# Recycling of a Starch-Based Biodegradable Polymer

*F.P. La Mantia, R. Scaffaro, C. Bastioli*†

Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo Italy
Tel: + 39 0916567203, Fax: + 39 0916567280, email: lamantia@dicpm.unipa.it

†Novamont, Via Fauser 8, 28100 Novara
Tel: + 39 0321699.602, Fax: + 39 09321699602, email: Bastioli@materbi.it

**Summary:** A new starch-based polymeric system, ZI1OU from Novamont, mainly composed of starch and polycaprolactone, was reprocessed several times in an extruder to investigate the recyclability of this biodegradable polymer. A previous investigation of the thermomechanical degradation in a mixer has been also done. The degradation is mostly due to the thermal stress but the presence of the mechanical stress strongly increases the degradation kinetic. During melt processing two concurrent processes take place: the first is the degradation, i.e. the breaking and shortening of polymeric chains, mostly occurring in the PCL phase; the second is the formation of some crosslinked structure in the starch phase. The rheological and mechanical properties, measured on samples subjected to repetitive extrusion operations carried out in a single screw extruder, clearly indicate that, in the adopted processing conditions, no significant modifications are observed. Only after five extrusions some decrease of these properties was measured.

## Introduction

Synthetic polymers are used in many technological applications and their use is continuously growing. Unfortunately, among many great advantages , there are also some properties, like the low density and the high ageing resistance, that can give a serious environmental impact. This is the reason why in the last years a “plastic waste science” has grown up to try to minimise the negative effects of the presence of plastic materials in the environment at the end of their life cycle. Nowadays two main paths, trying to solve this problem, can be individuated. The first is recycling, that is either recovery of the material for a further “re-use” (primary and secondary recycling), monomers or feedstock recovery (tertiary recycling) or energy recovery (quaternary) [1-5]. The second possibility - complementary, not alternative at all - is the use of biodegradable plastics; these are polymer systems that can be by bacteria which are able to oxidize them to transform the materials into carbon dioxide, water and biomass [6-7].

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For these peculiar characteristics, to enhance the economic of these materials and to further reduce the environmental impact, the mechanical recycling of these biodegradable polymers is particularly convenient, but only if the recycled materials show properties that are not poor. A previous work present in literature[8] deals with the recycling of blends of polyethylene and starch i.e. a partial biodegradable material.

The aim of this work is to study the properties of a commercial starch based biodegradable polymer after multiple processing steps in an extruder, simulating recycling and processing operations. In particular, a completely biodegradable material will be used.

## Experimental Part

The biodegradable polymer used for this work is an injection moulding grade of MaterBi series Z (ZIO1U) manufactured and kindly supplied by Novamont. It is constituted for about 50% of corn starch and for the remaining of polycaprolactone, a synthetic, biodegradable aliphatic polyester. The polycaprolactone (PCL) is a high molecular weight polymer commercially known as PCL 878 manufactured by Union Carbide and has been characterized for comparison. Like other similar systems [9], this material is characterized by an interpenetrated structure where low molecular weight organic compounds break the H-bonding avoiding the formation of a cross-linked material. This sample is completely biodegraded in 45 days following ASTM 5338.

Before processing, the material has been dried in order to avoid hydrolytic scission. The processing apparatus is a single screw extruder (Brabender) with a thermal profile of 100-130-170-170 °C and a rotational speed of 100 rpm. Under these conditions the estimated residence time is about 90 sec. Degradation tests were done in a batch mixer (Brabender Plasticorder) under different processing conditions. This temperature has been chosen as it is only slightly higher than the typical processing temperatures that are in the range 130 °C – 150 °C.

The rheological measurements were carried out using a CEAST, (Italy), constant rate capillary viscometer, mod. Rheoscope 1000. All of the tests were performed at 170 °C with a capillary having 1 mm diameter and length-to-diameter ratio (L/D) equal to 40. The Bagley's correction was not applied because of the large length-to-diameter ratio, while the Rabinowitsch correction was applied throughout.

