Macromol. Symp. **152,** *201–210 (2000)*

Re-stabilization of recycled polymers

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SUMMARY: During recycling operations in molten state, polymers can undergo drastic degradation phenomena due to the thermomechanical stress acting on the melt. Rheological and mechanical properties change deeply and the secondary materials show scarce processability and poor properties. Re-stabilization is therefore a necessary step to avoid the dangerous effects of these phenomena. In this work the properties of polypropylene and polyvinylchloride reprocessed in presence of different stabilizing agents are reported. When the stabilizer is added before each reprocessing step the molecular weight changes only slightly with the melt operation and the properties remain very similar to those of the virgin polymer.

Introduction

Degradation during the reprocessing operations is one of the more important problems in the recycling of both homogeneous and heterogeneous polymers1). Thermomechanical degradation, provoking mainly the decrease of the molecular weight, reduces the mechanical properties, drastically changes the rheological characteristics of the polymers and consequently their processing behaviour1).

Re-stabilization can avoid or better slow down the degradation phenomena due to the thermomechanical stress undergone by the melt polymers during reprocessing2-6). Therefore, the rheological and mechanical properties are less influenced by the processing and remain similar to those of the virgin materials.

Degree and type of degradation depend on the processing conditions and on the nature of the polymer, but severe processing conditions, polymers with high molecular weight and repeated processing operations can cause significant decreases in the polymer characteristics. In particular, variation of molecular weight and molecular weight distribution, formation of chain branching and of oxygenated compounds, unsaturations,

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etc. are observed. It is worth to notice that the change of molecular weight can induce also changes in the crystallinity. As a consequence of these modifications, the degradation leads to deterioration of the mechanical properties (decrease of elongation at break and of the impact strength, in particular) and to discoloration and other surface damages. To protect the materials against the thermomechanical degradation stabilizer agents must be then used. Re-stabilization is particularly important for those polymers, like polypropylene (PP) and polyvinylchloride (PVC), very prone to undergo thermal degradation also because the stabilizing agents added to the virgin polymer before the first processing loss their effectiveness and are not able to protect the polymer during the recycling and reprocessing operations and during the next lifetime.

In this work the effect of antioxidant and stabilizing agents on the rheological and mechanical properties of recycled polypropylene and polyvinylchloride is reported as a function of the number of reprocessing operations and of the processing conditions, of the molecular parameters of the polymer samples and of the type and content of the stabilizing agent.

Experimental

Polypropylene [6)]

The two polypropylene (PP) samples, produced and kindly supplied by MONTELL (Italy), are commercially known as D60P (Mw = 680,000) and X30G (Mw = 270,000). The first sample is a typical extrusion grade material whereas the second sample is an injection moulding grade.

The two stabilizing agents are known as Irganox B900 (produced and kindly supplied by Ciba), and Sandostab P-EPQ (produced and kindly supplied by Sandoz). The first stabilizing system is a mixture of 80% of Irgafox 168 (tris-[2,4-di-tert-butylphenyl]-phosphite) and 20% of Irganox 1076 (a hindered phenolic antioxidant), while the second stabilizer is a high molecular weight phosphonite compound (tetrakis [2,4-di-tert-butylphenyl] 4,4'-byphenylylene-diphosphonite).

The processing of the virgin materials and the recycling operations were carried out in two different apparatuses. The injection grade PP was processed in a small injection moulding machine, MCP RABBIT 2/3 at a temperature of 240 °C. The D60P polypropylene, extrusion grade material, was processed in a Brabender compounder model 42/7, attached to a Brabender Plasticorder PLE 651, with a thermal profile of 135-180-240 °C and a rotational speed of 50 rpm. This machine is an intermeshing counter-rotating twin-screw extruder that allows intensive high shearing and cross flow.

The polymer was extruded or injection moulded, granulated, added with the stabilizer, when necessary, and processed again more times. After each operation a fraction of the material was used for the rheological and mechanical tests.

The melt index was measured with a melt indexer CEAST at 230 °C under a weight of 2.16 Kg following ASTM D-1238.

The mechanical properties were measured using an Instron mod 1122 on samples cut out from sheets prepared by compression moulding in a laboratory press at 210 °C.

Polyvinylchloride 7)

Post-consumer PVC beverage bottles (RBPVC) and rigid PVC pipes (RPPVC), used about 5 years, were granulated into pellets through a 3 mm screen.

