RHEOLOGICAL DETERMINATION OF POLYOLEFIN ARCHITECTURES: RHEOPOLAR

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The RHEOPOLAR project is a cooperation between the University of Naples and ETH of Zurich. The project is financed by the Dutch Polymer Institute (DPI, Eindhoven).

The aim of the RHEOPOLAR Project is to study the molecular details of polyolefin–based systems through an innovative rheological approach.

The knowledge of material properties such as MWD, degree of branching, etc. has an important impact at industrial level, in terms of both processability and final material properties. However, this goal is not always easy to pursue. From a rheological point of view, the characterization of polymer melts is hindered by molecular weight effects, degradation, and crystallization phenomena. When dealing with high molecular weight melts, rheological measurements can be affected by shear induced fracture due to normal stresses differences, or technological issues related to normal force or torque overload. In addition, problems may occur during the loading of the sample into the rheometer due to the long relaxation time of these materials.

The choice of the temperature range during rheological measurements is crucial for the characterization of polymer systems. In fact, the wider the range, the grater the amount of information closely related to the molecular architecture that can be obtained from the measurements. However, for semi-crystalline polymers, as most polyolefins are, the phenomenon of crystallisation can prevent characterisation at low temperatures. The thermal stability of these systems is a further problem, in fact, by increasing temperatures during testing, the polymer inevitably degrades. These phenomena narrow the temperature range available for rheological measurements.

Diluting the polymer melt into an appropriate solvent may overcome, or at least limit, the experimental issues described above. In this perspective, rheology is used as a tool to relate the macroscopic viscoelastic response of polymer systems to their molecular architecture. linear and non-linear rheology of polymer solutions will be measured instead of melt state. Furthermore, the use of molecular models and constitutive equations for polymer solutions will enable to extrapolate information about the original melt.

Ultra-High Molecular Weight Polyethylene (UHMWPE) is used in various industrial sectors such as, for example, textile industry for the production of gears and sliding guides, medical field for the manufacture of orthopedic joint replacements, defense applications such as ballistic protection. Its applicability in these different sectors is due to its special and unique properties, mainly related to its high molecular weight, which leads to high resistance to impact, abrasion, low friction coefficient, chemical resistance and stress resistance. Further, the molecular weight of UHMWPE is inevitably associated with a large number of entanglements per chain, resulting in sustained elastic modulus and melt viscosity. This may represent a limit during the viscoelastic measurements. In the last years, several methods were reported in literature to decrease the viscosity of UHMWPE and improving its processability.

The study of the molecular weight of UHMWPE is, typically, carried out by dissolving it in good solvents such as decalin or xylene and measuring the intrinsic viscosity of the resulting solutions. Alternative methods such as light scattering, osmometry and size exclusion chromatography are unreliable when the molecular weight exceeds one million Daltons.

Finding an appropriate solvent for diluting polyolefin melts is one of the objectives of this project. Solvent selections for the provided PE, optimization of the dissolution process, study of the stability and homogeneity of the prepared solutions, determination of the best experimental conditions (temperature and concentration) are the main activities during the first year.

The use of polymer solutions instead of melts has advantages in that it:

- Reduces temperatures during testing, avoiding degradation;
- Reduces crystallization phenomena, because of the plasticizing effect of the solvent;
- Reduces phenomena of instability, such as edge fractures;
- Reduces the torque and normal force required during tests, because of the decreasing of system viscoelasticity.

