

In-situ thermoset polyurethane coating of glass beads dispersed in polystyrene by reactive extrusion

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The condensation reaction between hydroxyl terminated polybutadiene and an uritonimine modified 4, 4' diphenylmethane diisocyanate (liquid MDI) was carried out by reactive extrusion in the presence of γ propyl triethoxy amino silane treated glass-beads and polystyrene. Reactants were selected having a surface tension favoring the glass bead coating using the spreading coefficient concept. FTIR, SEC (size exclusion chromatography) and rheological analysis of the resultant material showed that condensation reaction had occurred leading to crosslinked Polyurethane located principally around the glass beads.

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1. Introduction

The mechanical behavior of composite materials does not depend only on the properties of each component but also on the interfacial regions. In fact in the last decades, numerous work has been carried out to show interphases in the vicinity of the filler or fiber surface. The interface (zero thickness) depends on the chemical and/or physical interactions between the polymer matrix and the inorganic surface. The term interphase refers to a 3D region with different properties than the bulk matrix, these resulting from the presence and the surface treatments of the fillers or fibers [1, 2]. As a consequence numerous papers have been written to model the mechanical behavior as a function of the interphase characteristics (thickness, modulus, ...) of composite materials based on particles [3–5] or fibers [6–8]. Using these models new ways of improving the mechanical properties of the composites could be investigated by tailoring these interfacial zones. By such a way for improving the tailored interphases (between the filler or fiber and the matrix) with controlled properties can be introduced in thermoset-based composite materials instead of adding a reactive rubber or a thermoplastic to the matrix leading to a separated dispersed phase [9, 10]. It has been reported that the insertion of such an interphase in particulate and fiber based composites is able to reduce the stress concentration during the application of external and/or internal stresses. Using this approach, the mechanical properties, such as the impact and fatigue strengths, can be improved without any decrease in the elastic mechanical—Young's modulus—and thermal—glass transition temperature—properties of the composite

materials [11, 12]. For epoxy-based composites the concept of the introduction of rubber interlayers has been widely investigated. For example the synthesis of crosslinkable soft interlayers prepared from carboxyl-terminated acrylonitrile-butadiene copolymers with different ways of being chemically bonded to glass surfaces has been described [13]. The crosslinking of such interlayers around the filler is required in order to be sure that the rubber remains at the interface during processing. The main characteristics of the interlayer controlling the mechanical properties of epoxy/glass bead composites are the interphase thickness and the presence of functional groups able to react with the glass surface [11–14]. The fracture properties depend on the interlayer thickness and an optimum thickness is found in agreement with the rheological models developed in the literature [3, 4].

The same concept can be used for amorphous thermoplastic based composites [15–21]. Most of the studies devoted to the encapsulation of fillers within rubbers concerned composite materials based on a polypropylene matrix and grafted ethylene-propylene rubber. The rubber coating for thermoplastic based materials can be made during the processing (extrusion) due to the preferential interactions which could exist between the filler surface and the grafted rubber [18]. For example, Marosi *et al.* [18] prepared ternary composites based on PP and fillers such as kaolin or barium sulfate (BaSO_4) and an ethylene-propylene-diene terpolymer (EPDM). For kaolin-based systems most of the EPDM rubber is localized at the interface, thus encapsulation takes places during the melting of PP, whereas a separate dispersion of EPDM and filler is observed with BaSO_4 . In

