High temperature interfacial tension measurements of PA6/PP interfaces compatibilized with copolymers using a spinning drop tensiometer

(short title: PA6/PP interfacial tension with copolymers)

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ABSTRACT

Interfacial tension measurements of polyamide/polypropylene (PA6/PP) interfaces are reported at high temperature, using a spinning drop tensiometer. Copolymers in different amounts are included in the PP drop, and their migration towards the interface is inferred from the evolution of the drop diameter during the experiment. The importance of the compatibilizer is studied; small amounts of copolymer give rise to a significant decrease of the interfacial tension. Above a critical concentration, the interfacial tension increases again, possibly due to the presence of micelles in the bulk which prevent the copolymer migration.

(Key-Words: interfacial tension; copolymer; spinning drop tensiometer; high temperature)

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INTRODUCTION

The influence of copolymers at interfaces has been studied intensively during the past decade, they are shown to be very effective in improving the mechanical properties of blends of immiscible polymers[1] as well as the adhesion between two immiscible polymers[2]. A very small amount of copolymer added to the blend can produce drastic changes[1]. However, it is still common in the industry to compatibilize blends with large amounts of copolymers.

When dealing with molten polymers, the addition of copolymers has an effect on the morphology of the blend. Desired mechanical properties[1] (yield stress, elongation at break) may be obtained corresponding to different morphologies. These morphologies are very dependent on the addition of diblock or triblock copolymers. Well-dispersed small phases (domains) are generally desired when manufacturing a polymer blend[3]. The effect of concentration of the copolymer on the morphology has been discussed by many authors. The effect of the type of copolymer seems to be well understood, as well as the influence of entanglements[4], chain length[5-6], areal density[5,7-8], and architecture[9-11]. Diblock copolymers seem to be more effective in changing the blend properties, because they locate easily on one or the other side of the interface, whereas a triblock copolymer has to lie across the interface and is therefore less efficient. Molecular theories have been developed[12-14], to take these factors into account. Furthermore, the addition of surfactant can be done in two ways: it can be mixed with the polymer beforehand or included so that the copolymer is formed by chemical reaction *in situ*. The last method is therefore more efficient because it permits one to locate the copolymer where needed, especially at the interface[15-16].

The energy G_c required for the separation of the interface[5,7-8] (double cantilever beam test) may be attained by the introduction of a copolymer A-B, at the interface between two immiscible polymers A and B. The effect of chain density Σ can also be measured by adapting this well-known test for solid samples.

When dealing with melts, the interfacial tension is an important parameter which changes non-linearly due to the presence of compatibilizers. Several studies have shown that small quantities of compatibilizer reduce interfacial tension of polymeric systems by sometimes up to 80%[17-22]. In a strict analogy to water-surfactant systems the critical micelle concentration (cmc) is an important parameter[23]; the cmc is a typical concentration above which micelles are present in the system. Interfacial tension is sometimes found to decrease linearly or logarithmically until the cmc is reached, then it levels off; however measured results for higher concentrations at high temperatures are not available.

The measurement of interfacial tension between molten polymers is difficult[18,19,23-27]. The difficulties are associated with high viscosities and small density differences which make it difficult to reach equilibrium, impurities present in the sample and the high temperatures required. Therefore, methods like drop volume, pendant drop and breaking threads, which rely on small driving forces which cannot be controlled, like gravity or capillarity, are less reliable than the spinning drop for which centripetal gravity is controlled and can be driven to high levels.

In this paper, we propose to investigate the influence of the addition of a copolymer at the interface between two molten polymers. This gives rise to new data which may be applied to previous theories. We use polypropylene-polyamide (PP/PA6) systems, and a copolymer containing polypropylene (PP) and polyacrylamide (PA6), the major part being PA6. The materials used are described in the first part.

We make use of a spinning drop tensiometer[28-29] (US. Patent # 4,644,782, www.SDTensiometer.com) and its recent improvements[30] to determine the interfacial tension between polymer melts. The apparatus is described in section two, as well as an original device for melting polymers in order to manufacture the samples to be used in the tensiometer.

We shall study the effects of adding copolymer to a drop (PP) in a PA6 matrix. The influence of including copolymer to both the drop (PP) and matrix (PA6) will also

be investigated. The main variable for these studies is the volume concentration of the copolymer. This is studied in the next two sections.

