Determination of the Polymer-Solvent Contact Angle by the Capillary Raising Curve, Applied to the Field of Supports for Homogeneous Catalysts

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ABSTRACT: A comprehension of the phenomenon that controls the diffusion of an organic solvent to the pores of a polymeric matrix is fundamental for optimizing the operating conditions to distribute a homogeneous catalyst, which has to be supported on it. The traditional sessile drop method is impossible to use when a high polymer-solvent affinity exists. In this case, a different determination technique, similar to the Wilhelmy static mode method and based on the direct observation of the capillary raising curve of the solvent on the polymeric surface, has been set together with an experimental apparatus specifically built to perform measurements at a desired temperature and atmosphere. Such a technique has been demonstrated to be easy and promising for differentiating the behavior of different polyolefins [polypropylene (PP), high density polyethylene (HDPE), heterophasic copolymers (COPO)] at equal solvent and different temperatures. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1622–1625, 2007

Key words: contact angle; surface tension; inert conditions; temperature; polyolefins; homogeneous catalysts; catalysts supportation

INTRODUCTION

In the field of polyolefins, heterogeneous Ziegler-Natta catalysts permit one to produce materials with different proprieties. They can also be used on reactors in series, modifying, in real time, the monomer composition necessary for obtaining polymeric blends with improved performances with respect to the traditional mechanical ones.

Despite the flexibility of the process and, partially, of the catalysts, Ziegler-Natta systems are not the best solution in all cases. In the last decades, new classes of catalysts have been discovered that allow the production of known materials with reformed properties or materials with new interesting application fields.

These new catalytic systems are homogeneous while most of the existing processes require a heterogeneous catalyst; thus, their industrialization requires a suitable support.

In the patent literature there are a great number of different solutions for catalyst supportation, which differ depending on the nature of the supports used (inorganic or polymeric) and the supportation technique. In all of the cases, the operation could be described as the impregnation of a porous solid with the solution of the catalytic system.

The use of porous polymeric particles obtained from a Ziegler-Natta catalyst is reported in the patent literature.[1] When using a polymeric support, the affinity between the catalytic solution and the polymer surface can strongly affect the homogeneous impregnation of the particles. How changing parameters, such as the temperature or the chemical nature of the solution, modifies this affinity is hence very important.

The contact angle measurement is one of the most direct techniques to evaluate the environment-dependent proprieties of material surfaces[2,3] and, in particular, get a deep insight into aspects such as homogeneity, roughness, hydrophilicity–hydrophobicity balance, etc.[4–6]

Among the various methods available for measuring contact angles, both static and dynamic, it has been decided to take inspiration from the static Wilehlmy balance method, whereby one records measurements at a solid/liquid interface, which is not in motion.[7,8]

Other conventional methods, like the sessile drop, do not easily permit us to obtain data for preliminary studies of the wettability of polyolefins (such as polypropylene or high density polyethylene) with nonpolar or low polar solvents (for example, toluene which is typically used for homogeneous catalysts). In fact, the fast spreading of the droplet on the surface does not permit any measure.

Therefore, the objective of this work is to overcome these difficulties and contemporaneously to set-up a simple measurement equipment, which is able to operate under an inert atmosphere and at a controlled temperature.

EXPERIMENTAL SECTION

Preparation of the polymer samples

The necessity of setting up a new analytic technique for measuring contact angles comes in some cases, as previously mentioned, from the failure of the traditional method of the sessile drop.

The possible alternative technique here is based on a modification of the original Wilhelmy Plate Method (known to be suitable for both static and dynamic contact angle measurements) and, in general, on the physical phenomenon of the capillary raising. Thanks to this phenomenon, dipping a plate of polymer (with defined dimensions of 1.5×1 cm^2 and thickness of 0.05 mm) in the solvent (whose contact angle has to be measured), the liquid rises along the faces of the plate generating a meniscus. The contact angle can be derived from the measurement of the geometry of this meniscus.

Three different kinds of polymers, with a crystallinity composition between 50 and 60%, have been taken in consideration:

- Polypropylene (PP) (Melt Index MIL: 15)
- High Density Polyethylene (HDPE) (Melt Index MIE: 1)
- Heterophasic Copolymer between PP and HDPE (COPO) (Melt Index MIL: 1.5)

The correct preparation of the plate is carried out according to the following conditions:

- Statistic sampling (for progressive inquartation) of some grams of polymer
- Hot pressing ($T = 200°C$ for PP and COPO (PP-HDPE); $T = 175°C$ for HDPE) on a CARVER press between two aluminum sheets for 10 s, so that a first raw sheet could be obtained
- Cutting of the raw sheet in small fragments and deposition of some of these on a steel stainless die (SPECAC Film Maker) preheated up to a temperature of 200°C
- Aging of the system for 10 min at 200°C
- Imposition of a pressure (1–1.5 metric tons) on the Film Maker for 40 s
- Cooling of the Film Maker under a current of cold water for 8 min
- Extraction of the plate
- Storage of the plate in sealed polyethylene bags

Figure 1 Experimental apparatus used: from the left, the camera, the microscope and the jacketed glass chamber can be seen. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Setup of the experimental equipment

A jacked glass chamber has been specifically built to perform the measurements at the desired temperature and atmosphere (nitrogen or argon) Figure 1.

