Diffusion and self-adhesion of the polyimide PMDA–ODA

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The relationship between the interdiffusion of two layers of the polyimide PMDA–ODA and the adhesion between the two layers has been examined. The polyimide layers were made by successively depositing a polyamic acid layer from solution and then curing the layers at elevated temperature to the polyimide. Diffusion occurred during the curing process of the second layer and was controlled by the cure schedule. The interdiffusion was measured using forward recoil spectrometry (FRES) and the adhesion measured by peel tests. Good correlation was found between the interdiffusion distance and the adhesion. It was found that a large diffusion distance, at least 200 nm, was required to obtain a bond whose strength was equal to that of bulk material.

(Keywords: diffusion; self-adhesion; polyimide)

INTRODUCTION

The adhesion of polymers to themselves (self-adhesion or autohesion) is a subject of technical importance that has inspired considerable scientific interest. There seems to be general acceptance of the primary role of diffusion across the interface to allow chains to entangle as the main mechanism of adhesion in most situations[1-3]. These situations include the adhesion (tack) that is observed when two surfaces of an uncrosslinked elastomer are pressed together and the welding or crack healing that occurs when a rigid polymer is heated above its glass transition or melting temperature. Several theories of tack or healing have been proposed recently based on the reptation model of polymer diffusion[4-10]. The main differences between these models are in the assumptions that have been employed on the relationships between failure stress or energy and the number of chain segments or total length of the polymer chains crossing the interface. Although differing in detail these theories all assume that the time necessary for one tube renewal, which corresponds to a diffusion distance of a radius of gyration of the chain, is sufficient to return the strength of the interface to that of the bulk material.

The experimental situation is not entirely clear, even in non-crystallizing elastomers where the failure processes are not as complex as those found in glassy or semi-crystalline polymers. From studies on mixtures of uncrosslinked polyisobutylene with a crosslinked butyl rubber, Ellul and Gent[11] delineated the relative importance of adsorption and diffusion in that system. Bothe and Rehage[12] and Wool[13] have summarized the evidence for the diffusion model of tack but in neither case were accurate measurements of diffusion available so that the theories, and particularly the assumptions of diffusion

distance required for complete healing, could not be evaluated quantitatively. Recently, however, Roland and Böhm[14] measured the diffusion across an interface of polybutadiene using neutron scattering and found that the autohesion of the polybutadiene continued to increase over times two orders of magnitude greater than that required for diffusion distances of one molecular radius of gyration. They speculated that a minor quantity of branched chains that diffuse very slowly might be responsible for the interfacial strength.

Welding or crack healing experiments on glassy polymers have been published by Kausch and co-workers[15-17] and Wool and O'Connor[9]. Both groups found that the strength (as measured by critical strain energy release rate) of an interface increases as the square root of healing time, a result that is consistent with the diffusion theory. Again the diffusion was not measured directly under the same conditions as the crack healing and, therefore, the assumptions on the amount of interdiffusion required to restore full strength were not tested. In addition crack tip studies using optical interference techniques[16] show that the failure mode of partially healed materials is complicated. This complexity probably occurs because there is no driving force for a crazing type of failure to follow precisely along the weakest line as the onset of strain softening ahead of the craze tip may not be greatly affected by reduced entanglement. Experiments by Robertson[18] using thin films of low molecular weight polystyrene to bond two acrylic sheets where the locus of failure did not necessarily keep to the polystyrene re-emphasize this point.

The self-adhesion of the aromatic polyimide made from pyromellitic dianhydride and oxydianiline (PMDA–ODA) is technically important. It is not, however, a

simple problem as the polymer is laid down from solution as an amic acid that converts to the imide on curing at elevated temperature. The interfacial strength is expected to depend on the interdiffusion of the two layers, which itself is controlled by the cure temperatures and times of the first layer and the combined system. The aim of the work described in this Paper is to explore the relationship between interdiffusion and adhesion in PMDA–ODA via a combination of diffusion results obtained using ion scattering techniques with adhesion results from mechanical testing.

EXPERIMENTAL TECHNIQUES

Protonated and deuterated PMDA–ODA based polyamic acids were synthesized from the corresponding sublimed monomers in dry N-methylpyrrollidone as described previously[19]. The polymers used for the diffusion experiments had a weight average molecular weight, M_w, of 30 000 and $M_w/M_n = 2$. Films of the amic acids were prepared by spin coating solutions containing 10 wt% of the polymer onto chromium-coated silicon wafers. The mechanical experiments were done with samples made from the PMDA–ODA Pyralin 2540 purchased from Du Pont. This polymer has a weight average molecular weight of 25 000 and $M_w/M_n = 2$.

