Wettability of glass substrates by molten nylon-6

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A study of the adhesion of molten nylon-6 to glass, vitreous silica and dehydrated silica is performed by the sessile drop method at 243°C. The influence of polymerization conditions, nature of substrate, thermal pretreatment of the polymer and lithium chloride addition on wettability is examined. The most relevant results show that thermal pretreatment of the polymer is a determining step in wettability and that LiCl addition causes an increase of contact angle, as a consequence of the decrease in the substrate–molten polymer interactions. The results are interpreted by means of an interfacial model based on additive polar and dispersion forces.

INTRODUCTION

The relevant development of research on the interactions at interfaces over the last fifteen years, is evidenced by the number of scientific reports. Great interest has been shown in the interactions between a polymeric phase and a solid substrate, which is related to potential applications to reinforced polymeric materials and particularly to composites[1-6].

Studies on wetting, spreading, and liquid to solid adhesion have been reexamined by carefully controlled experiments. Specifically, studies on adhesion of molten polymers (polyethylene, polystyrene, polyamides) to glass have been performed in order to evaluate the parameters which influence wetting kinetics[7-9] and explain the chemical and physical phenomena of adhesion[10,11].

In our laboratories we are at present carrying out studies on wetting and adhesion phenomena[12-14], as well as the effects of inorganic salts on the chemical, physical and mechanical properties of aliphatic poly-amides. In particular, we are studying the nylon-6–lithium chloride system, for which we have already found that LiCl depresses the polymer melting temperature[15], reduces the crystallization rate[16], and increases the melt viscosity[17], Young's modulus[18,19] and glass transition temperature[19,20]

The aim of the present work is to obtain further information on the behaviour of 'salt-added' nylon-6 by testing the influence of LiCl on the adhesive properties of this system to glassy substrates, especially because anomalous adhesion phenomena had been found after anionic polymerization of caprolactam in the presence of LiCl, giving rise to an implosion of the glass reactor.

This study has been performed using the sessile-drop technique[21] and measuring the contact angle between molten polymer and the solid glassy substrate. The value of the contact angle depends on the interactions between phases.

At equilibrium, Young's relation[22] states that:

$$\sigma_{SV} = \sigma_{SL} + \sigma_L \cos\theta \qquad (1)$$

where σ_{SV} and σ_{SL} are the solid–vapour and the solid–liquid interfacial tensions, respectively, σ_L is the surface tension of the liquid phase and θ is the contact angle between solid and liquid phase (*Figure 1*).

Equation (1), which may be rewritten as:

$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_L} \qquad (2)$$

clearly shows that the contact angle may be smaller or larger than 90°, depending on the sign of the difference $(\sigma_{SV} - \sigma_{SL})$. In particular, if we are dealing with a given substrate $(\sigma_{SV} = \text{const})$ the liquid wets or does not wet the solid depending only on the interfacial tension value.

Following Dupre[23] we can define the work of adhesion, W_{SL}, between the liquid and solid phases as:

$$W_{SL} = \sigma_S + \sigma_L - \sigma_{SL} \qquad (3)$$

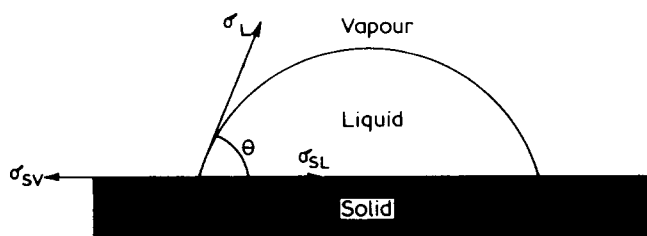where σ_S is the surface tension of the solid.

Figure 1 Contact angle and surface tensions for a liquid drop on a solid surface

By substituting equation (1) into equation (3), we have:

$$W_{SL} = \sigma_S - \sigma_{SV} + \sigma_L(1 + \cos\theta) \qquad (4)$$

i.e.

$$W_{SL} = \sigma_L(1 + \cos\theta) + \pi_e \qquad (5)$$

where $\pi_{e'} = \sigma_S - \sigma_{SV}$ is the spreading pressure.

If π_e is known or negligible, equation (5) enables us to obtain a thermodynamic value (W_{SL}) which is a true measure of wettability in the given system.

The solid substrates employed in our experiments have similar surface tension values as have the liquid phases. For the above reasons, the fundamental parameter which governs the wetting of glasses by our molten polymers is the interfacial tension (if π_e is similar, as shown later). This quantity is the result of the different types of interfacial forces built up at the solid–liquid interface.

