditions, a degradation through chain scission and/or cross-linking of macromolecules also happens.

The dependency of  $E_a$  on the melt flow conditions and blend's composition reveals that, regardless of the load value, the required energy to flow is higher if the temperature is smaller (between 125°C and 135°C) and the starch content of the blend is low. The higher energy to flow required by the melted blends with equal to or less than 50% starch can be a sign that, at small temperatures, the PVOH chains do not have enough flexibility to flow easily. These blends require smaller energy to flow when the temperature is ranged within 135°C–145°C and need higher energy to flow at increased temperature between 145°C and 170°C, probably because of the chain cross-linking. These results prove that

the processability of the two polymers vary significantly and that is why, depending on the composition, each blend requires special attention to find the own window of melt processing conditions. These results show also that in the used extrusion conditions the degradation is not a very large process because  $E_a$  do not have significant variation for those situation in which this process happens.

The colored extrudates had cross-linking degree of 0.2–0.6% and contained many voids, probably consequence of the formation of double bonds and volatiles as a result of degradation [17, 22, 25]. The extrudate's color and the voids content sustain the idea that the degradation of the studied blends means scission and cross-linking of macromolecules but also double bonds formation and volatiles elimination.

All the above presented results prove that, at extrusion of the studied blends, even the ShS is small ( $55 \text{ s}^{-1}$ – $450 \text{ s}^{-1}$ ); two processes are occurring, one of blends fluidization and another simultaneous one of degradation by cleavage or/and cross-linking of the macromolecules. The two processes



depend both on the extrusion conditions and on the blend's composition. These results are new evidences that the blends based on starch and PVOH are process sensitive materials. These results also prove that the blends with PVOH as major component seem to be more temperature sensitive and degrade mainly through chain cross-linking and those with starch as major component appear to be more mechanically sensitive and degrade predominantly by chains scissions. The extrusion conditions in which the degradation is avoided and the resulting extrudates are colorless depend on the blends composition, each blend requiring individual analysis to find the best formulation and the own window of melt processing conditions. The value of the ShR smaller than  $55 \text{ s}^{-1}$  [44] for the blend with 20% starch shows that this blend can be melt processed considering only the extrusion procedure. The blend with more than 50% starch can be extruded and/or injected because the shear rate reaches almost  $450 \text{ s}^{-1}$  [44].

The qualitative rheological testing on melted starch based renewable materials, according to the MFI method, leads to credible information about their degradability and moldability because, based on these results, it was possible to achieve new, undegraded renewable starch based materials [12–14, 45, 46] including nanocomposites [12–14] and foams [45]. These results are a good proof that the MFI method is a good path in studying both the degradability and moldability of new polymeric blends based on starch.

#### 4. Conclusions

- (1) The study of melt rheological behavior of some new renewable materials based on starch and polyvinyl alcohol (PVOH) correlated with other material properties as color, cross-linking degree, or voids content provides useful information on their degradability and processability
- (2) The obtained results show that, at the same level of additivition, under identical extrusion conditions, the melted blends with corn starch as main component are more mechanically sensitive and degrade mostly by chains scission and those with PVOH as major component are temperature sensitive and degrade generally by cross-linking. The conditions in which the degradation is avoided and the melt processing is possible depend on each blend composition and the conditions in which the extrusion was done. Each PVOH-starch blend requires particular formulation and individual melt processing conditions.
- (3) The obtained results were used in achieving of new, undegraded, colorless, renewable starch based materials like nanocomposites, foams, and so forth.
- (4) These results are a good proof that the estimation of the degradation considering the melt rheological properties measured using the MFI method is a good path for studying the degradability and moldability of polymeric blends based on starch.

#### Conflict of Interests

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

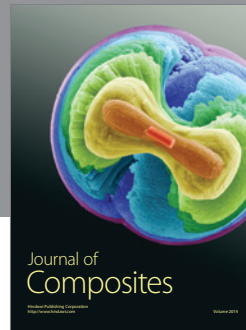
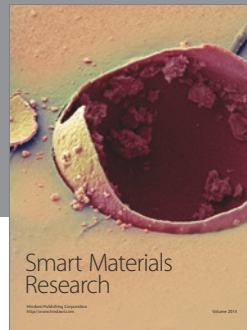
#### Acknowledgments

These researches were supported by UEFISCDI Romania from Grant no. 59/2012. The authors thank colleagues who have made the rheological measurements.

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