Samples for the adhesion experiments were made by spin coating the solution onto glass slides, and then curing on a hot plate or in a vacuum oven. For those peel tests where good adhesion to the substrate was required an adhesion promoter, A1100, was applied to the substrate before spin coating the amic acid solution. For both studies the first layer of the polymer was dried at 80°C for 30 min and then cured at a temperature T_1 between 150 and 400°C for 1 h. Finally a second layer was spin coated onto the first and the sample cured at a second temperature T_2, also between 150 and 400°C. In the discussion the samples are normally described by the T_1 and T_2 values, e.g. sample label 150/400 refers to a material where $T_1 = 150$°C and $T_2 = 400$°C. For the ion

scattering experiments the first layer was a 6 μm thick film of the protonated polymer and the second layer was a 20–30 nm thick film made from deuterated material. Mechanical measurements were made on samples where both layers were 7 μm thick.

The interdiffusion of the material was measured using forward recoil spectroscopy* (FRES)[21–24]. In this experiment, which is shown schematically in *Figure 1*, a monoenergetic beam of He ions is directed towards a sample at an angle of incidence α. Collision of these ions with target nuclei may result in the ejection of those nuclei at angle θ with respect to the incident beam. Conditions of energy and momentum conservation at the collision determine the relationship between the energy of the He ion and the ejected nucleus. Hence ejected deuterium nuclei carry away a greater proportion of the energy of the He ion than do hydrogen nuclei. The in-going He ions and the ejected nuclei lose energy at a known rate as they travel through the sample so any nuclei arriving at the detector have an energy that depends on the isotope and on the depth in the sample from which it came. Deuterium nuclei can recoil from depths approaching 0.8 μm before their energy is decreased to a point where they can be confused with hydrogen nuclei recoiling from the sample surface.

The energy loss rate in PMDA–ODA was obtained from a table of stopping cross sections[25] for H, D and He nuclei to permit conversion of a yield *versus* energy plot to one of concentration of deuterated polymer *versus* depth. The 43 keV energy resolution of the instrument limited the depth resolution to about 66 nm, although the application of a computer algorithm[26,27] which simulated the FRES spectrum expected for a given concentration *versus* depth profile and instrumental energy resolution is capable of measuring diffusion distances that are considerably smaller than this limit. Further details on the technique may be found elsewhere[20–22].

Peel tests were done at room temperature using an Instron 1120 testing machine. The results presented were obtained using a 'trouser leg' test on a free standing film as is shown on the insert in *Figure 3*. This is generally known as a T test. Despite exercising a large amount of care in the sample preparation we observed that the data show a considerable amount of scatter. Usually the samples were made in batches so that all the samples used to test one particular variable were made together under identical curing conditions.
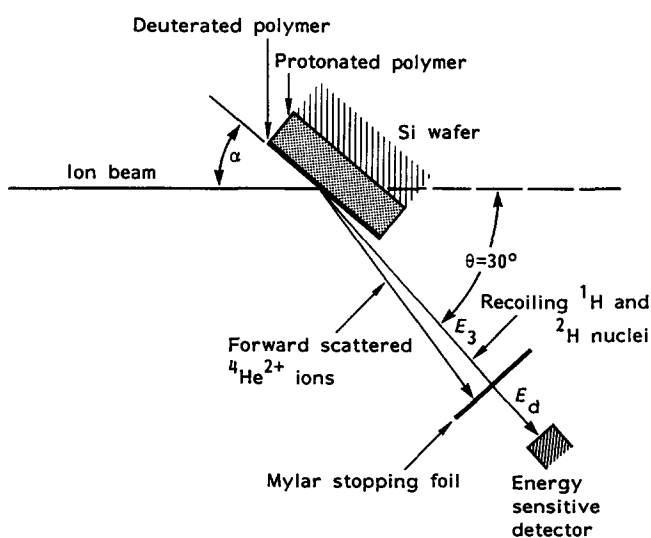