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this later case non interactions exist between EPDM and filler. In such a method of on-line coating during the extrusion process, the formation of an interphase around the filler particles is controlled by thermodynamic parameters; i.e. polar or non polar nature of the filler, but also on the viscosity of the components [19]. In fact for low molar mass additives, the coating process is mainly controlled by thermodynamics, whereas for high molar mass modifiers, i.e. high viscosity components, the kinetic of the diffusion to the interface becomes more predominant. These effects were verified on composites based on PP, calcium carbonate, and additives such as EPDM, copolymers of ethylene and vinyl acetate (EVA), polyisobutylene, or polychloroprene [19]. Coating of CaCO_3 was performed for both polar rubber such as EVA and non polar rubber such as polyisobutylene. In this case the encapsulation of filler can be carried out due to the low viscosity of the polyisobutylene at the melting temperature of the polypropylene. The same type of concept was used by Jancar and DiBenedetto for PP/ethylene-propylene rubber/inorganic fillers (CaCO_3 and $\text{Mg}(\text{OH})_2$). The encapsulation can be carried out using maleated ethylene-propylene rubber (MEPR) as an additive, whereas separated phases were observed in the case of maleated PP as matrix and EPR as additive [20]. In fact by controlling the surface characteristics of the filler (acidic or basic) and by changing the level of the interactions between the filler surface and the rubber additive, three different types of ternary composite materials can be processed: (i) separated filler and rubber phases; (ii) encapsulation of filler with the rubber phase. Long and Shanks [21] noticed that by studying PP/modified rubber (maleic anhydride modified EP or SEBS)/filler (calcium carbonate, talc or Nylon 12) systems that separated microstructure increases the stiffness of composites whereas a Core-Shell microstructure (encapsulation) improved toughness.

Nevertheless, in most of the cases, the processing of such ternary composite materials by encapsulating fillers does not involve chemical reaction and involves only the existence of preferential thermodynamic interactions between filler and additives. Rösch *et al.* [16] prepared composite materials by extrusion of PP in the presence of amino-silane treated glass beads and various rubbers. Significant improvements to the mechanical properties were obtained with EPM-g-MA or SEBS-g-MA rubber additives. This effect can be explained by a better interfacial adhesion resulting from the reaction of amine surface groups on glass with maleic anhydride functions to form imine links during melt-processing of PP.

The aim of this work is to apply the concept of *in-situ* encapsulation of fillers during melt-processing of thermoplastics and to use reactive extrusion for that purpose. In fact, as reported, such an approach required

control of the thermodynamic interactions between the filler surface and the modifiers and to promote the formation of the interphase layer in the melt. Such a diffusion of the additives to the interface can be easier for low molar mass modifiers than for macromolecular ones. As a consequence, reactive extrusion can be used to synthesize *in-situ* rubber around filler particles. In this paper, this concept was applied to model ternary systems based on an amorphous thermoplastic (polystyrene) and amine functional glass beads. A polyurethane was synthesized from a hydroxyl terminated polybutadiene and a diisocyanate in the PS-melt during extrusion.

2. Experimental

2.1. Materials

The diisocyanate used was uritonimine modified 4,4'-diphenyl methane diisocyanate (liquid MDI) (Caradate-30) having an isocyanate index $E = 134.5$ g/eq (NFT52132). Hydroxyl terminated polybutadiene (HTPB) was supplied by Elf Atochem (PolyBd R 45 HT, $\bar{M}_n = 2830 \text{ g} \cdot \text{mol}^{-1}$, $\bar{M}_w = 7190 \text{ g} \cdot \text{mol}^{-1}$). The number average and functionality average functionality were $\bar{F}_n = 2.7$ and $\bar{F}_w = 2.93$, respectively. Polystyrene (PS) was from Elf Atochem (Lacqrene 1340, $\bar{M}_n = 107\,500 \text{ g} \cdot \text{mol}^{-1}$, $\bar{M}_w = 204\,250 \text{ g} \cdot \text{mol}^{-1}$). Glass beads treated by γ aminopropyltriethoxysilane were provided by Sovitec (Microperl A 050 20). The number average diameter was $\bar{D}_n = 20 \mu\text{m}$.

