Macromol. Symp. ***147****, 167–172 (1999)*

MECHANICAL PROPERTIES OF RECYCLED POLYMERS

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SUMMARY: Modifications of structure and morphology of the polymers induced by the thermomechanical stress (or by the presence of water for some polymers) during reprocessing can cause a drastic deterioration of mechanical properties of the recycled material. The property – reprocessing relationships are an important tool to determine not only the properties of the recycled polymers but also the strategies to use (processing conditions, stabilizers, fillers, compatibilizers, etc) in order to obtain recycled polymers with good mechanical properties. In this work, typical behaviour of some mechanical properties as a function of the number of reprocessing operations is discussed and correlated with their structure and morphology. The influences of the type of apparatus and of the processing conditions are also considered.

INTRODUCTION

Polymers undergo, during recycling operations, changes of the structure and, in some cases, of morphology (Ref. 1). Changes of structure mean a decrease in the chain length as well as formation of chain branching and functional groups while crystallinity can vary depending on the changes in molecular weight. Thermomechanical stress, the presence of oxygen and, for condensation polymers, the presence of water or of other small molecules is responsible for these modifications. Changes of both structure and morphology induce drastic variations of some properties and, in particular, of rheological and mechanical properties, outdoor resistance and thermal stability. Clearly, the level of degradation and then deterioration of the properties depends on the amount of "stress" and on the number of reprocessing operations. The knowledge of variations of properties with the number of reprocessing steps and with the stress level is, therefore, an important tool in the use of these secondary materials.

In this work, typical behaviour of some mechanical properties as a function of the number of reprocessing operations will be discussed for some important polymers and correlated with their structure and morphology, with the type of apparatus and with the processing conditions (thermomechanical stress level). Finally, the influence of stabilizers is also considered.

PROPERTY – REPROCESSING RELATIONSHIPS

The behaviour of properties of the recycled polymers as a function of the number of reprocessing operations depends on:

CCC 1022-1360/99/$ 17.50+.50/0

- chemical nature of the polymers
- level of the thermomechanical stress
- presence of water or of other substances.

Chemical nature of the polymers

The chemical nature and structure of polymers influence both the degradation kinetics and interactions with other substances. In Figs. 1 and 2, the values of the elastic modulus (E) and of the elongation-at-break (EB) are reported as a function of the number of extrusions for a sample of polypropylene (Ref. 2) and for a sample of high-density polyethylene (Ref. 3). The values have been obtained by dividing the values after each reprocessing step by that of the virgin material.

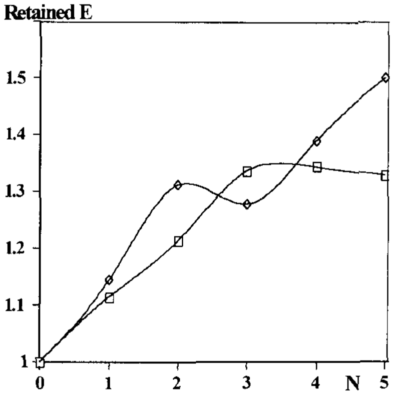

Fig. 1 Dimensionless modulus of PP (□) and HDPE (◇) samples as a function of the number of extrusions

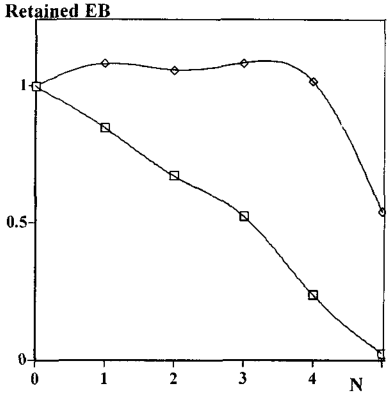

Fig. 2 Dimensionless elongation-at-break of PP (□) and HDPE (◇) samples as a function of the number of extrusions

Two opposite behaviours are observed: the modulus increases with the number of reprocessing steps while the elongation-at-break drastically decreases. The first point has been correlated with an increase in the degree of crystallinity due to a decrease in molecular weight while a reduction in EB is mainly due to a decrease in molecular weight and the concurrent increase in the crystallinity.

The changes in crystallinity and molecular weight of the PP sample are reported in Fig. 3 (Ref. 2). The crystallinity rises while the molecular weight decreases with the number of processing steps. Significant differences are also observed in the behaviour of the two polymers; in particular, the elongation-at-break of PP decreases faster than that of HDPE. This result is confirmed by a larger decrease in the viscosity and then in molecular weight (Refs. 2,3). The reprocessing steps have been carried out in the same apparatus (twin-screw compounder) under the same processing conditions and then with about the same thermomechanical stress applied to the molten polymers. The higher sensitivity of PP to the thermomechanical stress can be attributed to the tertiary carbon atom present in the PP chain that induces poor thermal stability.

