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Degradation of Polyolefines During Various Recovery Processes

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SUMMARY: The purpose of the presented research was the investigation of the stability and differences of degradation of polyolefines during various recycling processes. In modeling the recycling process during melting, extrusion with a one-screw extruder was used. Recycling through selective dissolution was modulated by two different solvents (xylene and a definite mixture of *n*-alkanes). Materials used for the investigations were polypropylene (PP), low-density polyethylene (LDPE) and high-density polyethylene (HDPE) (Ziegeler-Natta technology with vanadium catalyst). Changes in the chemical structure of polymers were measured with infrared spectroscopy and differential scanning calorimetry (DSC). Flow properties were characterized by melt flow index, and mechanical characteristics by tension. Experimental results show that for PP and HDPE , utilizing all investigated recycling technologies, chain scission prevailed over branching. For the LDPE chain branching was obtained. By the same token, differences in crystallinity (and as follows, in molecular mass) between the same materials, recycled by extrusion and selective dissolution, was obtained. During selective dissolution changes of properties and morphology in dependence of the solvent used were observed with the trend being that the amount of the admixture of *n*-alkane used in this investigation was more considerable with regard to the amount of material destruction as compared to xylene. Any reduction of the mechanical properties of any of the investigated polymers as a result of the various methods used was comparable.

Introduction

The bulk (about 70%) of postconsumer plastics waste obtained through municipal waste collection are polyolefines: PP, HDPE and LDPE. Inspite of numerous investigations in the aging of polyolefines and their degradation during recovery in

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the molten state,(for example[1) - 5)]), no serious comparison of the myriad recovery methods - especially through dissolution - has been done.

Since the recovery of polymer materials is of great interest, knowledge concerning polymer destruction during various technological processes would be of the utmost importance. One of the main objectives to be targeted here is the development of our understanding of the evolution of changes in material properties and their relationship to the recovery method and/or technological parameters. It is only then that the one or the other recycling method may be deemed preferable. Most published studies deal with the effect of reprocessing on mechanical properties or oxidation intensity. Models for the prediction of the influence of recycling and aging on the mechanical properties of materials by repeated extrusions have been developed [6)].

As an alternative for the traditional recycling of commingled postconsumer plastics in melt, the method of selective dissolution in tetrahydrofuran (THF), and later in xylene, was developed[7)]. This process allows for the production from mixed plastic waste of practically pure homopolymers instead of commingled (oft multiphase) blends. At the same time, unsoluble fractions such as fillers or reinforcements can be easily eliminated through simple filtration. Ignoring at this time the enormous potential of industrial applications of these methods and their reaction with other solvents, a thorough study of the effects of material degradation has yet to be done.

Materials and methods

For these investigations, commercial-grade polymers - PP from Solvay (Eltex P HL 402), HDPE from Vestolen GmbH (Vestolen A 6042) and LDPE from BASF (Lupolen 1800 H) - were used.

Repeated extrusions were carried out on a Collin 3200 one-screw extruder with a compounding screw (20x30D) at 20 rotations per minute. Temperature settings were 170/190/200°C for LDPE (melt temperature 200°C), 210/220/230°C for HDPE (melt temperature 230°C) and 215/225/235°C for PP (melt temperature 235°C), which were parameters reflective of actual performance processes. After each extrusion, a part of the material was removed for investigation and the rest without additives or restabilization returned for repeated extrusions.

Recycling through dissolution was carried out in xylene at 125°C and a previously-defined *n*-alkane mixture at 140°C. The materials were dissoluted and kept by stirring of the solution at 1, 2, 5, 10 and 24 hours at these temperatures.

The melt flow index (MFI) was measured on Meltfixer^{LT} from Polymertechnik, Krefeld. Temperature settings were 190°C for HDPE and LDPE and 230°C for PP, and loadings were 2,16 kg for PP and LDPE, and 5 kg for HDPE.

The cristallinity degree ($X = H_c/H$, where H_c was the measured melting enthalpy and H the known melting enthalpy for a 100% crystalline polymer) was evaluated through differential scanning calorimetry (DSC) on TA-DSC-2920CE (TA Instruments) in a nitrogenous atmosphere. The scanning rate was 10°C/min and, for data analysis, results of the second heating cyclus, in order to exclude different thermal pre-histories, was used.