Before processing 1-3 parts of stabilizer (dibasic lead hydrophosphite hemihydrate) were added to 100 parts of RBPVC and RPPVC by using a Brabender laboratory twin screw Brabender Compounder mod. 42/7 attached to a Plasticorder PLE651. The thermal profile was 140-155-165 °C for RBPVC because of its low viscosity value and 150-165-180 °C for RPPVC. The screw speed was 60 rpm.

The samples for mechanical tests were obtained by compression moulding in a laboratory press at 190 °C for RBPVC and 200-205 °C for RPPVC.

The Dynamic Thermal Stability Time (DTST) was measured from torque-time curves using a Brabender mixer, 65 g sample, running at 190 °C and 60 rpm. DTST is the time at which the torque in a mixing test starts to rise. The increase of the torque is a sign of the change of the structure. The material, then, can be processed for times lower than DTST.

Tensile measurements were carried out by means of an Instron machine (model 1122) at room temperature. A crosshead speed of 10 mm/min and a gauge length of 3 cm were used in all the measurements. All the reported results are average of at least seven measurements.

Results and discussion

Polypropylene [6)]

In Fig. 1 the melt index of the extrusion grade PP is reported as a function of the number of extrusions for both unstabilized and stabilized samples[6)]. In the abscissa 0 means virgin polymer, 1 polymer after the first processing, 2 after the second processing operation, and then after the first recycling step, and so on. MFI increases dramatically and this means a dramatic reduction of the molecular weight of the polymer because of considerable chain scission during processing. After the first extrusion the MFI increases of about two times and after four recycling steps MFI is about ten times the initial value. The dramatic increase of MFI is drastically reduced by adding the stabilizing agents before each recycling step. Indeed, MFI of the stabilized samples increases with the number of extrusions but the measured values are considerably lower than that of the unstabilized sample. B900 seems to show a slightly better efficiency, but the MFI values of the two systems are very close and then the two stabilizers show a similar behaviour. Similar comments can be made for the injection moulding grade PP.

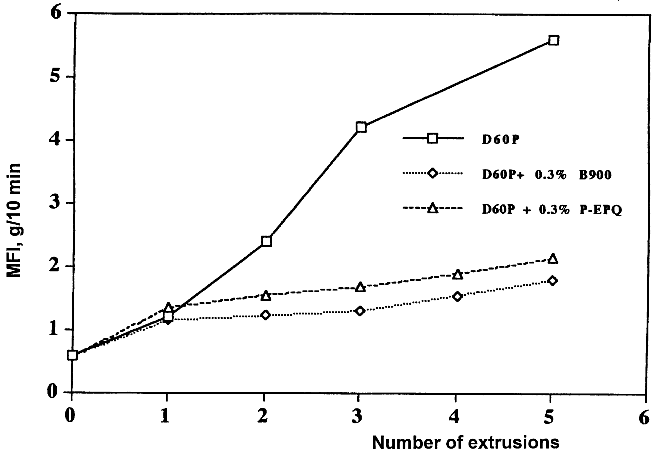

Fig. 1: MFI of stabilized and unstabilized PP samples as a function of the number of extrusions

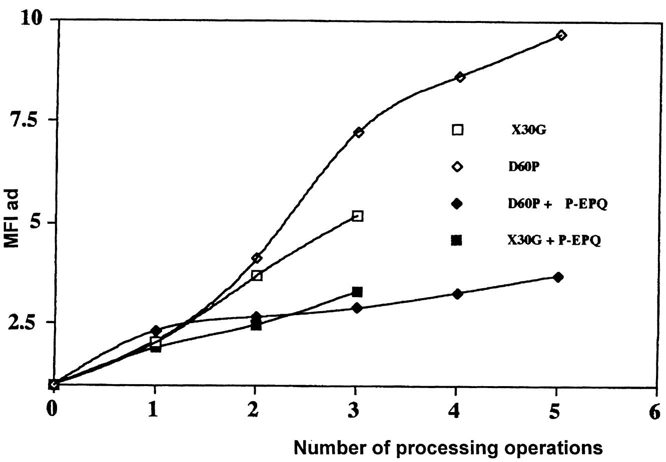

Fig. 2: Dimensionless MFI of unstabilized and stabilized PP samples as a function of the number of reprocessing operations

To better evidenciate the effect of the grade (molecular weight) on the degradation and on the stabilization of the PP, dimensionless MFI values are reported in Fig. 2, taken from[6], for the unstabilized samples and for the same samples stabilized with the P-EPQ stabilizer. The increase of MFI of the high molecular weight sample is more pronounced than that of the low molecular weight material. This can be attributed to more severe processing conditions during extrusion or, more probably, to the larger mechanical stresses applied to the melt due to the higher viscosity of this sample.