Finally, in the last section of this paper, the influence of the speed of migration of the copolymer towards the interface is estimated using diameter versus time diagrams with the aim of determining the effect of surface covering by copolymers.

EXPERIMENTAL SECTION

Materials: PP, PA6 and copolymer

The polymers used are commercial ones, and their properties are listed in table 1. The compatibilizer used in this study is a copolymer which contains parts of polyamide and parts of polypropylene. The major component is polyamide.

The morphology of similar PP/PA6 systems including such copolymer has been investigated previously using ultrasound[31]. In this case, PPmal-g-PA11 was used, and good emulsification was obtained. Such copolymers seem to be good candidates for reducing domain sizes (micron size). The morphology of PA6-PP blends modified with maleated rubbers can also be changed drastically[32-33]. The effect of bonding temperature and time during *in situ* formation of block copolymers in such systems is also important[16], for it allows the mobility of the copolymer. The viscosity ratio between polypropylene and nylon 6 has been shown not to be significant for predicting phase inversion in such blends, but it leads to different particle sizes[34]. Finally, the effect of the mixing procedures[35] shows that improved phase morphology is obtained when using single-step blending. Therefore, such systems are expected to show a significant interfacial tension change, when adding such copolymers.

The copolymer has been mixed with PP or PA6 during separate extrusion processes. The volume concentration of copolymer in each sample varies up to 30% (1%-5%-10%-20%-30%). The PA6 and PA6-copolymer systems are still transparent at the operating temperatures, and will allow visualization of the drop inside, as will be

explained in the next section. Higher concentrations are used, for there are no experimental studies looking at the effect of higher copolymer concentrations.

Density measurements are given in table 2. The density was determined using a capillary rheometer (Göttfert 2001). Using a constant velocity for the piston, the flow rate Q (m^3/s) can be determined. In addition, the mass rate ($\dot{m}$) is calculated using an automated precision balance (kg/s), therefore the ratio $\dot{m}$ /Q gives the density for the different polymers and blends.

There is considerable data for usual polymeric systems[37-43], but none for the PP-PA6 systems. Comparable interfacial tension of about 10-15 mJ/m^2 is available for an EP/PA6 system[24] (ethylene-propylene copolymer vs. polyamide-6) at our working temperature (260°C).

The spinning drop tensiometer

The spinning drop tensiometer is widely used for measuring interfacial tension and considered to be one of the best methods for measuring small values of tension[36-37]. If the speed range of the motor is wide and the testing tube permits the formation of a large bubble, the spinning drop tensiometer can be used to make accurate measurements of both small and large tensions. Unlike other methods, it can be used to measure tension in fluids with high viscosity and/or small density difference; with an adequate oven measurements can be taken in a wide range of temperatures. The spinning drop tensiometer we used (see figure 1) has all these desirable features and is one of the most versatile instruments presently available to measure interfacial tension and is particularly adapted to measurements required for melted polymers.

Most of the so-called shape methods rely on gravity to deform a drop in order to measure interfacial tension; long times are required for reaching equilibrium due to high viscosities but these polymeric systems undergo risks of polymer degradation. The spinning drop tensiometer uses centripetal acceleration to control shape; the time to equilibrium can be controlled by over and under spinning[44].

A spinning polymer drop (small density) is rotated inside another immiscible polymer (high density). The balance of inertial and interfacial forces leads to Vonnegut's formula[36] for the interfacial tension γ (J/m^2)

$$\gamma = \frac{(\rho_2 - \rho_1)\omega^2 d^3}{32} \tag{1}$$

where ρ_1 (kg/m^3) is the density of the drop, ρ_2 (kg/m^3) is the density of the heavier fluid, ω (rad/s) is the angular velocity of rotation and d(m) is the diameter of the drop. Equation (1) is valid under the assumption that the drop is in equilibrium and its length is larger than four times its diameter.

Images of the drop are captured from the camera with a frame grabber in a Pentium II computer. Pictures may be collected every second and played in real time, stored in the computer for later processing using dedicated NT Microsoft^{TM} software. The software measuring system is calibrated using a post with known diameters embedded in the heavier fluid. This allows the measuring of the drop diameter without corrections of index of refraction. This procedure has been described before[28-30] and will not be detailed here.

