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Innovative molecular modeling approach to up-grade polymeric materials from post industrial rejects

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Introduction

In the frame of MOMO project, polymeric blends, from post-industrial rejects have been studied. Industrial scraps cannot be reused in an advantageous way, mainly because of their degradation. Post industrial rejects constitute a major problem both from the standpoint of the European legislation and policy and from the economic side where enterprises are concerned.

To reach the goal molecular modelling has been integrated in product-process design, in a context of tailor made materials development ("virtual manufacturing").

Materials

The materials considered in this study are polycarbonate (PC) Makrolon 2447 and acrilonitryle-butadiene-styrene (ABS) Lustran H950 (Bayer Plastics) from industrial fields.

Modelling

Polymers are complex macromolecules whose structure varies from the atomistic level of the individual backbone bond of a single chain to the scale of the radius of gyration, which can reach tens of nanometers. The corresponding time scales of the dynamic processes relevant for different materials properties span an even wider range, from femtoseconds to milliseconds, seconds or even hours in glassy materials, or for large scale ordering processes such as phase separation in blends. No single model or simulation algorithm currently available can encompass this range of length and time scales. In order to simulate a polymeric system one must consider models that range from those including quantum effects and electronic degrees of freedom to chemically realistic, classical models.

One of the most important issue in computational materials research is the multiscale simulation, namely the bridging of length and time scales, and the linking of computational

methods to predict macroscopic properties and behaviour from fundamental molecular processes [1, 2]. A relevant issue in polymer technology is the possibility to predict the morphology, the phase behaviour and the mechanical properties for immiscible blends. Multiscale modeling is suitable to this aim, since atomistic models can give information on the interaction that occurs between the component of the system as well as on the chain characteristics (e.g., characteristic ratio and Khun length). The information may be used as input for the mesoscale level of simulation in which the system is treated as a density field. The simulation at mesoscale gives as output an order parameter (OP) and a distribution of single component densities in space, thus evidencing morphology and phase behaviour. The last element in this chain is given by the FEM simulation that calculates, from the morphology provided by the mesoscale simulation, the mechanical properties of interest.

This procedure has been applied to several systems based on PC/ABS blends as ABS/PC 70/30, ABS/PC 50/50, ABS/PC 30/70, (and also neat ABS and neat PC), with the aim of studying the structure-properties relationships in order to reach the most suitable material for industrial applications [3].

Experimental

The blends were prepared using HAAKE PTW24 (40:1) extruder from HAAKE PolyLab System (Thermo Electron Corporation, Germany). The temperature range was 225–280°C and the extruder speed 60 RPM. Samples for Izod impact and DMTA measurements were prepared using injection molding machine, type Babyplast 6/10 (CRONOPLAST S.L., Spain). Izod impact tests were performed using Resil Impactor Junior (CEAST, Italy), up to ISO 180 standard. DMTA test were performed using DMTA V instument (Rheometric Scientific Inc., USA) under the following conditions: sample dimensions 10x8x1.5mm, mode “bending”, frequency 1Hz, strain 0.01%, ramp velocity 5°C/min.

Results and discussion

The possibility to model the new materials from recycled waste polymers by molecular modelling methods was investigated by comparision of the results obtained from the simulation process and the experiments. Mesoscale simulations results show phase segregation for all systems, revealing the presence of small, circular domains with dimension of 10 – 20 nm, varying with the concentrations of the two components (Fig.1). There is a good agreement between the simulated and the experimental structure [4], confirming the simulation consistency.

The density field distributions obtained by mesoscale simulations have been used to perform finite-element calculations to obtain the following mechanical properties: (i) elastic modulus, (ii) elastic constants, and (iii) thermal expansion coefficient. As example the calculated Von Mises stresses in z direction are illustrated in Fig. 2 for PC 15/ABS 85 blend.