The tensile tests were conducted with a MTS tensile machine on standard, injection molded, specimens. The clamp travel speed was 50 mm/min. From each material 8 - 14 specimens were used for measurements.

IR spectroscopy investigations were carried out on a Nicolet IR 800 spectrometer on films of approximately 100 μm thickness.

Results and discussion

Repeated extrusions

The polymer recovery in melt is the most used recovery method. During this recycling method employing high temperatures and mechanical stresses, material degradation is to be anticipated. Depending on material, temperature and shearing stresses, thermomechanical degradation in the form of chain scission or crosslinking as well as chain branching can prevail. One of the characterization methods for molecular weight changes can be obtained with DSC by evaluation of the crystallinity degree. For the investigated PP and HDPE, the crystallinity degree after repeated extrusions increased (Fig. 1). That allows, according to Van Krevelen[8)], the

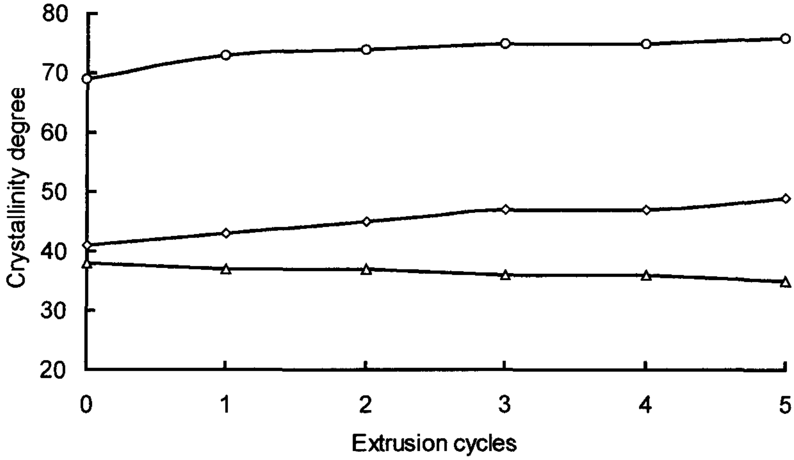

Fig. 1. Crystallinity degrees after multiple extrusions for PP -◊- , HDPE -o- and LDPE -Δ-

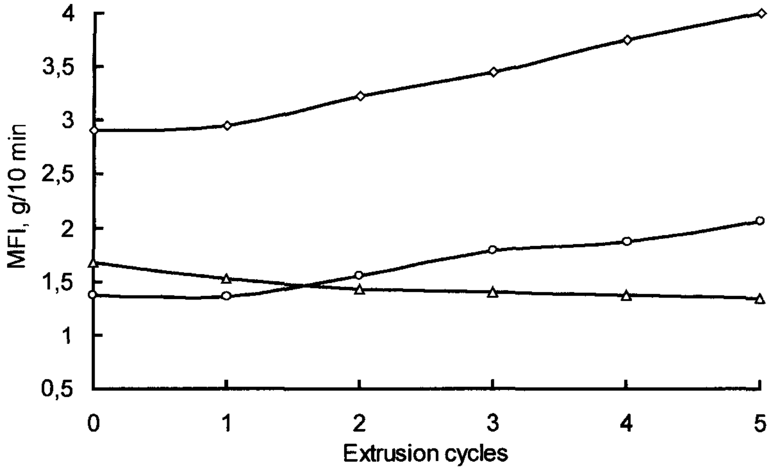

Fig. 2. MFI after multiple extrusions for PP -◊- , HDPE -o- and LDPE -Δ-

presumption that molecular mass decreases as a result of the chain scission for both materials under extrusion. Contrastingly, for LDPE the degree of crystallinity decreases. Such an effect can be obtained as well as a result of increasing molecular weight, short-chain branching (scission of long- chain branching) or crosslinking$^{9)}$. The increase in MFI with extrusion cycles for PP and HDPE (Fig. 2) confirms the results of DSC measurements of chain scission for these materials. The decreasing MFI values for LDPE allows us to conclude that, for this material, crosslinking by repeated extrusions prevails.

For all investigated materials, reductions in both stress at break and elongation at break were obtained. These results are in good agreement with similar studies undertaken previously by other researchers$^{2)-4)}$.