In the design of the tensiometer, special care has been taken to insure good temperature control, absence of vibrations at high velocities, and data acquisition done on the computer[30]. Also, measurements of diameter versus time allow the determination of relaxational and extensional properties of polymeric systems[29] as well as characteristic times (migration of a compatibilizer is an example).

Manufacturing solid samples

Most polymers are solid at room temperature and are available commercially in the form of beads, flakes, powders or chunks. Starting with these raw materials, we have manufactured samples to be used in the spinning drop tensiometer by melting and forming the polymers in an oven. A special oven was built for this purpose and a method was developed to form different samples. This method is very reliable, inexpensive and produces samples under vacuum, free of contamination and no

oxidation. With this method we were even able to form rods of very brittle polymers (polystyrene) with a molecular weight of 50,000 g/mole.

The forming-oven is shown in figure 2. It consists of an aluminum cylinder with a central chamber. The cylinder contains heating elements (2kW). The polymer is molten in a glass tube (12 mm diameter), which is centered inside the cylinder and positioned vertically using two guides. The top-plug has a small hole (0.5 mm in diameter) through its center that can be connected to a vacuum pump. The lower guide is spring loaded to accommodate for different glass tube lengths. It also has a through hole where a rod pushes the sliding-plug with post from the bottom, when the polymer is molten. The sliding-plug at the bottom seals the glass tube. The glass tubes used to form the polymer samples are not necessary identical to the high precision tubes used in the tensiometer; cheaper ones (same diameter) can be used.

A sample consists of three parts (figure 3). Part A (denser polymer) is the lower one, which has the calibration post. Part B (denser polymer) is the upper part; it contains the drop of lighter polymer (Part C).

The beads (flakes or powder, about 8 grams) are loaded into the glass tube (figure 2) and the other end is sealed with the top-plug. First a vacuum is achieved. Heating the system takes about 15 minutes and cooling about one hour. In general, the target temperature should be a value 10 to 20°C above the melting temperature of the polymer. When melting the polymer, the spring loaded pushing rod (bottom) moves up so that the polymer is compressed. When cooling, the pushing rod also moves down to compensate for volume change.

Figure 2 shows a situation where a sliding-plug with post has been used at the bottom, therefore part B is obtained after melting the beads. For making part A, the same procedure is used, except that the sliding-plug with post is replaced in figure 2 by a sliding-plug with the calibration post. Finally, the last part C is made using a special Teflon^{TM} cylindrical die to form a rod of lighter polymer.

The whole process takes about two hours and a half, producing a good sample in about 80 % of the trials. After putting the different pieces together in the glass tube (Figure 3) which is then set on the tensiometer, vacuum is achieved and the experiment can start.

INFLUENCE OF THE LOCATION OF THE COMPATIBILIZER

In studying the effects of copolymers it has first to be decided whether the copolymer should be inside or outside the drop, or both.

The first set of experiments were carried out with the copolymer inside the PP drop (1%). The interfacial tension was found to be 13.4 mJ/m^2 ± 1 mJ/m^2 (see label 1 on figure 4 or table 3), which is a clear reduction, compared to 15.8 mJ/m^2 which is the value obtained without any compatibilizer.

In a new set of experiments, the copolymer was located both in the PP drop (1%) and in the PA6 matrix (1%). These experiments show that interfacial tension equals roughly 9.0 mJ/m^2 ± 1 mJ/m^2 and is reduced even more, as expected because there is more copolymer present at the interface. These experimental points are also shown in figure 4 (label 1+). This labeling is used because the copolymer concentration in the PP drop is still 1%. Nevertheless, there is actually more copolymer because of the extra molecules situated in the outer polymer.

This result is important and shows that covering of the interface is not achieved completely with 1% copolymer included inside PP, but optimal reduction may be expected when going to higher concentrations.

INTERFACIAL TENSION VS. COPOLYMER CONCENTRATION

Interfacial tension data as a function of copolymer concentration is collected in table 3. At low concentrations (below 5%), the experiments were carried out twice, as indicated in the same table. The concentration of the copolymer is expressed as a

fraction of the total volume of the drop of PP. The graph of interfacial tension vs. concentration is depicted in figure 4.