The tensile properties were evaluated with an Instron equipment mod. 1122 on specimens (thickness about 0.50 mm, width 10 mm) cut out from compression moulded sheets, prepared by using a Carver laboratory press at 170 °C.

The morphology was studied by scanning electron microscopy (SEM) using a Philips mod. 501 apparatus. The samples were fractured in liquid nitrogen and coated with gold using an SPI sputter coater. Calorimetric tests were performed using DSC7, Perkin Elmer.

Solubility tests and intrinsic viscosity measurements have been carried out by using chloroform (for the solubilization of PCL) and dimethyl solfoxide (for the solubilization of starch) at the temperature of 30 °C. The separation has been carried out in two steps, firstly solubilizing the PCL, and then solubilizing the residual precipitate constituted by starch.

## Discussion of the Results

Before analysing the behaviour of the material after recycling operations it is useful to study its thermomechanical degradation as a function of the most important processing parameters. The three parameters that, together with structure and chemical nature of the polymer, influence the degradation of the materials during the processing operations are temperature, mechanical stresses and residence time inside the apparatus.

In Fig. 1 the flow curves of samples processed in the closed mixer under different processing conditions are reported.

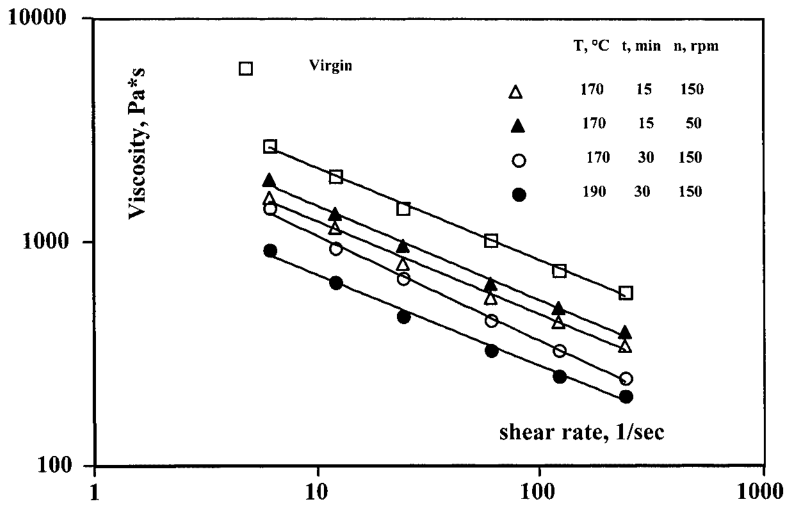

Fig. 1: Flow curves of samples processed in the mixer in different processing conditions.

As expected, the viscosity of the material decreases with increasing time, temperature and also by increasing the rotational speed which increase the mechanical stress applied to the melt.

The above data clearly indicate that some degradation occurs during these severe processing operations. However, it is not possible to discriminate if the degradation occurs because of a decrease in the molecular weight or if the decrease of the viscosity is also due to some change in the morphology, for example due to some reduction in the compatibility, as occurred, because of degradation, in other blends [10]. This last hypothesis, however, is not confirmed for this interpenetrated system, by the SEM observations. Indeed , the morphology does not change as a consequence of the melt processing undergone in these conditions. A reduction in ~~of~~ the molecular weight, as a result of the thermomechanical stress, is then responsible for the decrease of the viscosity. This last observation, together with the fact that most part of the degradation occurs at low processing times, suggests that this is a thermomechanical degradation. The degradation rate is, indeed, decreasing with time and with decreasing the molecular weight. It is worth to remark that the mechanical degradation increases with stress and then with the viscosity of the melt. However, it is not possible to discriminate which of the two components of this multicomponent system is more prone to degrade

The dimensionless viscosity (at 170 °C and at a shear rate of 12 $s^{-1}$) relative to samples of ZIO1U and of pure polycaprolactone processed in different conditions are reported in Table1. The dimensionless viscosity is obtained by dividing the value of the processed sample by that of the same virgin material.