2.2. Apparatus

Size exclusion chromatography (SEC) was carried out using a Waters device equipped with UV and refractive index detectors. The solvent was THF at a 1.5 ml/min flow rate and a pressure of 5×10^6 Pa. Columns from Polymer Laboratories, gel 1000, 500 and 100 \AA , were used. Number and weight average molar mass were calculated using a calibration from polystyrene standards. Scanning electron microscopy were carried out on liquid nitrogen fractured surfaces or on powders using a Philips XL 20 microscope. A Rheometrics RDA II viscoelastimeter equipped with a cone-plate tool having a diameter of 25 mm and a $50 \mu\text{m}$ -gap was used for the measurement of the viscosity of the specimens at 210°C .

2.3. Extrusion

A modular intermeshing corotating twin-screw extruder CLEXTRAL BC21 was used in this study. Screw diameter were 25 mm and the total barrel length was 900 mm. The used screw profile is presented in Fig. 1. PS and Glass beads were introduced through extruder



Figure 1 Screw profile used for *in-situ* coating of glass bead in PS.

hoppers placed on barrel 1 and barrel 5 respectively. The liquid MDI was injected through one side of barrel 5 and the HTPB through the other side of the barrel 5. The isocyanate to alcohol ratio was one. The PS contained 0, 3, 4.5, 6 wt % PU and/or 25, 30, 45 wt % glass bead. Screw rotation rate was 200 rpm. The total impute was 4 kg/h. The stationary state (constant pressure and temperature) was established in approximately 20 min. The extrudate was then taken from the extruder die, cooled at room temperature and pelletized.

3. Results and discussions

The polyurethane which is expected to be synthesized during melt processing results from the reaction of an hydroxyl terminated polybutadiene and a diisocyanate. The mean residence time of the polyurethane monomers is lower than 4 min [27]. A detailed kinetic study of such reactions was made previously [22]. Using the kinetic modeling developed in this study and the kinetic data, a total conversion is expected in 4 min at 190 °C (temperature selected for PS processing).

3.1. Choice of components and reaction conditions

The morphologies which could result form the reactive extrusion are (Fig. 2):

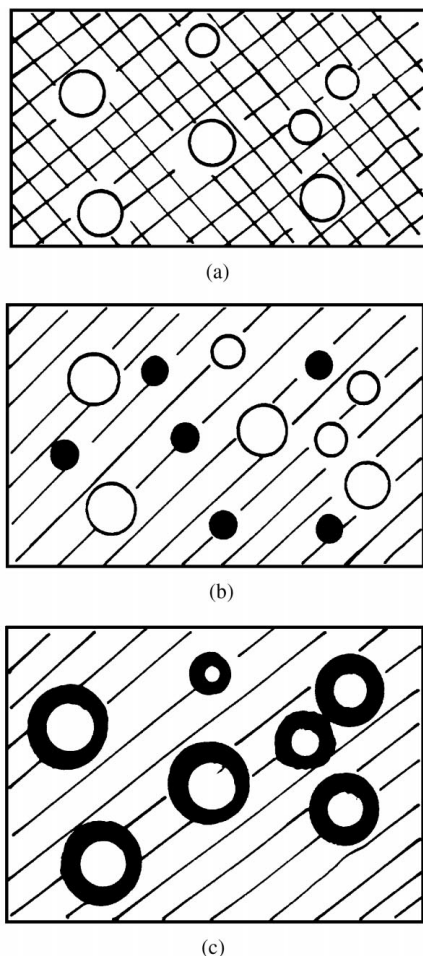


Figure 2 Morphologies of the polystyrene/polyurethane/glass beads materials.

(i) Two phase-structure based on a PS-matrix where HTPB and MDI remained dissolved filled with glass beads (Fig. 2a).

(ii) Three phase-structure with filler and polyurethane dispersed phases in a PS continuous medium (Fig. 2b).

(iii) Three phase-structure with encapsulated filler (polyurethane interlayer) (Fig. 2c).

For preparing the later one, some requirements for the components are necessary:

(i) The interactions between the polyurethane reactants (PB-OH and MDI) need to be higher than those developed between these components and the polystyrene and the reaction time needs to be lower than the residence time in the extruder.