The rapid decrease of the tension with copolymer concentration is evident and is followed by an increase after a certain copolymer concentration in the neighborhood of 1% to 5%. The increase is not predicted by any theories known to us. In surfactant systems which are better understood, the surface tension levels off after the cmc. The last data point (30%) on the graph may be too high; the system may not have reached equilibrium; it is conceivable that micelles give rise to a yield stress or because of other reasons which we do not understand. Aqueous surfactant systems which give rise to a fall in tension with concentrations below the cmc followed by an increase for concentrations larger than the cmc have been reported[15]. In our case, the interfacial tension starts at a value of around 15.8 mJ/m^2, decreases to at least 8 mJ/m^2, then increases again to a plateau at about 14-15 mJ/m^2. These values are coherent with the only available literature data from Luciani[24] for EP/PA6 systems using a capillary breakup method.

It is probable that as in the case of aqueous surfactants the copolymers preferentially occupy the interface: after the interface is saturated it is likely that the copolymers associate with each other in micellar aggregates. Though the data here is not sufficient to establish which of several theories gives a valid description of the action of copolymers, we may conclude that in the system studied here, the optimal concentration for tension reduction lies between 1% and 5%. Of course, when using industrial systems where more drops exist, it may be better to use higher amounts of copolymer to cover larger surfaces.

DIFFUSION OF THE COPOLYMER. MIGRATION TIMES

Diffusion of the copolymer towards the interface is very important in terms of efficiency of one copolymer or another. Depending on the location of the copolymer, different results may be obtained. As seen recently[45], the way to lead the compatibilizer

to the interface is crucial: using a conical die in coextrusion for instance is more efficient for reaching equilibrium in interfacial tension measurements using the breaking thread method. In the present experiment, it is the centripetal acceleration which brings the copolymer to the interface, for its density lies in between these of the two other polymers. There is effective migration because we see a decrease of the interfacial tension by about 50%, at least for the low concentrations.

To investigate these effects better, diagrams showing drop diameter d(t) versus time t may be reported[28-29]. One can reduce the diameter data with the final diameter d_∞ and plot d/d_∞-1. A good dimensionless parameter[30] is $t\gamma/(\mu_1+\mu_2)d_\infty$ (μ_1 and μ_2 are the viscosities of PP and PA6 respectively). This representation is good to decide on the efficiency of the copolymer, since d/d_∞-1 will be seen to decrease to 0 in such a case.

The variations of d/d_∞-1 vs. $t\gamma/(\mu_1+\mu_2)d_\infty$ for four previous experiments are shown in figure 5. The significant decrease to zero shows that equilibrium is obtained. Cases with 1% interfacial agent or 1+% (both fluids) are slower and similar to each other and the reaching of equilibrium is probably mainly concerned with the migration of the copolymer on each side of the interface. Migration of the copolymer is slow, therefore longer migration times may be needed, compared to the case with no copolymer.

On the other hand, it seems that the reaching of equilibrium is faster for the 5% case. Actually, the system seems to stop rapidly at its final position (d_∞). An explanation of this can be based on physico-chemical principles. Polypropylene (PP), which involves mainly dispersive interactions does not have affinities with the Polyamide (PA6), which likes water and develops polar interactions. Copolymers located in the drop bulk migrate rapidly towards the interface in the low concentration cases (1 and 1+), because they do not like being inside PP. As soon as the concentration has reached the critical micellar concentration (cmc), the interface is completely covered with copolymers, and there is no more space for the copolymers to go there:

they will stay inside the drop and form micelles. This tends to create yield stresses, which eventually stop the migration, therefore, reaching d_∞ is rather fast.

In any case, this method of measuring interfacial tension together with d(t) diagrams seems very efficient for estimating migration times, and the efficiency of the copolymer has been clearly demonstrated at low concentrations. At higher concentrations, it appears that yield stresses due to the presence of micelles prevent further deformation of the system.

CONCLUSION

The evolution of interfacial tension as a function of compatibilizer concentration has been studied for PP/PA6 systems with a spinning drop tensiometer. The system also allows one to determine accurate diameter data, and the time needed for reaching an equilibrium diameter is the migration time of the copolymer to the interface. In addition, an original and inexpensive system for manufacturing samples has been described.