Figure 1 The geometry of the FRES experiment. The incident ion ($^4He^{2+}$) beam impinged on the layered specimen, supported by a Si wafer substrate, inclined at an angle α to the incident beam. The recoiling ^1H and ^2H nuclei were detected by a Si surface barrier detector. A Mylar stopping foil was used to filter forward scattered $^4He^{2+}$ ions and heavier nuclei
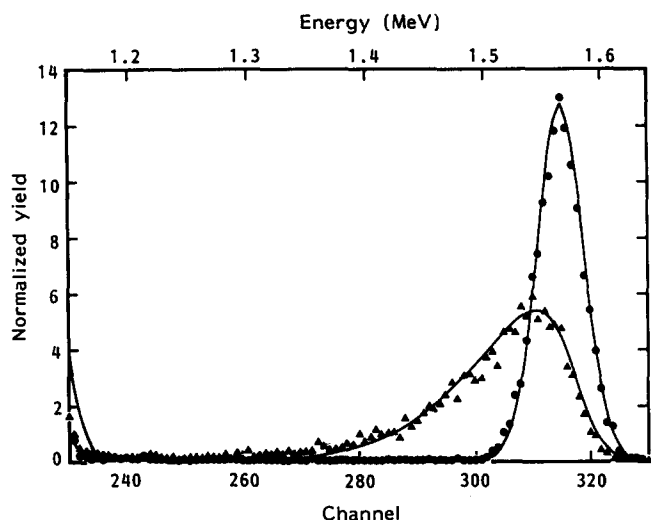
RESULTS AND DISCUSSION

Effect of cure temperature on interdiffusion

FRES spectra from two different samples are shown in *Figure 2*. The spectrum for the 400/150 sample exhibits a sharp peak at approximately 1.55 MeV, which corresponds to a thin layer of PMDA–ODA confined to the surface. We will show later that no measurable diffusion occurred in this sample. The other spectrum, from the 150/400 sample is quite different from the first in that the peak height has decreased significantly and there is now a tail that extends to lower energies. Significant diffusion has occurred in this sample.

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* This technique is identical to that developed by Doyle and Peercy[20] to profile ^1H and ^2H in metals

Figure 2 FRES spectra for 400/150 (●) and 150/400 (▲) samples. The solid lines are simulated FRES spectra corresponding to diffusion distances w of 22 and 156 nm, respectively

The data can be analysed quantitatively using the simulation program referred to above[26,27]. The solid lines in *Figure 2* are fits to the spectra using the Fickian solution to the diffusion equation for the thin film case which is given by[22,28]:

$$\phi(x) = \frac{1}{2}\{\text{erf}[(h+x)/w] + \text{erf}[(h-x)/w]\}$$

Here h is the original thickness of the layer of deuterated PMDA–ODA, which is obtained by matching the simulated FRES deuterium spectrum to the experimental FRES spectrum. The diffusion distance $w = 2(\langle D\rangle t)^{1/2}$, where $\langle D\rangle$ is the time averaged diffusion constant, is adjusted to find the w that corresponds to the least squares minimum of the difference between the experimental and theoretical spectra. The reasons for the use of w rather than D will be discussed later. The solid lines for the two spectra correspond to such least squares fits. This procedure is more accurate than the procedure previously employed[29] in which the FRES spectrum was converted into a smeared volume function *versus* depth profile and then fitted to $\phi(x)$, especially for small values of w.

The physical meaning of the diffusion distance w is easiest to consider with respect to diffusion in the adhesion situation, i.e. the interdiffusion of two infinite slabs. In this situation w corresponds to the distance from the interface at which the concentration of the minor component had dropped to 8%. Also, only about 9% of the material that crosses the interface travels a distance greater than w.

A compilation of the results obtained from the FRES measurements is shown in *Table 1*. As can be seen there is little diffusion if $T_2 < T_1$. When $T_2 \geqslant T_1$, some diffusion was always observed but it decreased rapidly with increasing T_1. The fact that the interdiffusion at various T_2 was about the same for the lowest T_1, 150°C, suggests that at the highest T_2 diffusion only takes place for the first few minutes at T_2; as the polyamic acid imidizes (and solvent is lost) its diffusive mobility decreases rapidly. Experiments on similar materials have shown that very little diffusion occurs after the first few minutes. For this reason the diffusion distance has not been converted into

an average diffusion constant. It is clear from these results that the degree of interdiffusion can be controlled by choice of the curing temperature T_1 of the underlying PMDA–ODA film.

Effect of cure temperature on adhesion

The data in *Figure 3* show the effects of T_1 and T_2 on the T peel strength of the bilayer samples. It was not possible to obtain peel strength data on the materials with $T_1 = 150°C$ as the arms of the samples normally broke. These results do not imply that the interface under these curing conditions was as strong as the bulk material but just that it was not the lowest energy crack path in the peel test. The fact that it was possible to peel off small sections of the interface shows that the interface was still weaker in spots than the bulk.