(ii) A phase-separation between the polyurethane and the polystyrene is required for structures a and b.

(iii) The thermodynamic work of adhesion between glass filler and the polyurethane needs to exceed the interactions between glass and polystyrene for encapsulation.

According to the solubility parameters of the polybutadiene, the diisocyanate and the resulting polyurethane, a phase separation will occur in the presence of polystyrene. In addition, using this screw profile, the mean residence time is about 5 min and as a consequence, a full conversion of isocyanate is expected during the melt-processing. Thus, the morphology corresponding to Fig. 2a cannot be prepared.

Because of the low molar masses of the reactants, diffusion kinetics of PB-OH and MDI to the interface is not the main parameter for *in-situ* encapsulation of glass beads with polyurethane. The driving force is the level of interactions between glass, PS, and polyurethane in the melt. The ability of the polyurethane to be prepared at the interface and/or to the components to migrate to the glass surface is favored by using aminosilane-treated glass beads. In addition the use of glass beads treated by an aminosilane coupling agent results in amine reaction with the isocyanate monomer. This reaction is much faster than the alcohol-isocyanate reaction [23]. Thus one can expect that Isocyanate-amine condensation reactions will occur first on the glass bead surface leading to urea and the polyurethane layer will grow further due to isocyanate alcohol reactions leading to a polyurethane layer chemically bounded to the glass.

The spreading of PU onto glass surface can be estimated using Hoops's equation [24]: the spreading coefficients, λ , are given by the following formula:

$$\lambda_{31} = \gamma_{12} - \gamma_{32} - \gamma_{13} \quad (1)$$

1, 2 and 3 indexes refer to glass beads, PS and PU, respectively. λ_{31} is the spreading coefficient of component 3 on 1. γ_{ij} are interfacial tensions. If λ_{31} is positive, the PU should coat glass beads in a PS matrix. If λ_{31} and λ_{13} are both negative, the dispersed phases

remains separated. A fairly good approximation for the γ_{ij} calculation is given by the harmonic equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 + 4 \left(\frac{\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} + \frac{\gamma_1^{nd} \gamma_2^{nd}}{\gamma_1^{nd} + \gamma_2^{nd}} \right) \quad (2)$$

γ^d and γ^{nd} are disperse and non disperse terms of the surface energy.

Using data from literature [25] and assuming that the temperature dependence of γ_1 and γ_3 is $\frac{d\gamma}{dT}$ about $-0.06 \text{ J} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$, interfacial tensions were estimated at the reaction temperature (190°C).

$\gamma_{12} = 4.57 \text{ J} \cdot \text{m}^{-2}$, $\gamma_{32} = 4.41 \text{ J} \cdot \text{m}^{-2}$ and $\gamma_{13} = 0.04 \text{ J} \cdot \text{m}^{-2}$. A positive λ_{31} was obtained. It is obvious

that the precision of the numerous different data reported in literature and the errors introduced by extrapolating the interfacial tensions from room temperature to 190°C does not allow such precise λ_{31} calculation. Anyhow, the only other possibility is that γ_{32} is higher than γ_{12} which leads to the non realistic case where glass covers PU.

3.2. *In-situ* synthesis by reactive extrusion of the polyurethane interlayer

The control of the synthesis is much more complicated than a classical reaction made in a batch reactor or in solution. In this case, the reaction takes place in an