Copolymer has been included in the drop of lighter polymer (PP). It is shown that, as in other systems, the presence of a copolymer reduces the interfacial tension, and this can occur at very low concentrations. Above a certain concentration ($\approx 5\%$), the presence of micelles prevents diffusion of the copolymer.

This method seems very promising for predicting the influence of various compatibilizers, and their molecular weight, architecture, randomness may be further investigated. It could be also very helpful for testing various theoretical models.
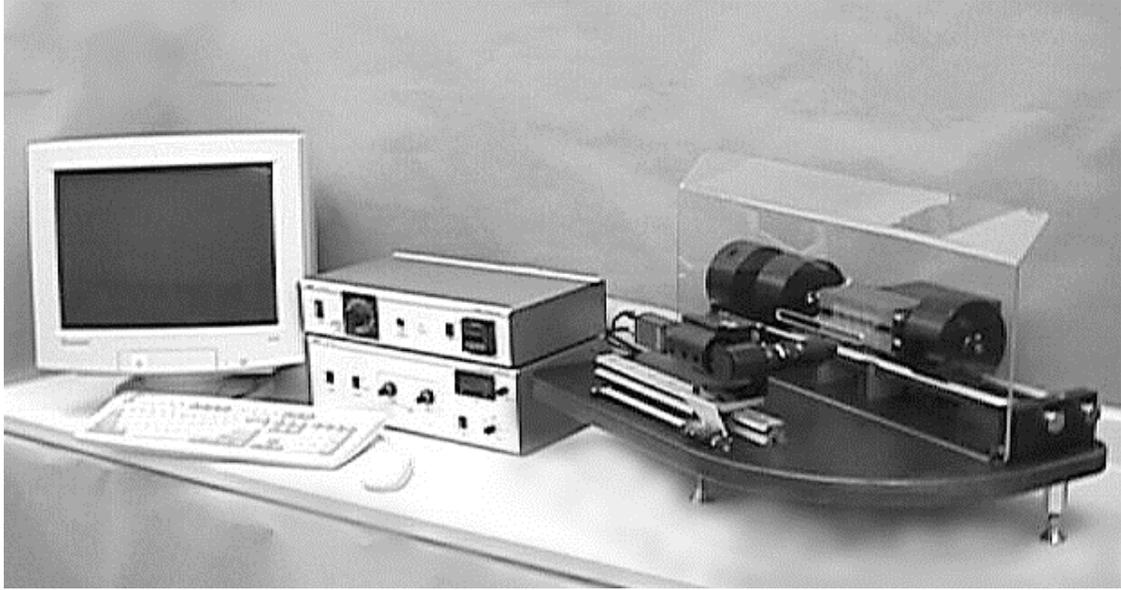
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FIGURE CAPTIONS

Figure 1   General view of the tensiometer.

Figure 2   Oven to form polymer rods. A glass tube with sliding plug and post has been included. In this case, part B is made after melting and cooling.

Figure 3   Solid sample assembled in the glass tube and ready for loading in the tensiometer. Part A: dense polymer with calibration post. Part B: dense polymer with hole for the drop. Part C: drop of light polymer

Figure 4   Interfacial tension vs. concentration of copolymer in PP drop. Label 1 corresponds to a 1% concentration in the drop, Label 1+ corresponds to 1% both in the drop and the outer polymer. The dotted line is a guide for the eye.