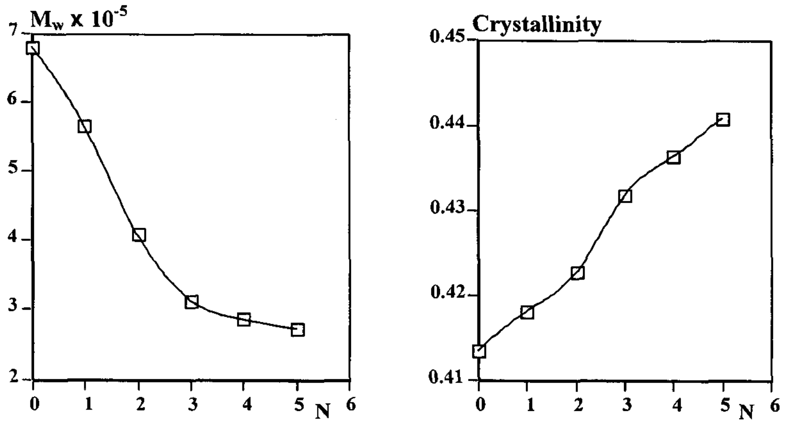

Fig. 3 Molecular weight and crystallinity of a PP sample as a function of the number of extrusions

Restabilization

The elongation-at-break of unstabilized and stabilized PP samples is reported in Fig. 4, as a function of the number of extrusion steps.

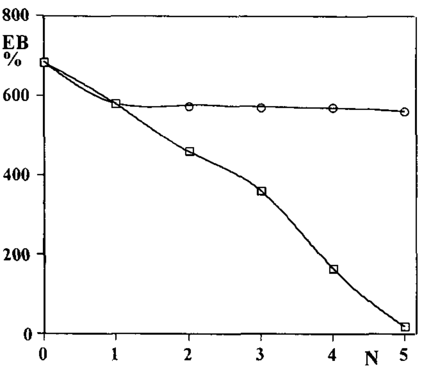

Fig. 4 Elongation-at-break vs. number of extrusions for stabilized (○) and unstabilized (□) PP

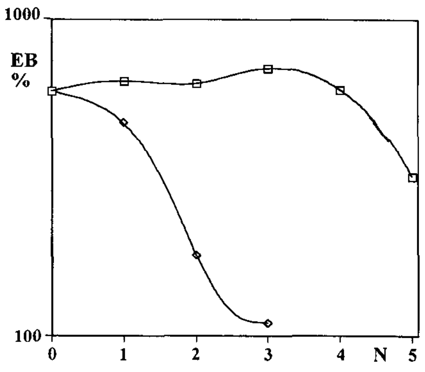

Fig. 5 Elongation-at-break as a function of the number of extrusions for a sample of HDPE reprocessed in single-screw (◇) and twin-screw extruder (□)

The stabilizer (a high-molecular-weight phosphonite) is added before each processing step. The elongation-at-break of the unstabilized sample falls down dramatically after four processing steps and the ductile polymer shows a fragile behaviour. This dramatic worsening can be drastically reduced by adding the stabilizer. The stabilizer is able to maintain the value of the elongation-at-break at a level similar to that of the virgin material. Clearly, this effect is due to the fact that the molecular weight of the polymer does not decrease when protected by the stabilizer.

It is worth mentioning that the beneficial effect occurs only if the stabilizer is added before each processing step. On the contrary, the kinetics of degradation is reduced only for the stabilized step then starting to increase like for the unstabilized sample.

Thermomechanical stress level

Temperature, residence time and mechanical stress are the most important parameters determining the degradation kinetics of molten polymers. For polymers undergoing thermal degradation, an increase in these parameters gives rise to a large amount of degradation, while lower temperatures increase the degradation kinetics for polymers sensitive to mechanical degradation. The elongation-at-break of an HDPE sample reprocessed in a single-screw extruder (SE) and in a twin-screw extruder (TE) is strongly influenced by the recycling apparatus (Fig. 5; Ref. 3).

The sample reprocessed in SE undergoes a more extensive degradation and, after two extrusions, HDPE shows a fragile behaviour while EB of the material extruded in TE is about the same as that of the virgin HDPE. The main difference between the two apparatuses is in the length of the extruder and the residence time of the melt: the residence time in SE is about twice that measured in TE. The material is subjected to a higher thermal stress and, therefore, the degradation in the first extruder is more rapid as observed from the EB data.

Presence of water or other substances

Condensation polymers undergo extensive degradation when the processing is carried out at high temperature in presence of water. Clearly, this is due to the hydrolytic chain scission of condensation polymers. The effect of the presence of water during reprocessing steps is shown in Figs. 6-8 where the values of modulus, tensile strength and elongation-at-break are reported as functions of the number of extrusions for a sample of polycarbonate (Ref. 4).