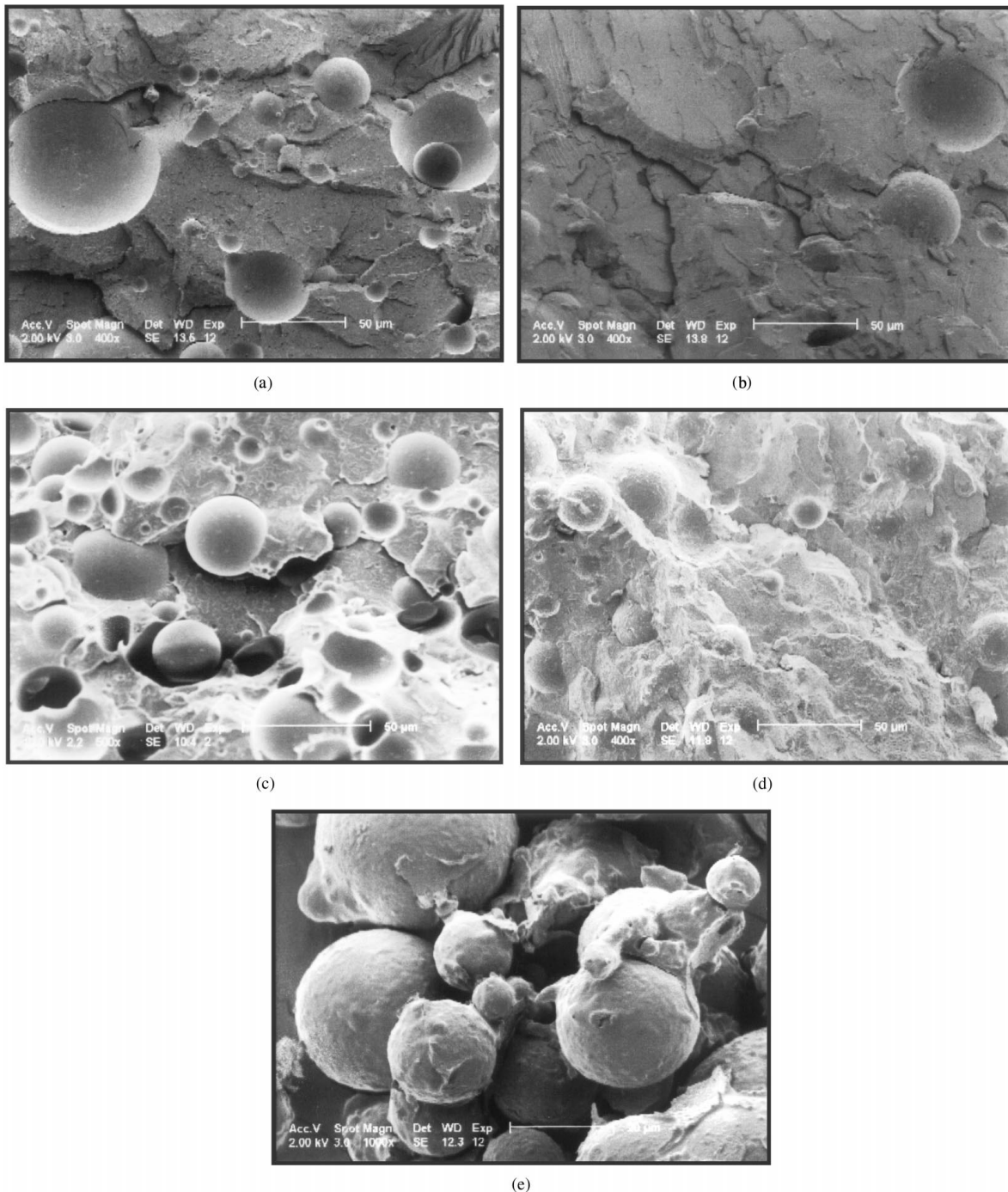


Figure 3 SEM micrographs of fractured surfaces: (a) PS + 25 wt % glass beads; (b) PS + 25 wt % glass beads + 4 wt % PU; (c) PS + 48 wt % glass beads; (d) PS + 48 wt % glass beads + 4 wt % PU; and (e) Non-soluble part of material of Fig. 3d.

heterogeneous medium, and the stoichiometry of the reactants is only constant if none of the reactants is soluble in the matrix and if the morphology equilibrium of the dispersed phase is established in a short time. A twin-screw extruder, equipped with kneading-discs blocks, is an efficient mixing tool [26]. This makes a rapid homogenization of the reactants possible within the rest of the components. On the other hand, because the average functionality of the reactants is higher than 2, a gelation of the polyurethane reactive system will occur. Such reaction is possible in a twin-screw extruder because a phase separation will occur between the PS and the PU and the expected PU network will be as a dispersed phase in the PS matrix. According to the selected morphology (Fig. 2c), it is necessary to verify that (i) the HTPB reacts with the diisocyanate and that (ii) the PU is localized as a thin layer on the glass beads.