Figure 5   Typical reduced diameter vs. reduced time diagram at different compatibilizer concentrations
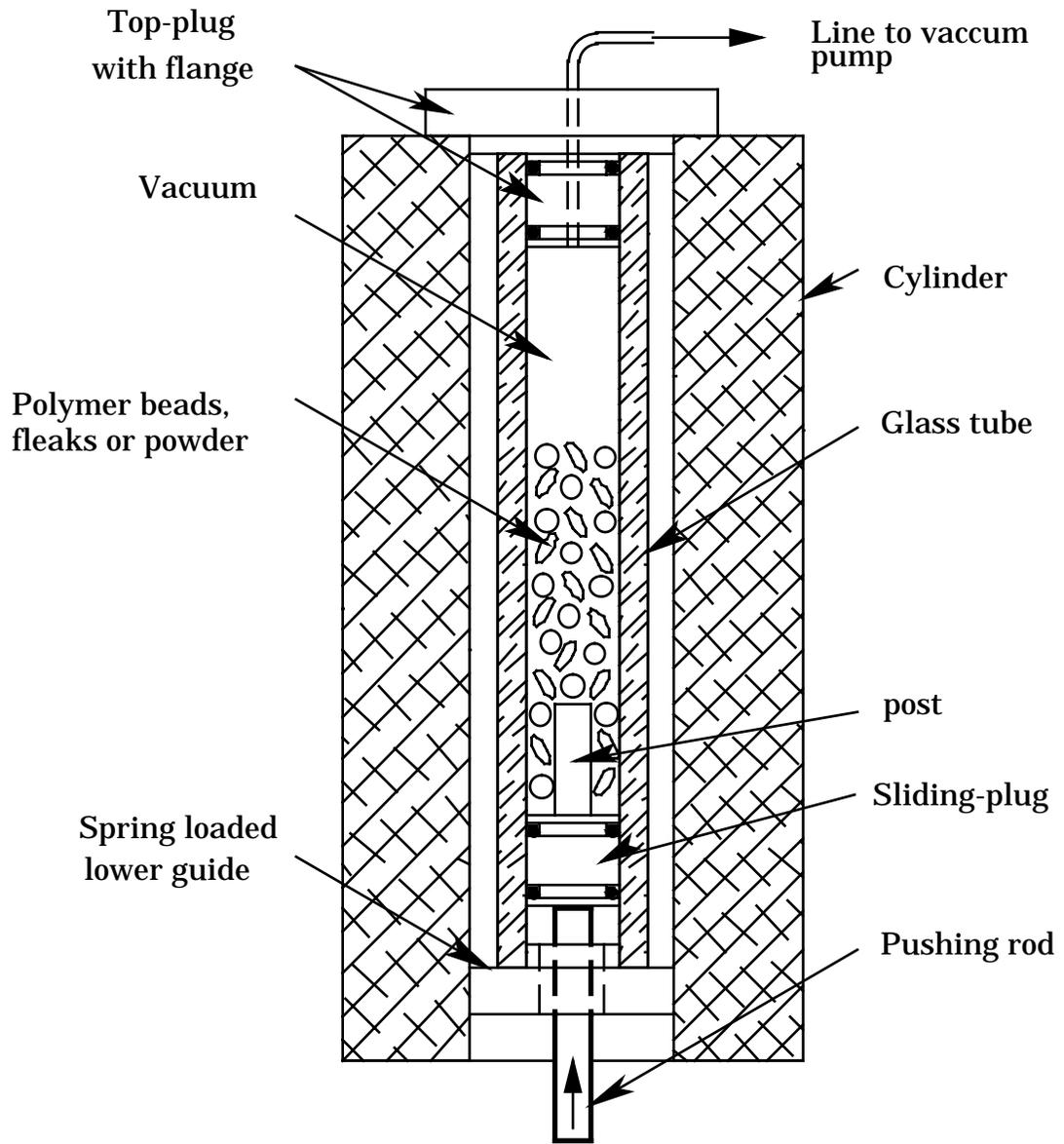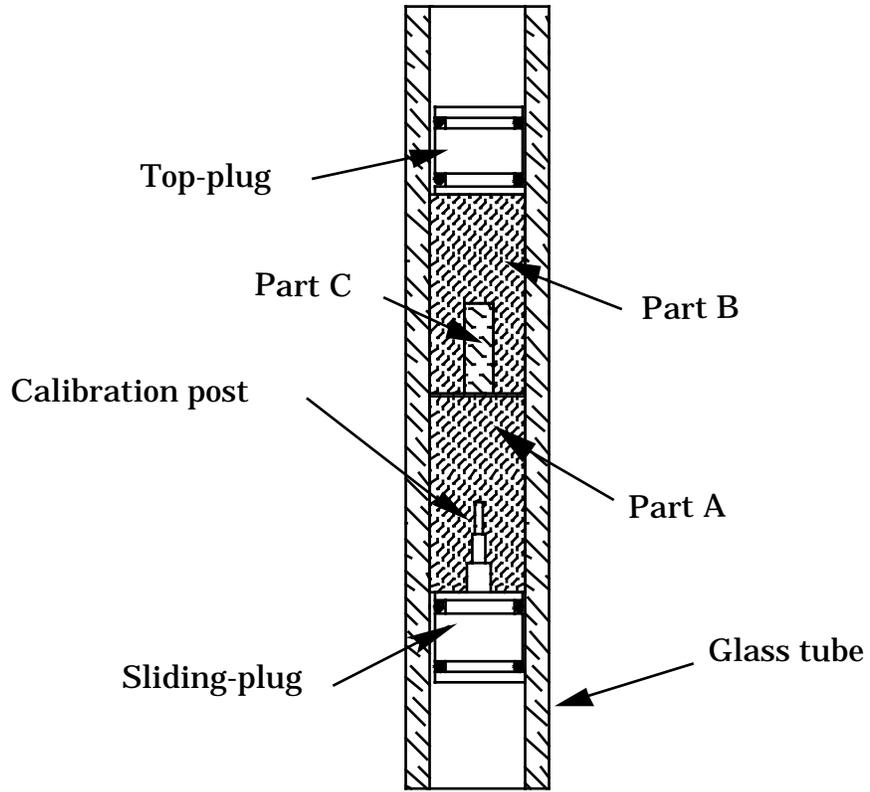
FIGURE 1