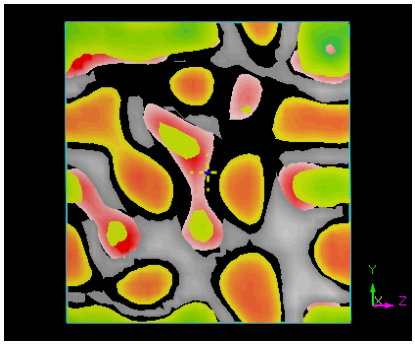
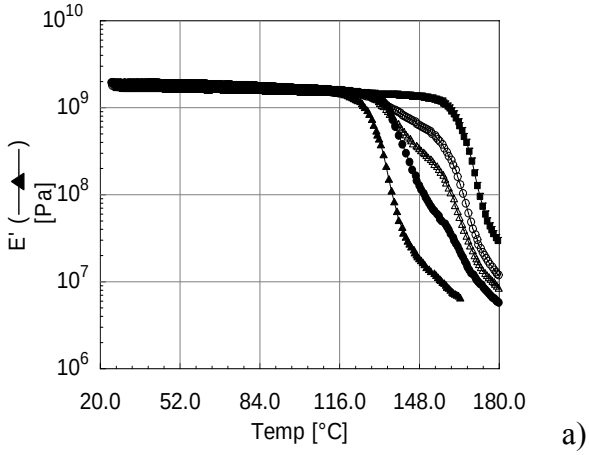
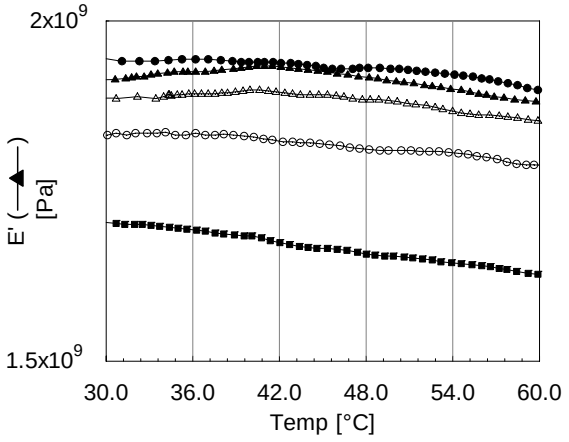


Fig. 1. Mesoscale section morphology of PC 15/ ABS 85 blends at 298K.

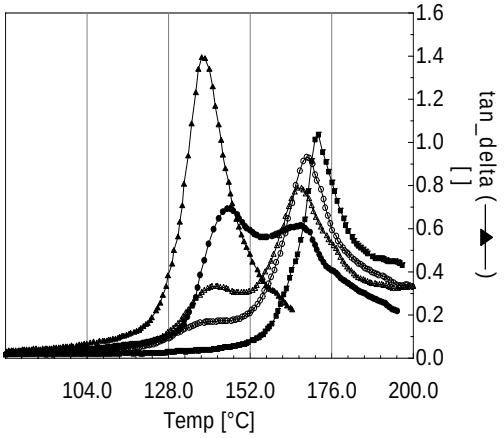
In order to compare the results obtained from molecular modelling, DMTA measuremenst of extruded PC/ABS blends were performed. These results are presented on fig. 2 which represents the modulus behaviour as a function of temperature (Fig. 2a, 2b) and influence of the polymers ratio on glass transition temperature of PC/ABS blends. At room temperature the storage modulus of PC/ABS 30:70 blend is bigger than both neat polymers. The glass transition temperature (Fig. 1c) is characteristic for each, neat polymers. However, for the blends is possible to observe that there are two different peaks which position and intesivity depends on polymer ratio and miscibility.



a)



b)



c)

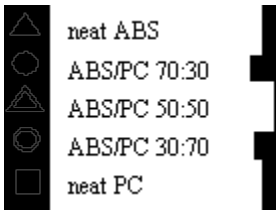


Fig. 2. Storage modulus (a, b) and tan(delta) (c) vs temperature for different blends

Using the results which are presented in fig. 1b is possible to check the molecular modelling capability to predict some behaviour of new materials. Fig. 3 represents the comparision between experimental values of storage modulus at 30°C and storage modulus of blends obtained from the simulation, assuming that the modulus values of neat polymers are known.

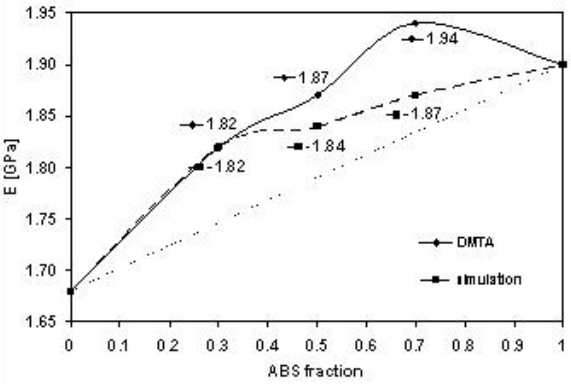


Fig. 3. Comparison between simulation and experimental values of storage modulus

Conclusions

The raising in the polymer prices and contemporarily the growing pressure coming from EU provisions concerning waste treatment, the recycling of polymeric materials is becoming of paramount importance.

With the present study, it is demonstrated that a design procedure for polymeric blends has been developed and applied to polymer recycling in a case of industrial interest, such as automotive field. The results give evidence that the design process can give substantial support to overcome the abovementioned industrial threats.

Future developmets will allow to extend such an approach to nanocomposite polymeric materials and to consider other industrial fields.

References

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