Dissolution in xylene

Usually, dissolving temperatures are essentially lower than those in the molten state, which should as a result decrease the degradation intensity. During polymer recovery through dissolution, instead of shear stresses, chemical/catalytical influence of the solvent itself can influence chemical degradation of the polymer. Not to be excluded is the possibility of extraction of the stabilisators in the solvent, which can further influence the performance of recovered material and oxidative stability during the lifecycle.

Fig. 3 presents the results of the DSC measurements for the investigated PP, HDPE and LDPE. Similar to repeated extrusions, the crystallinity degree for PP and HDPE increases and for LDPE decreases with the dissolution time. The differences between the values through dissolution are comparable with those after multiple extrusions. The MFI values of the dissoluted materials show the same regularities as after extrusion. The aforementioned decrease in the stress at break and elongation at break after different dissolution times was obtained. A direct comparison of the changes in the properties in form of mastercurves between dissolution and extrusion is not possible, because of the obvious impossibility of comparing mathematically thermomechanical influences through extrusion with chemocatalytical at dissolution.

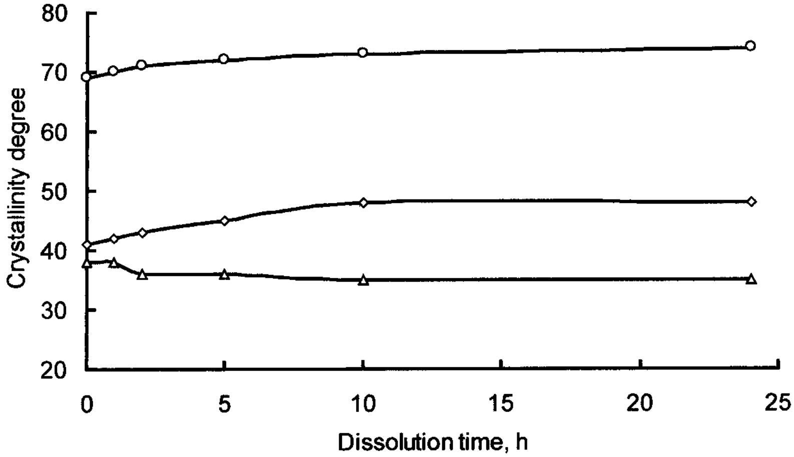

Fig. 3. Crystallinity degrees for PP -◇- , HDPE -o- and LDPE -Δ- after different dissolution times in xylene

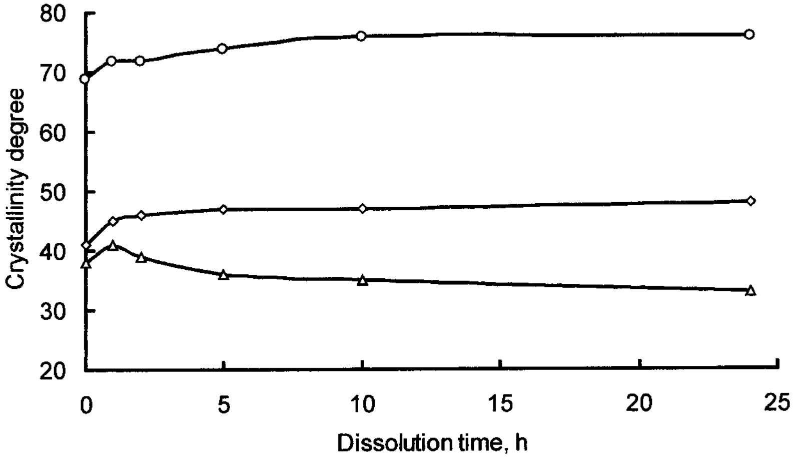

Fig. 4. Crystallinity degrees for PP -◇- , HDPE -o- and LDPE -Δ- after different dissolution times in *n*-alkane mixture

Dissolution in *n*-alkane mixture

The method of mixed postconsumer polymer waste recycled through selective dissolution in a previously-defined *n*-alkane mixture was developed at the Institute of Polymer Performance (Kunststofftechnikum), TU Berlin. In contrast to the dissolution in xylene, the full process is carried out under normal atmospheric pressure, and the solvent is less environmentally dangerous as THF or xylene.