Table 1. Dimensionless viscosity of PCL and ZIO1U processed in different conditions.

| Processing conditions | PCL | ZI1OU |
|---|---|---|
| T = 170 °C, n = 50 rpm, t = 15 min | 0.80 | 0.65 |
| T = 170 °C, n = 150 rpm, t = 15 min | 0.70 | 0.51 |

The degradation level of the multicomponent system seems higher than that of the pure synthetic component. This means that the starch degrades faster or that the degradation of PCL is accelerated by the presence or by the degradation products of the starch, as observed in other multicomponent systems [11]. The decrease of the molecular weight of the PCL is confirmed by the intrinsic viscosity measurements reported in Table 2.

Table 2. Intrinsic viscosity of PCL and starch in virgin and recycled ZIO1U.

| Sample | $\eta_{in}$ PCL, dl/g | $\eta_{in}$ starch, dl/g | Remarks |
|---|---|---|---|
| ZIO1U virgin | 0.761 | 1.110 | |
| ZIO1U (150 rpm, 5 min) | 0.731 | 1.236 | partially insoluble |
| ZIO1U (150 rpm, 30 min) | 0.721 | 1.165 | partially insoluble |

On the contrary, the intrinsic viscosity of the amorphous starch phase, reported in the same table, increases and some insoluble material is also observed.

In Fig. 2 the viscosity of recycled samples up to five extrusions has been reported. It is worth noting that for the first three passages in the extruder no significant variation of the viscosity can be detected and only after the fourth passage there is a certain reduction in the viscosity especially at low shear rates, suggesting that for low processing times this materials can be reprocessed several times.

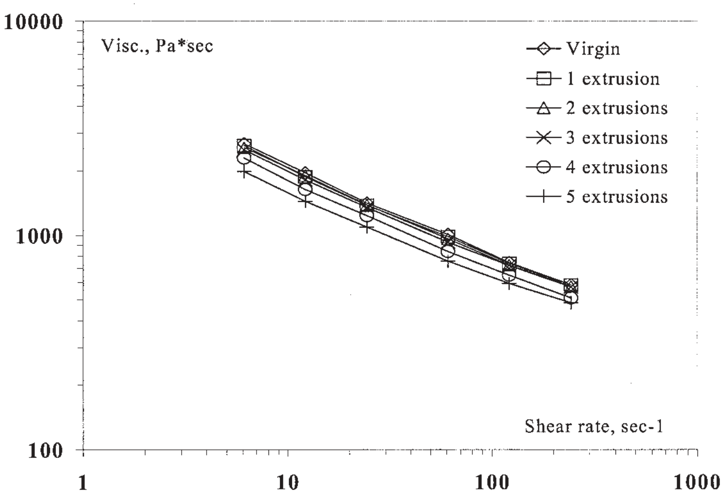

Fig. 2: Viscosity of MaterBi processed several times.

This behaviour is quite different from the one observed during the degradation tests where a remarkable degradation level was reached. In that case the tests were carried out in particularly severe conditions especially for the processing times that were no less than 15 minutes. Actually, in the extruder the average residence time is about one minute and the results indicate that during this time no important degradation effects occur. In the extrusion conditions, even after five passages the viscosity is quite similar to the one of the virgin materials. The rheological results are confirmed by the mechanical tests. In Fig. 3 the tensile stress, the elongation at break and the impact strength are reported for the virgin and for the recycled materials. Both tensile stress and elongation at break are not substantially worsened with respect to the virgin material and only a small reduction of the impact strength can be observed. However, the only property that seems to be slightly affected by the re-processing step is the tensile modulus. The viscosity at 12 $s^{-1}$, the elastic modulus and the heat of fusion ($H_f$) of the PCL phase for a specimen of virgin polymer and of the same material after 3 and 5 passages in the extruder are reported in Table 3. The heat of fusion was obtained by the analysis of the calorimetric curves which are not reported here.