In this case, all the investigated properties show the same decreasing trend and also the elastic modulus decreases with the increasing number of reprocessing steps. Indeed, PC is an amorphous polymer and a decrease in its molecular weight has the sole effect of reducing the value of the modulus because crystallinity does not play any role. The tensile properties of PC are almost uninfluenced by the reprocessing only if done after a careful drying of the polymer;

on the contrary, some degradation, leading to reduction in mechanical properties, is observed for the sample recycled in humid conditions.

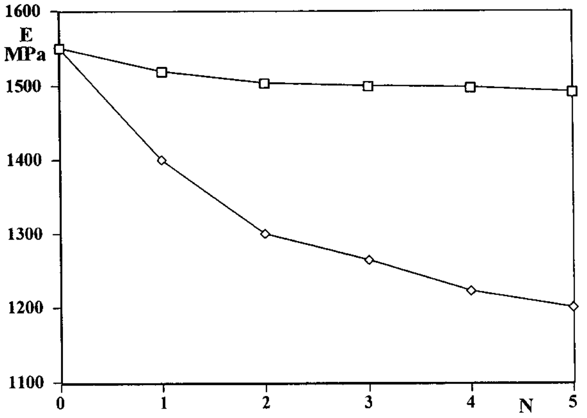

Fig. 6 Modulus as a function of the number of extrusions for an extrusion-grade PC

(□ dry, ◇ humid)

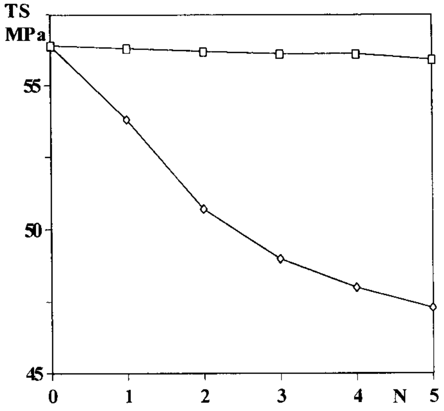

Fig. 7 Tensile strength as a function of the number of extrusions for an extrusion-grade PC (□ dry, ◇ humid)

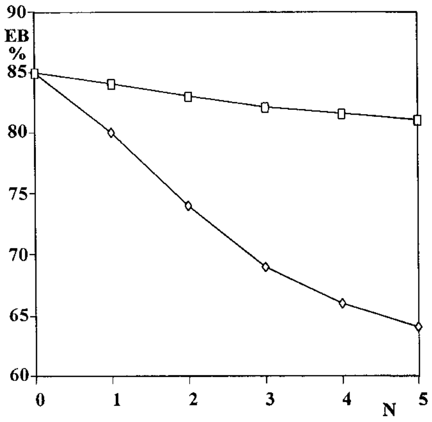

Fig. 8 Elongation-at-break as a function of the number of extrusions for an extrusion-grade PC (□ dry, ◇ humid)

Mechanical properties of heterogeneous recycled plastics

The main problem in the recycling of heterogeneous plastic waste is the incompatibility of different polymer phases. The lack of adhesion gives rise to brittle materials with very poor mechanical properties.

Elongation-at-break and impact strength of a 50/50 PET/PP blend uncompatibilized and compatibilized with a maleic-anhydride-functionalized SEBS rubber are reported in Fig. 9 as functions of the compatibilizer concentration (Ref. 5).

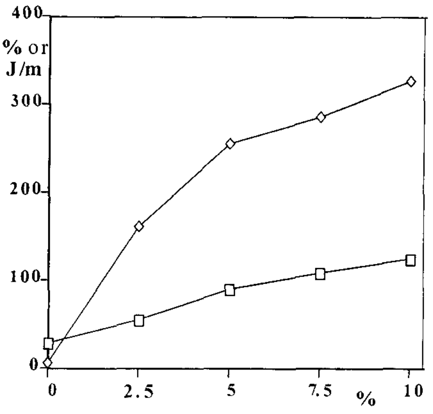

Fig. 9 Elongation-at-break (◇, %) and impact strength (□, J/m) of a PET/PP blend as functions of the content of a maleic-anhydride-functionalized rubber (%)

The tensile strength is almost constant or slightly decreasing with increasing the content of the rubber. Elongation-at-break and impact strength, on the contrary, increase in an impressive way with the increasing content of the functionalized rubber. However, it is worth noticing that the properties are enhanced mostly at low contents of the compatibilizer. The stress-strain curves of uncompatibilized and compatibilized PET/PP blends clearly highlight that the presence of the functionalized rubber induces a brittle-ductile transition making a brittle material ductile. The decrease in the tensile strength is expected because the rubber shows low values of these ultimate properties, whereas the impressive increase in elongation-at-break and impact strength can be attributed to both the high values for these characteristics of the elastomer and the compatibilization induced by the functionalized elastomer. While at high contents of the rubber, the first explanation can hold, at low concentrations, when the rate of increase in these characteristics is larger, the compatibilization has to be considered responsible for the enhanced values of these properties. It has been hypothesized that the compatibilization occurs because of polar bonds between the compatibilizing agent and the polyester.

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