Fig. 4 shows the changes in the degree of crystallinity of the investigated polymers after different dissolution times in the *n*-alkane mixture. These changes adhere to similar „rule"s as those obtained by extrusion or dissolution in xylene. The main difference is observed is at short dissolution times, where the differences are more pronounced. Similar jumps between the values of MFI (Fig. 5) of non- recycled material and those for 1 h dissolution were obtained. At the first moment it would appear to be the result of intensive material degradation. However, the prevailing mechanical properties do not confirm this thesis. Nether stress at break nor elongation at break show the jumps in property changes. Also, subsequent tests of the solvent evince no grounds for the suspicion of degradation. After the solid polymer upon cooling is sedimented and filtrated, the soluble material fractions in the solvent were found. The content of these soluble residues were about 5% of the initial polymer mass. The analysis of these substances show (Fig.6) that low-molecular fractions of the polymer and performance additives (waxes) were extracted. With that, the jumps in crystallinity degree and MFI may be be explained.

The IR spectroscopy measurements for all three investigated recovery techniques do not confirm the assumption concerning the oxidation of the materials. The investigations show only insignificant increases of carbonyl index (CI). At the same time, differences between CI changes in dependence of material and recovery method were obtained. A more detailed result of this study will be published later10).

Conclusions and ongoings

The results of the presented study show, independent of the recycling method, the same regularities with regard to the property changes. The values of these changes

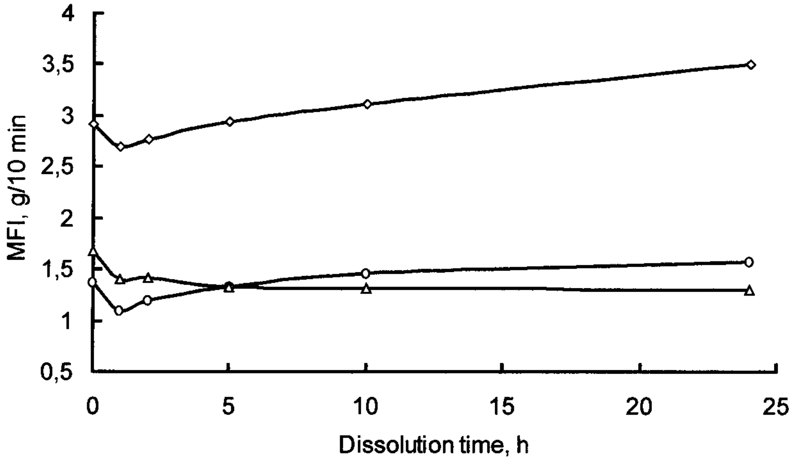

Fig. 5. MFI for PP -◊- , HDPE -o- and LDPE -Δ- after different dissolution times in *n*-alkane mixture

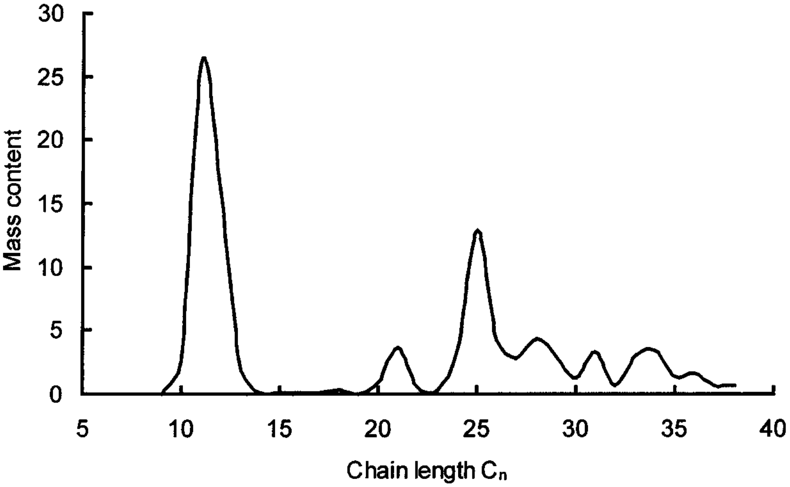

Fig. 6. GPC results of in *n*-alkane soluble rests after dissolution in *n*-alkane mixture

are comparable, but this comparison is only empiric: there are no methods to compare the influence of mechanical stresses by extrusion with the chemical activities of solvents on chemical bond recombination.

The presented study also shows, that only repeated recovery is not representative for an actual prediction of material degradation of postconsumer plastic waste. A combination of numerous aging and performance cycles should be used, especially for recovery through dissolution, because by this method a large portion of the stabilisators and other additives may be removed from plastic materials along with the solvent.

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