Figure 4 contains scanning electron microscope (SEM) images of fracture surfaces of 150/400 and 400/150 samples, selected because they have very good and very poor adhesion, respectively. The fracture surfaces are completely different. The high fracture energy surface is

Table 1 Diffusion distances*

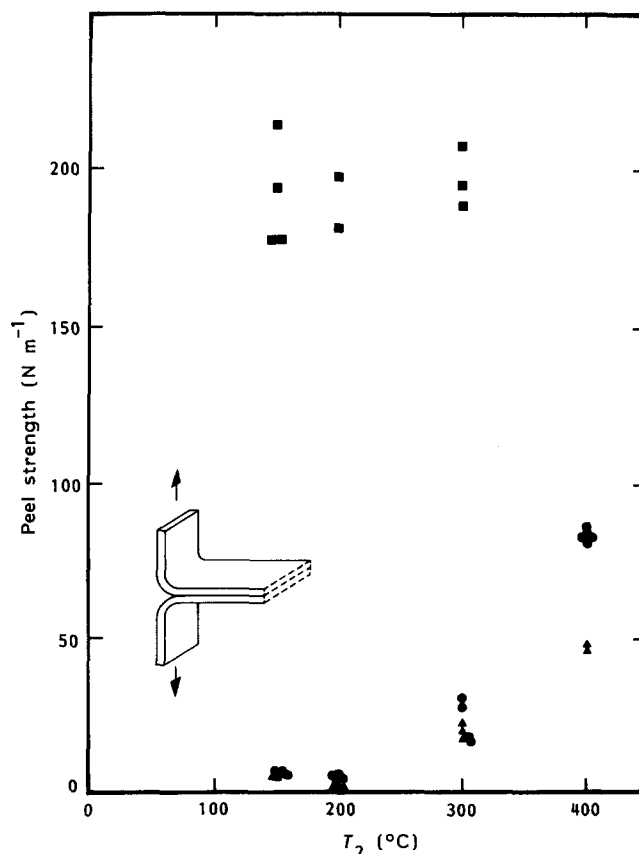| T_2 (°C)	T_1 (°C)			
	150	200	300	400
150	168 nm	42 nm	28 nm	22 nm
200	150	43	29	31
300	154	46	35	31
400	156	47	37	30

* Results are given in nm

Figure 3 T peel strength as a function of T_1 and T_2. T_1 (°C): ■, 200; ●, 300; ▲, 400
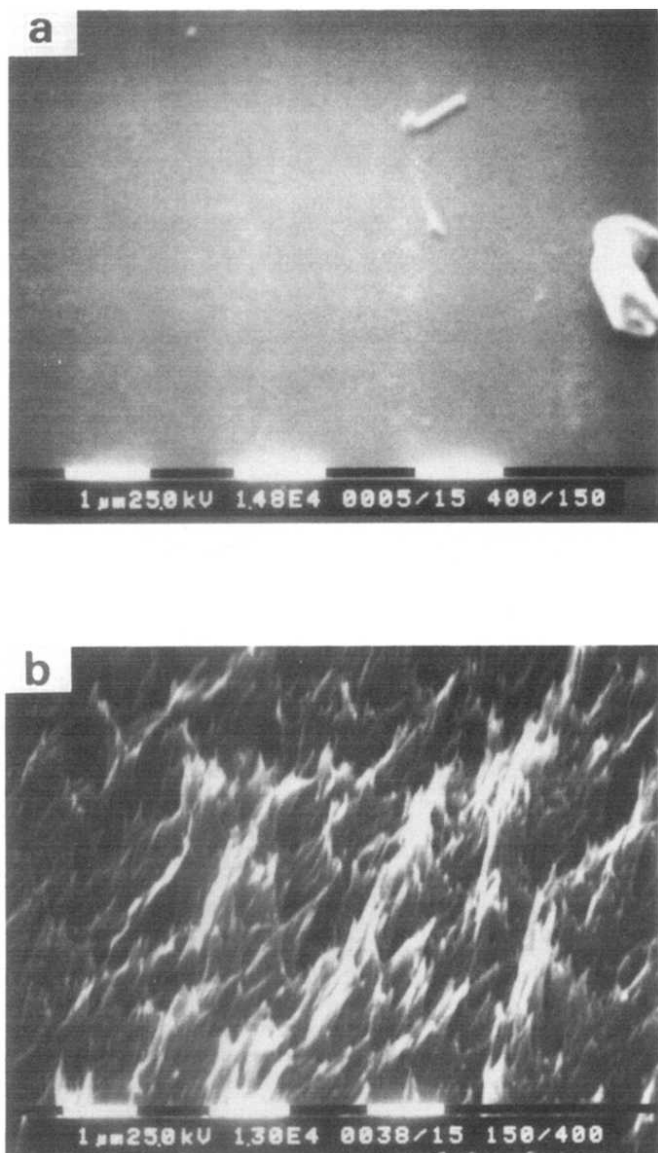
Figure 4 Fracture surfaces of (a) 400/150 and (b) 150/400 specimens