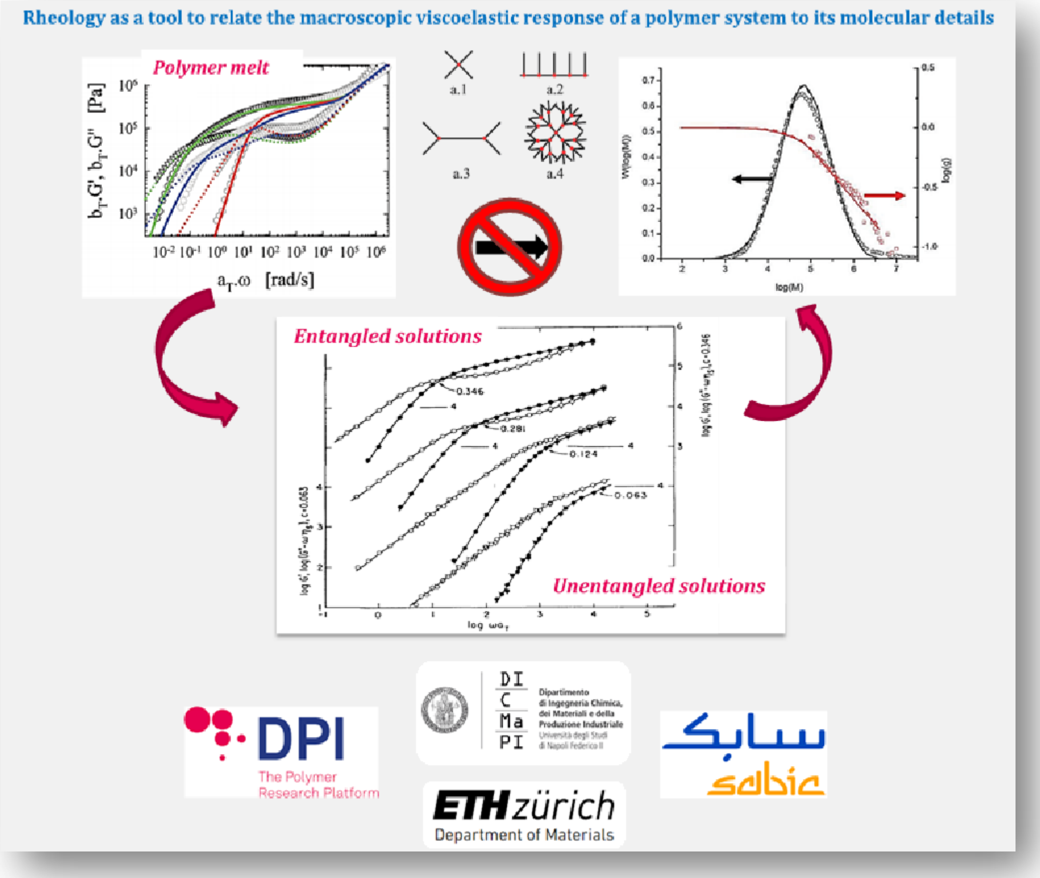
This means that, if phase separation phenomena are avoided, the window of viscoelastic characterization can be substantially widened.

However, other factors must be considered. The choice of the proper solvent may be a main challenge. Solvents for polyolefins are toxic, flammable, difficult to find, and to handle. Therefore, the preparation and use of such solutions need particular care. Determining the best operative conditions (e.g., type of solvent, polymer concentration, temperature) is a challenging task.

During the second year, rheological measurements will be performed on the prepared. Whenever possible, measurements on the corresponding melts will be also performed for comparison purposes. Rheological measurements will include (but will not be strictly limited to): - linear shear viscoelasticity (Small Amplitude Oscillatory Shear (SAOS), creep, stress relaxation) - non-linear shear viscoelasticity (transient shear flow experiments, orthogonal superposition of steady and oscillatory shear flow); - non-linear extensional viscoelasticity (such as squeezing flow and uniaxial extension) In view of the relevant rheometry issues expected, advanced rheological tools and state-of-the art techniques will be used.

The main objective of the last year is to relate the measured rheological properties of polymer solutions to the architectural molecular information and to the polymer melt behavior.

The evaluation of the linear viscoelastic response of polymer melts from the molecular weight distribution is the subject of a vast literature, but the inverse problem is an “ill – posed” one. Determining the available appropriate molecular models to interpret the rheology of polymer solutions, or develop new models along the same directions, is another challenging issue.



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