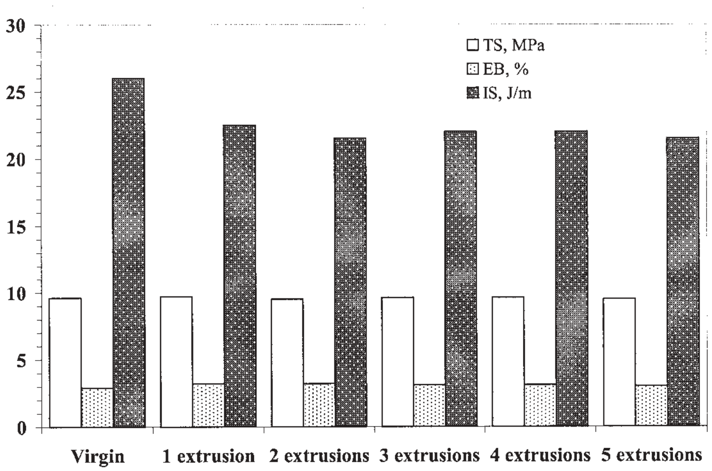

Fig. 3: Tensile stress, elongation at break and impact strength of virgin and recycled material.

As previously said, the viscosity shows relevant changes only after five reprocessing steps but on the contrary, the modulus is increasing. This behaviour was already observed in some semicrystalline polymers [12-14] and not in amorphous polymers[14]. It can be attributed to the increase of crystallinity due to the reduction of molecular weight of PCL, as demonstrated by the decreasing of the viscosity and confirmed by the increasing of the heat of fusion of the PCL semicrystalline phase .

Table 3. Viscosity and mechanical properties of virgin and recycled ZIO1U.

| Sample | Viscosity, Pa*s | Modulus, MPa | $H_f$, J/g |
|---|---|---|---|
| ZIO1U virgin | 1950 | 570 | 53 |
| ZIO1U (3 passages) | 1895 | 611 | 54.1 |
| ZIO1U (5 passages) | 1415 | 680 | 55.9 |

Considering the previous results, the decrease in the viscosity is mostly due to the reduction of molecular weight of the PCL, while the rise of the modulus to both the presence of small amount of crosslinked molecules in the starch phase and to the rise of crystallinity in the PCL phase.

It can be concluded that during melt processing two concurrent processes take place: the first is the degradation i.e. the breaking and shortening of polymeric chains, mostly occurring in the PCL phase; the second is the formation of some crosslinked structure in the starch phase. The first phenomenon is responsible for the decrease of viscosity and for ~~of~~ the slight increase of crystallinity, while the second is the responsible for ~~of~~ the increase of the modulus, property highly sensitive even to small changes in the polymeric structure.

The above data clearly demonstrate that, for this starch based biodegradable polymer, the conditions of temperature, mechanical stresses and residence time typical of extrusion operations allow to obtain reprocessed materials with properties similar to those of the virgin material. Such behaviour in not typical for all the recycled polymers that, due to the very high degradation rate, cannot often be re-used in the same processing apparatus and show very poor mechanical properties. It must be added that this class of polymer (MaterBi Serie Z) contains some plasticizers but the variation of the properties cannot be reasonably attributed to any change of structure of the molecules either to any interaction with the macromolecules because these compounds are chemically inert, thermally stable and lowly volatile at the processing temperatures used in this work.

## Conclusions

The starch based biodegradable polymer ZIO1U is relatively stable to thermal degradation and to the applied mechanical stress that can accelerate the degradation kinetic. The degradation is mostly connected with chain breaking of the synthetic component molecules and with the prevalent crosslinking of the starch phase. Nevertheless, the typical reprocessing conditions does not influence in a relevant way both rheological and mechanical properties. The material can be then reprocessed in the same apparatus used for the virgin polymers and for the same applications.

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