Top-plug
with flange

Vacuum

Polymer beads,
fleaks or powder

Spring loaded
lower guide

Line to vaccum
pump

Cylinder

Glass tube

post

Sliding-plug
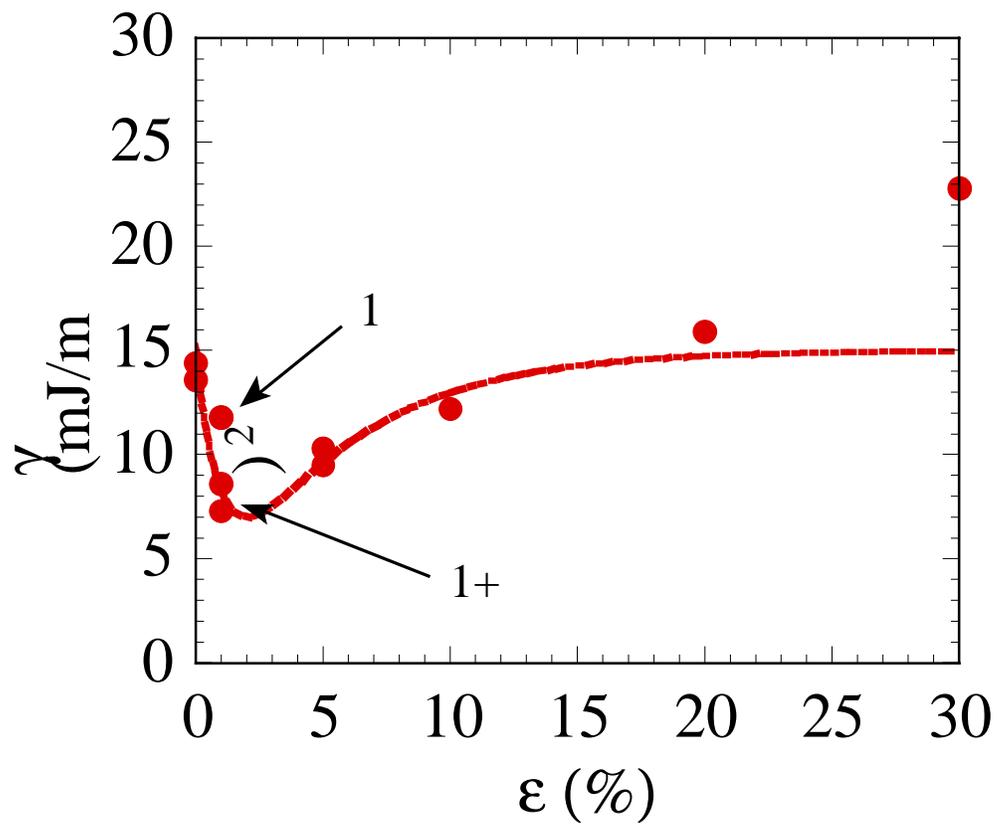
Pushing rod

FIGURE 2

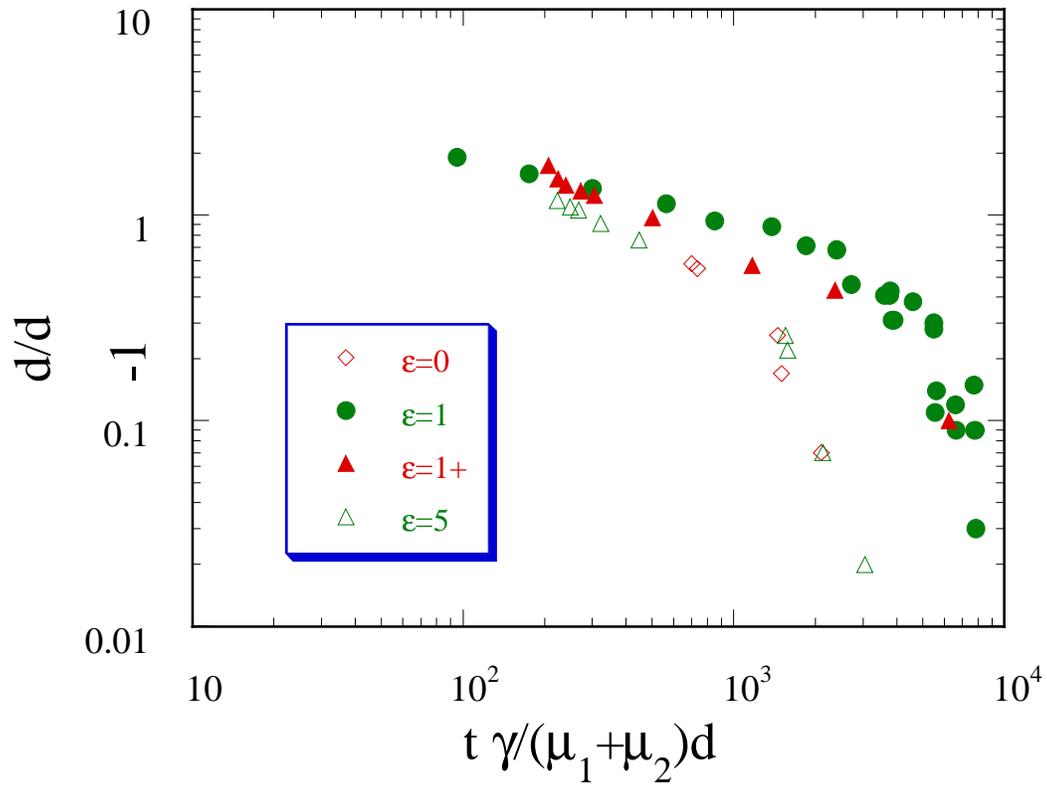**FIGURE 3**

FIGURE 4

FIGURE 5

TABLE CAPTIONS

Table 1 Polymer properties.

Table 2 Densities of polymers at different concentrations of copolymer at 260 °C.

Table 3 Data corresponding to interfacial tension vs. copolymer concentration (fig. 4)

Table 1

Polymer	Type	Viscosity μ at 260°C (Pa.s)
PA6	Ultramid B3	673
PP	Finasphere 1030S	1703
copolymer	-	-

Table 2

Concentration (% vol)	0	1	5	10	20	30
ρ_1 (kg/m^3)	730	731	730	733	743	749
ρ_2 (kg/m^3)	980	980[*]	980	980	980	980

([*] except for experiment where copolymer is also outside: ρ_2=975 kg/m^3)

Table 3

Volume concentration (%)	T (°C)	Final diameter d_∞ (mm)	ω (rpm)	γ (mJ/m^2)
0	260	2.236	4004	15.4
0	260	1.733	6040	16.3
1	260	2.139	4007	13.4
1	260	1.804	5168	13.4
1+	260	2.208	3009	8.1
1+	260	1.864	4220	9.6
5	260	2.001	4006	11.0
5	260	1.744	5117	11.9
10	260	2.126	4208	14.4
20	260	2.330	4298	19.0
30	260	2.268	5508	28.0