Several attempts have been made in order to evaluate σ_{SL} from a theoretical point of view[24-32].

Application of the additivity principle to intermolecular forces[27,28] led to simple equations relating the interfacial tension to surface tensions as well as polarity of the phases in contact. Intermolecular energies are assumed to be made of additive polar and dispersion components, the surface tension of ith phase is given by:

$$\sigma_i = \sigma_i^d + \sigma_i^p \qquad (6)$$

Thus we may write:

$$\sigma_{SL} = \sigma_S + \sigma_L - 2\varphi^d - 2\varphi^p \qquad (7)$$

where φ^d and φ^p are measures of the dispersion and polar contributions, respectively. Different averages of dispersion and polar contributions to the different surface tensions may be used in order to evaluate these parameters.

The expression most widely used and more appropriate for our system, is the 'geometric mean' equation:

$$\sigma_{SL} = \sigma_S + \sigma_L - 2(\sigma_S^d \cdot \sigma_L^d)^{1/2} - 2(\sigma_S^p \cdot \sigma_L^p)^{1/2} \qquad (8)$$

It has been noted[27] that the geometric mean equation gives good results for interfaces between polymers and high-energy materials (metals, metal oxides, inorganic glasses and mercury). Similar equations have also been suggested by Owens and Wendt[30], Kaelble and Uy[31], and Hata[32].

In cases where only dispersion forces operate (i.e. when the liquid and/or the solid is non polar), the polar term may be neglected and equation (8) becomes the Fowkes equation[29]:

$$\sigma_{SL} = \sigma_S + \sigma_L - 2(\sigma_S^d \cdot \sigma_L^d)^{1/2} \qquad (9)$$

EXPERIMENTAL

Materials

Polymer samples preparation   Our polymer samples have been synthesized by activated anionic polymerization in bulk carried out under adiabatic conditions[33]. To achieve a homogeneous distribution of the salt in the polyamide, the salted systems have been prepared by pre-

mixing the monomer (caprolactam) with the given amounts of lithium chloride (from 1.8 to 8.1 wt %), followed by polymerization. Both unsalted and salted samples have been synthesized with two different activator (A) to initiator (I) ratios $(r = [A]_0/[I]_0$ equal to one or three) keeping the activator to monomer ratio constant. Activator and initiator are N-acetyl-caprolactam, and lithium hydride, respectively. Experimental details for the polymerization are given elsewhere[34].

Table 1 collects some characterization data of the examined samples. Before contact angle measurements, polymer samples were conditioned to avoid gas bubble formation during experiments. The samples were degassed under vacuum at 260°C for ~3 h or compression-moulded at $T = 250$°C for a few minutes. The latter method is necessary for salt-added polymer owing to its viscosity. Homogeneous polymer pieces are cut out from pretreated samples and stored in a desiccator in the presence of phosphorous pentoxide until use.

Substrates   Soda-lime glasses (microscope slides) and vitreous silica in the form of square pieces ($15 \times 15 \times 2$ mm) have been used. Before use, the mirror-finished surfaces of the substrates have been etched by concentrated HNO_3, washed under distilled water and rinsed in acetone. In order to assess the influence of surface condition on wetting characteristics of our systems, part of the experiments have been performed on highly dehydrated silica specimens. This was done by heat treating the specimens under vacuum at ~850°C for 2–3 h. This treatment is irreversible and leaves the surface almost free from –OH groups (about one –OH for 100 $Å^2$)[36]. All the treated substrates are stored at ambient temperature under an argon atmosphere.

Sessile-drop measurements

The sessile-drop experiments were carried out in a resistance furnace in which a laboratory tube, made of vitreous silica, can be heated under vacuum or controlled atmosphere up to 1100°C. The temperature recorded by a Pt/PtRh thermocouple near the molten specimen, is maintained constant within ± 1°C. The system (*Figure 2*) can be evacuated after the introduction of the specimen in a cold chamber, and brought to the preset conditions of temperature, composition and pressure of gas. Afterwards, the specimen itself is carried into the working chamber by a push-rod operated magnetically from

Table 1 Characterization data of unsalted and salted polycaprolactam specimens

Sample	$r = \dfrac{[A]_0}{[I]_0}$	$[\eta]$ * (cm^3/g)	LiCl wt %	Pretreatment
A	1	215[a]	0	Degassed/Compression-moulded
B	3	–	0	Degassed/Compression-moulded
C_1	1	160[a]	1.8	Compression-moulded
C_2	1	150[a]	3.7	"
D_1	3	–	1.8	"
D_2	3	–	5.4	"
D_3	3	–	8.1	"