The stabilizing agent seems to act in a similar way for both samples. Indeed, the increase of MFI is similar for the two grades PP whatever the molecular weight is. This is due to the ability of the antioxidants to prevent the propagation of the radical reactions.

The effect of the concentration of the antioxidant can be evaluated by plotting, Fig. 3, the molecular weight as a function of the number of extrusions for samples containing different amounts of B900[6]. The stabilizing effect of the antioxidant in the concentration range 0.1 and 0.3% is very similar for the first three extrusions but, increasing the number of extrusions, the sample with lower content of antioxidant shows a more drastic reduction of the molecular weight that, however, remains much higher than that of the unstabilized polymer.

The worse behaviour of the less stabilized system does not give any significant worsening of the elongation at break(6), as reported in Fig. 4 where this characteristic is plotted for the same samples of Fig. 3. Indeed, the elongation at break of the unstabilized PP falls down dramatically with increasing the number of extrusions and this ductile polymer becomes brittle after five melt operations, whereas the elongation at break measured on both stabilized samples does not change significantly and remain very similar to that of the virgin polymer.

The effect of the concentration of antioxidants is, in this concentration range, almost negligible. This is due(6) to the fact that the brittle-ductile transition occurs at lower molecular weight (about 300,000) and then, if the antioxidant is able to maintain the molecular weight higher than this value, only small variations of the value of the elongation at break are observed.

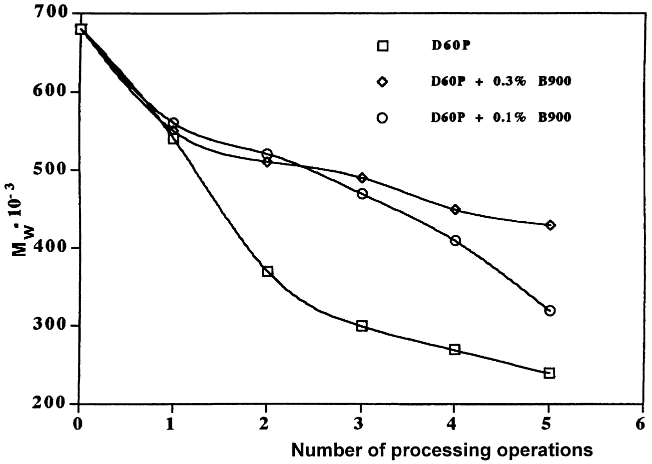

Fig. 3: Molecular weight of unstabilized and stabilized extrusion grade PP samples as a function of the number of extrusion

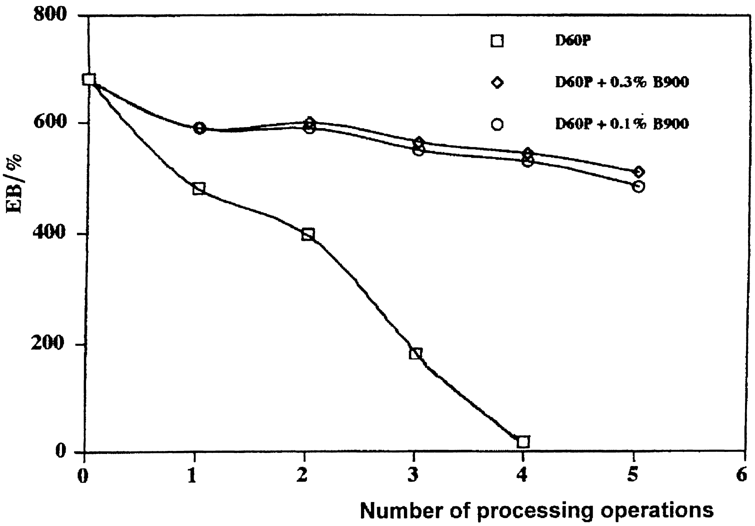

Fig. 4: Elongation at break of unstabilized and stabilized extrusion grade PP samples as a function of the number of extrusions

Polyvinylchloride 7)

The torque-time curves recorded during mixing of RBPVC - recycled PVC from bottles - are plotted in Fig. 5, taken from7). During melt processing PVC undergoes cleavage of the C-Cl bonds with evolution of HCl, rise of the viscosity and then of the torque. Dynamic Thermal Stability Time (DTST) is the time at which the torque in a mixing test at constant temperature starts to rise. PVC, therefore, must be processed for times lower than DTST. DTST of this PVC sample is less than 4 min and is, of course, dependent on the processing conditions and in particular decreases on increasing temperature and mechanical stress. The effect of these two parameters is put in evidence in Tab. 18) where the DSDT values of the same sample are reported as a function of the temperature for three different rotational speeds.