Several reactions were made with different proportions of reacting components. These experiments were defined in the experimental part. Results obtained in similar systems (PS/Glass bead or PS/Glass bead/PU) are rather similar. For this reason global results are reported here.

In order to analyze the microstructure of the resulting material (PS/Glass bead/PU), some of it was solubilized in THF. The non-soluble phase was filtered, dried and analyzed by FTIR using a diffuse reflection technique (DRIFT). Back-ground was taken with initial glass beads. The FTIR spectrum displays the band associated with the urethane function at 1728 cm^{-1} and

the absence of residual isocyanate at 2260 cm^{-1} . This shows that the isocyanate/alcohol reaction occurred in the extruder. The soluble fraction was also analyzed by SEC. The chromatogram corresponds to that of PS. This indicates that the thermoplastic was not affected by processing in presence of HTPBD and the diisocyanate, and the absence of residual HTPB and MDI. Since the initial concentrations of the reactants are very low ($<5\text{ wt}\%$), conclusions concerning the absence of these reactants in the final product should be moderated, specially for systems with lower PU concentrations.

This analysis does not exclude the possibility that some of the PU can also be in dispersed phase in the PS matrix. This possibility will be examined in the following paragraph.

3.3. Evidence of PU-encapsulation of glass particles

In the preceding paragraph, it has been clearly demonstrated that at least some of the isocyanate had reacted leading to the formation of a polyurethane. In the anticipated microstructure (Fig. 2c), the PU is located around the glass beads. Examining the SEM micrographs of the fractured surfaces of PS/Glass beads blends (Fig. 3a and c), the debonded surface of the glass beads can be seen indicating a poor adhesion at the interface between glass and PS (adhesion failure). The SEM micrographs of a PS/Glass beads/PU ternary system (Fig. 3b and d)