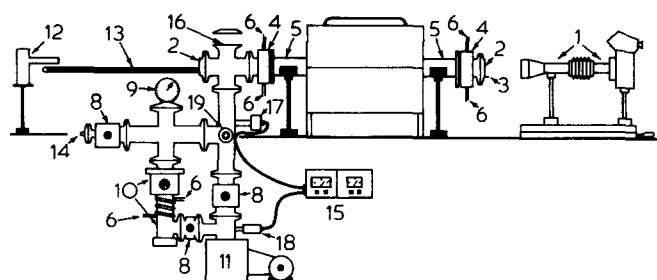* Data obtained before pretreatment of the samples
[a] Ref 35

Figure 2 Apparatus for the sessile-drop experiments. (1) Photographic system; (2) optical window; (3) thermocouple out-put; (4) water cooled vacuum seals; (5) laboratory tube; (6) water cooling; (7) furnace; (8—11, 14, 15, 17—19) vacuum system; (12) mercury lamp; (13) magnetic system for specimen input in the furnace; (16) window for specimen input
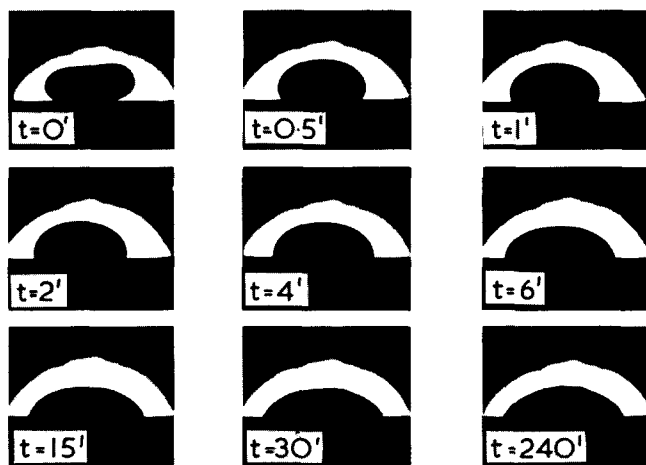

Figure 3 Behaviour of contact angle against time for degassed Ny A (r = 1) on glass

outside. The specimens, perfectly levelled, are photographed using a 200 mm telephoto lens with a mercury lamp as light source. Contact angles were measured directly on the negative film by means of a Leitz MCM Metrological microscope. All nylon specimens have been melted previously under a pressure of 300 Torr of helium on a steel plate in order to obtain a drop which could give a good cylindrical symmetry on the vitreous substrate. The experiments were carried out under helium at 700 Torr and at 243 ($\pm$2)°C. Photographs were taken at different time intervals until the equilibrium angle was obtained ($\sim$4–5 h; *Figure 3*). The reported contact angle values are an average over at least three measurements on different samples of the same batch.

RESULTS AND DISCUSSION

Our results are grouped on the basis of:
(i) the nature of the solid phase
(ii) the type of the pretreatment to which the polymers were subjected.

The effect of LiCl additions will also be considered.

Unsalted nylons on different substrates

The experimental values of equilibrium contact angles and the calculated driving force for wetting ($\sigma_{SV} - \sigma_{SL}$) are reported in *Table 2* for degassed specimens A ($r = 1$) and B ($r = 3$) on glass, vitreous silica and 'treated' vitreous silica.

The value of the driving force of wetting has been calculated by taking $\sigma_L = 36$ mN m^{-1}, which is a mean and rather reliable value for the surface tension of hydrolytic molten nylons[37].

The contact angle for specimen A is always smaller than 90°, while for specimen B it is always greater than 90°. In both cases the value of θ increases with the decrease in the number of active centres (heterocations and -OH groups) on the substrate. This is made evident by the simultaneous decrease of the driving force for wetting which becomes negative when we pass from A to B.

A degassed 'hydrolytic' sample of nylon-6 gives us a value of θ equal to 79° on a glass substrate.

Influence of polymer pretreatment on adhesion

In order to elucidate the possible effects of the thermal pretreatment on the stability and adhesion characteristics of our polymers, we tested samples treated as described in the experimental section. The r value strongly affects the degradation process of these polymers, as studied by Sebenda and Kouril[38]. In particular, they found that when $r = 1$ cleavage reactions predominate, as a consequence of the higher quantity of strong bases. However, when $r = 3$ one observes a decrease in the number of molecules as a function of time. This is probably due to condensation reactions which prevail over cleavage reactions.