In the chamber, a small glass vessel contains the liquid under examination in which the polymeric plate has to be immersed.

The chamber has two opposite quartz windows: from one side, the chamber is illuminated thanks to two optical fibers connected to a light; from the other side, a microscope Wild M3 connected to a Polaroid land camera, allows one to observe and take a picture of the meniscus formed by the liquid in contact with the polymer.

The chamber has two inlets, one for fluxing it with high-purity nitrogen gas to create inert conditions (fundamental for the direct investigation of the real catalytic solution) and a second one for depressurizing it through a vacuum pump.

Two other inlets were foreseen to be necessary in the upper part of the chamber to host a ''wire thermocouple'' which is necessary to monitor the inside temperature and a feeding syringe for pouring the liquid into the container. Finally, a ''hook'' is present to hang the plate of polymer on.

RESULTS

Qualitative evaluation of polyolefins wettability by toluene at ambient temperature (25°C)

A congruent number of points (at least 20) were obtained by scanning a picture of a capillary raising curve (Fig. 2) and introducing them in a graphic elaboration program (in our case Graphpad Prism 3.0) permits us to extrapolate the global trend.
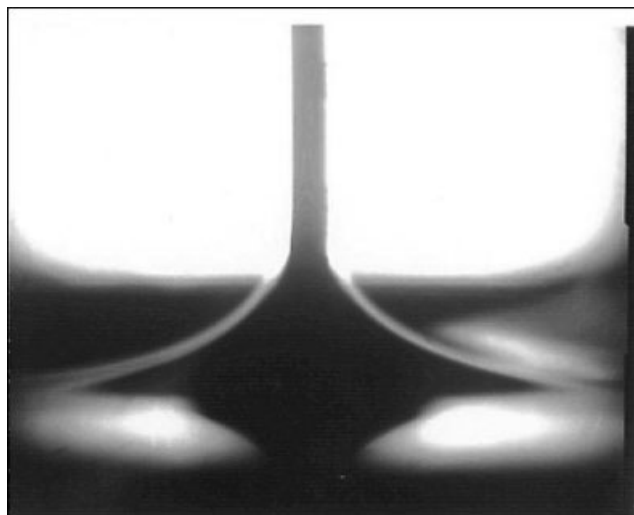
Figure 2 Photo of a capillary raising curve obtained from a polyolefin plate merged into the vessel filled with toluene and positioned in the jacketed glass chamber.

The calculus of the derivative at the zero point (the contact point between liquid and polymer) allows us to identify an angle (θ) that will depend on the course of this raising curve and then, indirectly, on the affinity among the polymer and the liquid under examination.

The general validity of the exponential equation:

$$Y = C_1 e^{-AX} + C_2 e^{-BX} \qquad (1)$$

with C_1, C_2, A, B as experimental constants as an interpolation curve of the experimental points has been verified.

The derivative of the eq. (1) (which is considered as representative of these capillary raising curves) could then be calculated at the zero point to obtain the value of the θ angle:

$$\tan\theta = -(AC_1 + BC_2) \qquad (2)$$

The limitation of these data concerns the reproducibility about the value of θ, which have been evaluated around ±3°.

Therefore, the absolute values obtained through this method can be affected by this error; either way, it clearly shows a "behavior trend" of the three different polyolefins with respect to the organic solvent under evaluation.

The curves obtained for the three different polymers at room temperature (reported in Fig. 3) also show that the copolymer has a consistently lower affinity toward the toluene, with respect to the other materials.

A possible explanation is that the presence of an amorphous component brings a high entropy contribution, determining a general decrease of the copolymer surface tension with respect to the
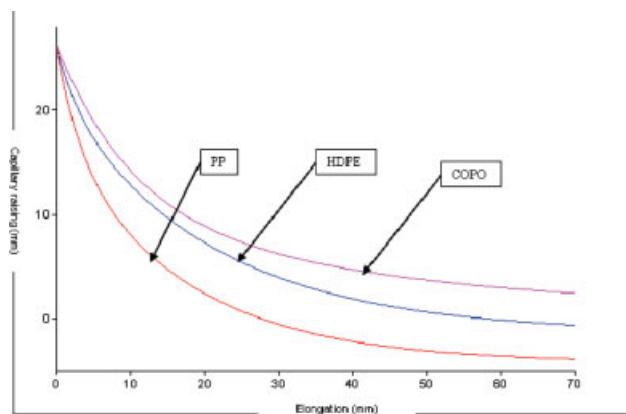
Figure 3 Capillary raising curves of toluene on the three different materials compared at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

two semicrystalline omopolymers. Furthermore, this amorphous component may partially obstruct the pores of the polymer, reducing the capillary phenomenon that is the base of the polymer-solvent adhesion.