DTST decreases with increasing temperature and rotational speed, that is with the mechanical stress. The effect of the mechanical stress is to increase the rate of formation of macroradicals and acts as a "catalyst" of the thermal degradation.

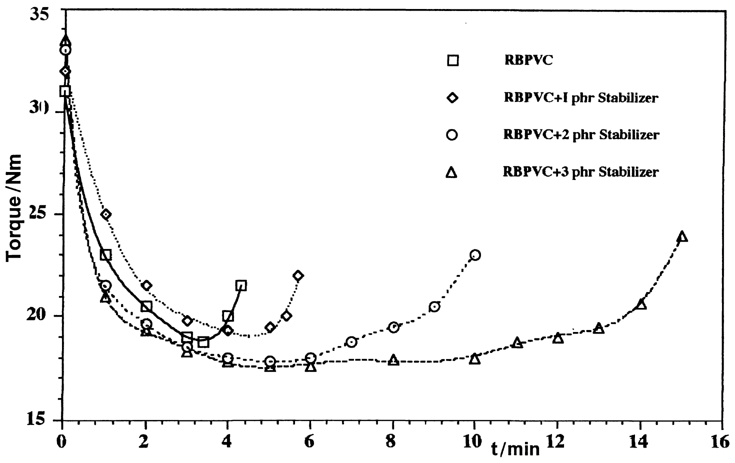

Fig. 5: Torque vs time for unstabilized and stabilized samples of PVC from bottles

The processability can become therefore very poor with increasing the speed of the screw and is necessary to improve the DTST value by adding suitable stabilizing systems. Of course the stabilizers added to the virgin material have been consumed both during processing and during the lifetime of the PVC products.

Tab. 1. DTST values of a PVC sample recycled in different processing conditions

	DTST, s		
T, °C	n = 20 rpm	n = 50 rpm	n = 100 rpm
180	765	405	205
200	436	250	119
220	180	130	68

The torque-time curves for the samples with 1-3 phr of stabilizer are reported in the same Fig. 5[7]. The time at which these curves start to rise (DTST) increases with increasing the stabilizer content. The values of DTST of RBPVC and of a sample of PVC recycled from pipes (RPPVC) are reported in Tab. 2.

Tab. 2. DTST values of two re-stabilized recycled PVC samples as a function of the concentration of stabilizing agent

	DTST, s			
sample	0 phr	1 phr	2 phr	3 phr
RBPVC	220	285	380	770
RPPVC	370	780	1250	--

The presence of small amounts of stabilizer remarkably improves the thermal stability of PVC and enhances the processability of the recycled PVC samples.

Some improvement of the mechanical properties can be achieved by re-stabilizing the recycled PVC. Modulus, E, stress, YS, and strain at yield, YE are reported in Tab. 3 as a function of the stabilizer content for two different processing temperatures[8)].

Modulus, stress and strain at yield increase with the content of stabilizer but, for all these properties, the improvement is evident but not very large because the processing time is below DTST.

Increasing the processing time above DTST the unstabilized PVC becomes very brittle and the mechanical properties cannot be measured. On the contrary, the mechanical properties of stabilized samples remain almost constant for longer processing times.

Tab. 3. Mechanical properties of RBPVC samples, reprocessed at two different temperatures as a function of the concentration of stabilizing agent

	T = 180 °C			T = 220 °C		
Stabilizer content, phr	YE, %	YS, MPa	E, MPa	YE, %	YS, MPa	E, MPa
0	10	51	925	9	50	880
1	12	53	940	11	52	895
2	14	54	955	13	53	905

Conclusion

The re-stabilization of polymers for recycling and reprocessing operations is a necessary step for those materials that undergo severe degradation phenomena because of the thermomechanical stress acting on the melt. As a consequence of this degradation, secondary plastic materials show scarce processability and poor mechanical properties. Like for virgin polymers, the use of stabilizing systems can strongly reduce the degradation level and retain the rheological and mechanical properties near to those of the virgin material provided that the stabilizer is added before each reprocessing operation.

As shown in this paper, polypropylene and polyvinylchloride can maintain their mechanical and rheological properties, even after many reprocessing operations, if suitable amounts of stabilizer are added.

Acknowledgement

This work has been financially supported by CNR Grant 97.02601.CT03 and Murst 60% 97

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