The results, shown in *Table 3*, refer to a single substrate, 'treated' silica, which enhances the differences in behaviour of the two polymer types (see below). The trend observed in equilibrium contact angles confirms that the thermal history of the two materials is the determining step in wettability. The compression-moulded samples behave similarly, giving contact angle values which agree within experimental uncertainty. However, the drastic degassing procedure makes the $r = 1$ specimens wet the silica substrate much better than $r = 3$ specimens. This may be due, in the case of $r = 1$, to a larger number of available active centres which can 'react' with the solid,

Table 2 Contact angles and driving force for wetting for molten polycaprolactam samples on several substrates

| | Degassed samples | | | |
| | A (r = 1) | | B (r = 3) | |
Substrate	Contact angle, θ (degrees)	$\sigma_{SV} - \sigma_{SL}$ (mN·m^{-1})	Contact angle, θ (degrees)	$\sigma_{SV} - \sigma_{SL}$ (mN·m^{-1})
Glass	65	15.3	103	−8.1
Vitreous silica	74	9.9	113	−14.1
Dehydrated vitreous silica	78	7.5	125	−20.7

Table 3 Influence of polymer pretreatment on contact angle of A and B samples on dehydrated vitreous silica

Sample	Pretreatment	Contact angle, θ (degrees)
A (r = 1)	degassed	78
	compression-moulded	91
B (r = 3)	degassed	125
	compression-moulded	94

Table 4 Interfacial tensions and spreading pressure values for different degassed nylon-6–substrate systems

System	σ_{SL} (mN·m^{-1})	π_e (mN·m^{-1})
Nylon-A–glass	191	123
Nylon-B–glass	218	120
Nylon-A–silica	146	144
Nylon-B–silica	164	150

decreasing the interfacial tension and the contact angle from 91 to 78. In the case of $r = 3$, decreasing the number of active centres makes σ_{SL} and θ increase from 94 to 125.

Sebenda et al.[38] have isolated several different species which can be formed during the base-catalysed degradation of polycaprolactam (keto-imides, keto-amides, diamino-ketones, uracils, isocyanates, etc.) rich in polar groups able to interact with the solid surface.

Adsorption on solid phases and wettability

Equation (8) may be used to calculate σ_{SL} for our systems, provided that the polar and dispersion contributions to the surface tension of the materials are known. From literature we have:

$$\sigma_{S, glass} = 330 \text{ mN m}^{-1} \text{ (ref 39)}*$$

$$\sigma_{S, glass}^d = 30 \text{ mN m}^{-1} \text{ (ref 40)}$$

$$\sigma_{S, silica} = 300 \text{ mN m}^{-1} \text{ (ref 41)}$$

$$\sigma_{S, silica}^d = 78 \text{ mN m}^{-1} \text{ (ref 29)}$$

Assuming that the surface tension of the ith phase is given by equation (6), we may obtain the polar contribution as the difference between $(\sigma_i - \sigma_i^d)$.

Owens and Wendt's method[30] was used on the degassed specimens A and B, to determine the relative contributions to solid surface tension of dispersion forces. This method consists of measuring the contact angles formed on a solid nylon substrate by two liquids with different polar and dispersion contributions to surface tension, namely water and methylene iodide. In our case, using the values:

$$H_2O \quad \sigma_L = 72.8 \text{ mN m}^{-1}; \quad \sigma_L^d = 21.8 \text{ mN m}^{-1}$$

and

$$CH_2I_2 \quad \sigma_L = 50.8 \text{ mN m}^{-1}; \quad \sigma_L^d = 49.5 \text{ mN m}^{-1}$$

we obtained the ratios:

$$\left(\frac{\sigma_S^d}{\sigma_S}\right) = 0.66 \text{ Ny A degassed}$$

$$\left(\frac{\sigma_S^d}{\sigma_S}\right) = 0.82 \text{ Ny B degassed}$$

These ratios are measured for solid samples, but, to a first approximation, they will be retained valid and unchanged for the polymers in their liquid state. Assuming that

$$\sigma_{L, Ny A} = \sigma_{L, Ny B} = 36 \text{ mN m}^{-1}$$

* Extrapolated from liquid values.

we calculated the interfacial tensions for the systems nylon-6-glasses, reported in *Table 4*.

Combining equation (8) with Young's equation (1), we derive an expression for the spreading pressure, π_e:

$$\pi_e = 2(\sigma_S^d \cdot \sigma_L^d)^{1/2} + 2(\sigma_S^p \cdot \sigma_L^p)^{1/2} - \sigma_L(1 + \cos\theta) \quad (10)$$

The values shown in *Table 4*, demonstrate that a large decrease in solid surface tension takes place when the polymers melt under non-oxidizing conditions. The π_e values are of the same order of magnitude as the spreading pressures measured on silica in contact with other single organic liquids (120-150 mN m^{-1})[42]. This suggests that the adsorbed species are low molecular weight compounds which come out of the molten phase because of the decomposition processes. However, σ_{SL} values increase, for the same substrate, when passing from $r = 1$ to $r = 3$ specimens.