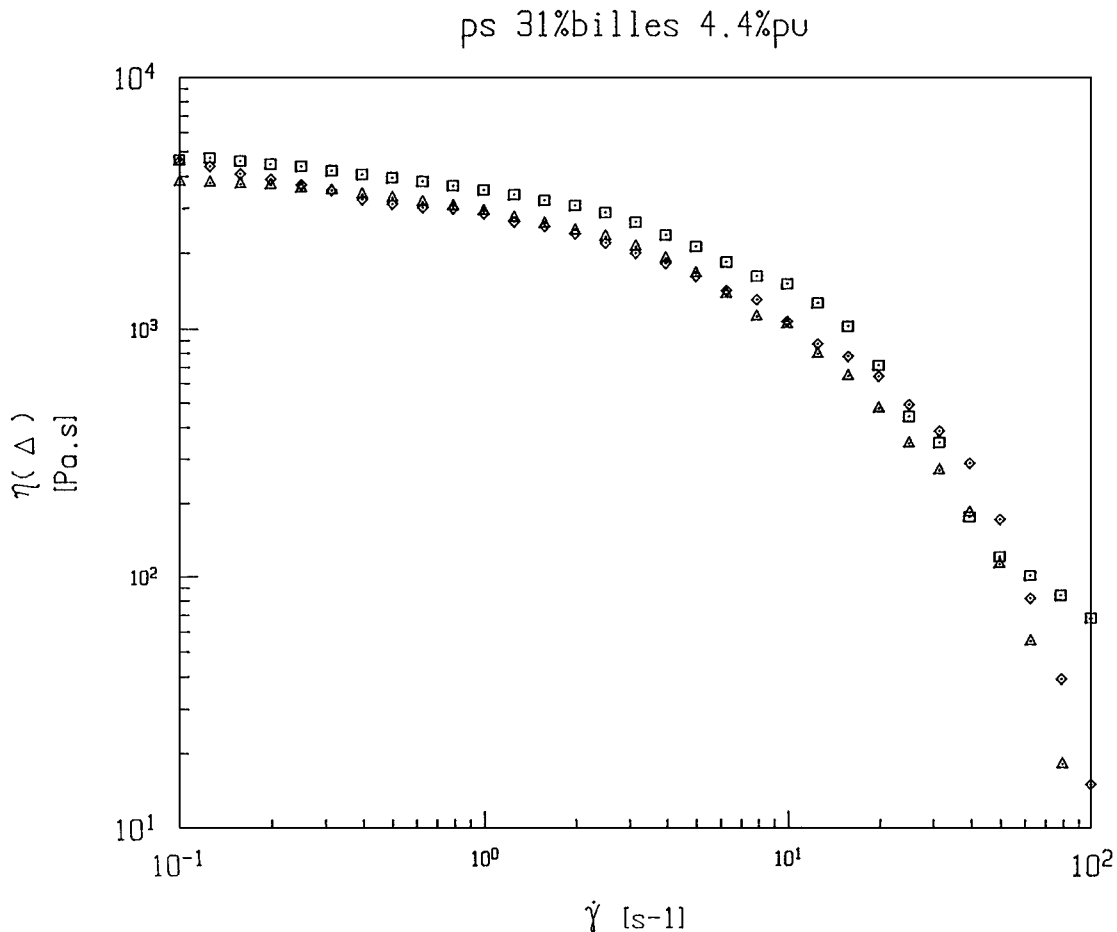


Figure 4 Viscosity evolution of PS (Δ), PS + 31 wt % glass beads (\diamond) and PS + 31 wt % glass beads + 4 wt % PU (\square).

show clearly that polymer fragments remain attached to the glass surface indicating a cohesive failure. As a matter of fact, in these ternary systems, the failure is not brittle since a large plastic deformation of the matrix around the filler particles can be noticed. This phenomenon is similar to that observed for rubber-coated glass beads embedded in a polyepoxy matrix [11]. All of these facts confirm that the polyurethane rubber is located as a thin layer at the glass surface. As a consequence, the desired microstructure, i.e., the encapsulation by the polyurethane of the filler in a pure PS matrix can be made using this method.

The same behavior was found by Friedrich *et al.* [15] for PS filled with aminosilane-treated glass beads processed in the presence of PS-co-MA as modifier.

The rheology of filled polymers in the melt is also very sensitive to the surface modification of filler. The rheological behavior of PS/glass beads/PU ternary blends is given in Fig. 4. As expected, the viscosity of the PU-modified filled PU is slightly higher than for unmodified systems. This phenomenon clearly indicates that the soft polyurethane is located at the interface instead of being a dispersed phase in PS [15]. In fact, Friedrich *et al.* [15] observed that the rheological behavior of PS melts filled with polymer-grafted beads is strongly dependent on the amount of surface grafted polymer. Thus, rheology of unmodified and PU-modified PS melts indicates that encapsulation occurs during processing of PS and glass beads in the presence of polybutadiene and diisocyanate.

This concept can be also used for reducing the volume fraction of rubber in filled materials based on a rubber-modified matrix. In fact, using this methodology, enhancement of fracture toughness is expected without any losses in thermal properties and stiffness of the composite materials.

4. Conclusions

This study showed that a filler coating by a thermoset polymer in a thermoplastic matrix can be carried out by reactive extrusion using a twin-screw extruder by controlling the surface tensions of components. Future studies will concern coating other types of fillers and the effect of such coating on the mechanical and thermomechanical properties of resulting materials.

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