Qualitative evaluation of polyolefins wettability by toluene at increasing temperature

In general, the contact angles could increase or decrease with the temperature[9]: the behavior depends on the relative value of the surface entropy of the involved phases.

In most of the cases, a small decrease (0.05° for each degree) could be noticed by increasing the temperature; however, at temperatures close to the boiling point of the liquid, its surface tension falls drastically and the contact angle goes quickly to zero.

The reduction of the surface tension of a liquid constituted by enough small molecules as a function
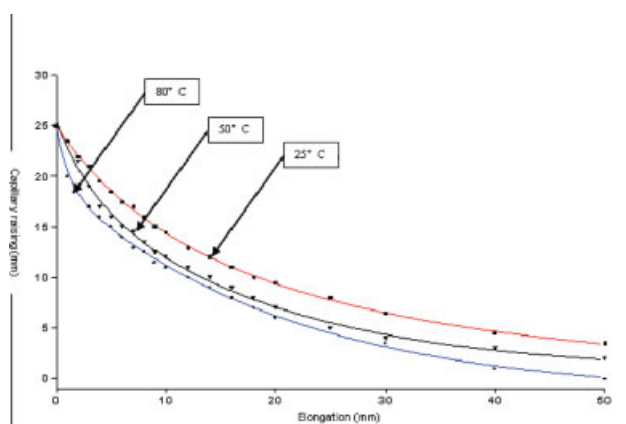
Figure 4 Capillary raising curves of toluene on the copolymer at increasing temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

TABLE I
Contact Angle of Different Polyolefins at Increasing Temperatures

	HDPE	PP	COPO
25°C	22°	16°	33°
50°C	11°	10°	22°
80°C	7°	5°	11°

of the temperature is expressed by the Guggenheim[10] equation:

$$\gamma = \gamma_0 \left(1 - T/T_c\right)^{11/9} \tag{3}$$

where γ_0 is the surface tension at zero absolute temperature and T_c is the critical temperature of the liquid.[11,12]

On the other side, with regard to the polymer itself, the wettability is the combined result of dispersion and nondispersion forces operating at the interface.[13] In fact, beyond the general decrease of the surface tension of the liquids involved, at high temperature, it is possible to have a general increase of the entropy due to progressive surface configuration changes: this determines a ''hydrophobic effect'' which favors an interaction with low polar solvents like toluene in this specific work.

Also, the mobility and the reactivity of the macromolecular chains depend on the temperature, with obvious consequences on the morphology and the chemical nature of the polymer surface, considering that most of the impregnation industrial processes don't require temperatures exceeding 70–80°C, the consequences could remain negligible.

Therefore, it has been possible to hypothesize a resultant decrease of the contact angle by increasing the temperature while maintaining the difference of affinity among the different polymers with respect to room temperature substantially unchanged.

This expected trend is shown in Figure 4 where the capillary raising curve of toluene on the copolymer at three different temperatures (25, 50, 80°C), which are included in the significant interval for what concern industrial catalyst preparation processes, is reported.

Table I reports the complete contact angle values obtained relative to the three materials at these temperature conditions.

CONCLUSIONS

Industrial laboratories always need more simplified discrimination methods to classify the available polymers for their potential application as supports. For this reason, an apparatus that allows one to obtain information on the wettability of the polymeric materials in terms of contact angle, operating under inert conditions and at a desired temperature, has been investigated.

Moreover, a raw easy measuring technique of contact angles between polyolefins and organic solvents (here, in particular, toluene), potentially interesting in the field of homogeneous catalysis, has been set up through an exponential interpolation of the scanned points obtained on a ''capillary raising curve'' of the liquid on the polymeric wall.

The positive effect produced by increasing the temperature has been confirmed in terminus of improved wettability of the aforesaid polyolefins: polypropylene and polyethylene demonstrate very similar behaviors. Vice versa, it is remarkable how the copolymer shows a lower wettability at the same temperature, probably due to the presence of an amorphous component that reduces the surface tension and, in general, the effectiveness of the capillary phenomena.

Future work needs to be done for a better understanding of these processes via performing systematic measurements as a function of time and aging or environmental conditions.

Furthermore, it will be necessary to investigate the chemical–physical meaning of the fit parameters of the equation used to interpolate the experimental data, and it could also be useful to study the hysteresis effect between the advancing and receding contact angles, which can be affected by surface roughness, surface-configuration changes, and chemical heterogeneity.

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