Salted nylons

Specimens C_1, C_2, D_1, D_2, D_3 have been examined on 'treated' silica. *Table 5* shows that the presence of lithium chloride depresses the wettability, increasing the contact angle from a value near 90 to around 110, independent of salt concentration.

For comparison we made some tests with salted polymers on glass substrates and obtained the following values:

$$C_2: \theta = 115$$

$$D_2: \theta = 108$$

which are very close to those obtained on 'treated' silica (*Table 5*). The presence of LiCl masks the different behaviour on various solid substrates.

There is considerable experimental evidence[43] that lithium ion coordinates with the carbonyl group of a polyamide. Consequently there should be a decrease in the number of interaction centres between polyamide chains and hydroxy groups of the vitreous substrate. This would explain the higher contact angle values shown by salted specimens with respect to pure samples. On the basis of the above arguments, θ should increase with increasing salt concentration, but this is not generally true. θ increases about 20° upon first addition ($\sim 1.8\%$) of LiCl, but does not show significant changes on further salt additions.

CONCLUSIONS

This paper is mainly aimed to study the behaviour of molten nylon-6 on glass and silica surfaces. It was not

Table 5 Contact angle values for salted polymer samples on dehydrated vitreous silica

Sample	LiCl (wt, %)	Contact angle, θ (degrees)
A	0	91
C_1	1.8	109
C_2	3.7	114
B	0	94
D_1	1.8	109
D_2	5.4	111
D_3	8.1	110

possible to deduce the exact role which the physico-chemical parameters plan in adhesion phenomena in our system. Nevertheless from the above results we can deduce the following points.

Degassed nylon-A has a much better adhesion than degassed nylon-B whereas the two nylons, when compression-moulded, show the same adhesion. This difference is not attributed to the value of r but to the different type of pretreatment. In fact, the r value affects the degradation processes that the polymers may undergo during their preparation. Polymers with $r=1$, which present a large residual concentration of base, may be subjected, during the degassing procedure, to cleavage reactions which generate a large number of short chains. However, polymers with $r=3$ show a decrease in the number of molecules with time, probably due to condensation reactions which take place when the basicity of the system is very low. This difference in behaviour suggests that a large number of short chains, outcoming from the degradation processes, maximize the interaction centres with the substrate. As a consequence the degassed nylon-A wets better than the corresponding nylon-B, as shown by the decrease in interfacial energy (see *Table 4*).

Compression-moulded specimens, however, which show similar contact angles, do not undergo large changes in the average molecular weight (probably because this type of pretreatment does not involve a long permanence of the polymer at high temperature). Therefore, they can interact in a similar way with the active centres of vitreous substrates.

The addition of LiCl to nylon-6 causes a large increase in contact angles as a consequence of the decrease in the solid–liquid interactions. Moreover, the presence of LiCl seems to suppress the difference shown by pure nylon-6 on different substrates. This may be caused by the coordinating action of Li ion with carbonyl groups of the polyamide — consequently the interactions between polymer chains and –OH groups of substrates are reduced. It has been shown recently[10] that polyamides interact with silica hydroxyl groups by means of hydrogen bonds between these groups and carbonyls of the amide functions, also the NH group of the polyamide does not interact with the vitreous surface. Nevertheless, the true mechanism of this phenomenon and the quantitative dependence of contact angles on salt concentration remain unknown.

Calculations have been made of the dependence of experimental contact angles on adsorption phenomena on solids by molecules coming from the liquid phase. These calculations have shown that adsorption does exist and that degassed nylon-A and -B present similar spreading pressure values, both on glass and on silica surfaces. This allows us to conclude that these fluid phases, at about 250°C, give rise to vapour phases, formed by molecules of the same type.

On the basis of the present results, we exclude that the breaking of the reactor glass walls is due to an improved adhesion of nylon to the glass surface, induced by the lithium salt. Direct evidence has been obtained by removing from the broken reactor the salted polymer sample and by surface cleaning and remelting it under the same conditions as for the polymerization. After cooling, no destructive tensions on the reactor were found and the solidified polymer mass was found completely detached from the wall. Other factors, such as specific adsorptions and links on the glass surface during the polymerization, must be invoked to account for the described phenomena.

A spectroscopic study of the adsorption during the various stages of polymerization could give, in our opinion, relevant answers to this point.

ACKNOWLEDGEMENTS

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