very rough with much evidence for local ductile deformation of the polymer. In contrast the low fracture energy surface is very smooth with almost no evidence of voiding and plastic deformation. It appears that there is a small difference between the two sides for the 150/400 bond with a little more ductile deformation evident on the material that has experienced both 150 and 400°C cures. This ductility difference is consistent with the observation of a slight increase in the ductility of a material that has experienced a series of increasing cure temperatures.

In *Figure 5* the peel strength results from *Figure 3* are plotted against diffusion distance, *w*, measured by FRES. It is clear from these results that there is a strong correlation between the interdiffusion and the interfacial strength in the PMDA–ODA system. Bilayers with less than 30 nm diffusion distances have almost no adhesion, whereas those with more than 50 nm distances are too strong to be measured reliably by the T peel test. Ellul and Gent[11] have suggested that is it necessary in glassy polymers, as it is in elastomers, to separate the effects of the kinetics of adsorption (contact formation) from those of interdiffusion when discussing the kinetics of crack healing or welding. In the experiments on the PMDA–

ODA system presented here the second layer was deposited from solution, so contact was established before curing. Nevertheless, the adhesion for the systems with high T_1 was very small and so it is unlikely that simple adsorption contributed significantly to the adhesion for these polymers.

Although the correlation between the FRES interdiffusion measurements and the adhesion results is excellent, other factors complicate their interpretation. The mechanical properties of the PMDA–ODA change with cure temperature, causing a small decrease in modulus and an increase in nonlinearity in the early part of the stress–strain curve with increasing cure temperature[30]. Hence an increase in inelastic deformation in the bulk sample with increasing cure temperature might be expected. Also, the failure strain of PMDA–ODA increases considerably with cure temperature so, if the failure energy at the crack tip (J or G) is related to this failure strain, then an increase of peel strength with T_2 would be expected. Materials with a T_1 of 200°C appear not to show this effect. There is little apparent change of either peel strength or interdiffusion distance when T_2 is changed from 150 to 200°C. When T_2 was increased to 400°C the interdiffusion distance increased and the adhesion was too strong to measure.

One interesting feature of the results discussed so far is the considerable depth of interpenetration that is required to cause a strong bond. This result is consistent with those described by Roland and Böhm[14] in polybutadiene. However, much smaller interdiffusion distances to restore the original toughness were calculated from literature values of diffusion constants by Wool in natural rubber[13] and Jud et al. in poly(methyl methacrylate)[15]. Small interdiffusion distances were also obtained from the analysis of healing in lightly crosslinked styrene-acrylonitrile (SAN) by Nguyen et al.[17]. As discussed in the 'Introduction', most theories of tack, welding or healing in uncrosslinked amorphous polymers tend to assume that relatively short diffusion distances, certainly no larger than the radius of gyration of a chain and perhaps just a few times the distance between entanglements, are required for complete strength recovery of the material. For a flexible polymer, such as polystyrene, at molecular weights of less than 100 000 this means diffusion distances of, at most, 10 nm, but PMDA–ODA does not obtain virgin strength with diffusion distances of about 200 nm!
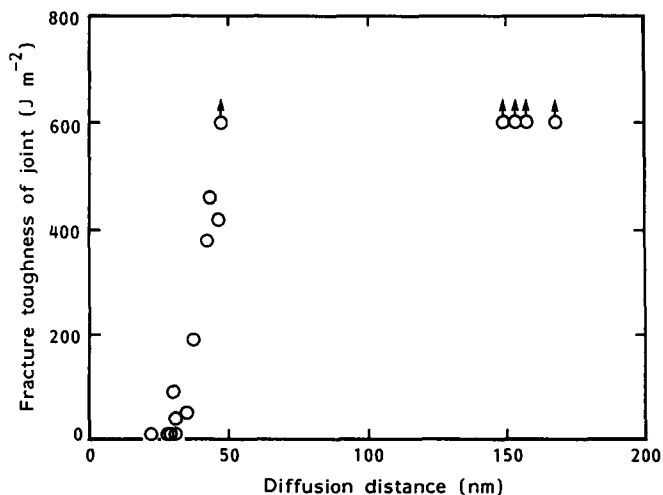

Figure 5 Variation of T peel strength with interdiffusion distance *w*

However, in the solid state PMDA–ODA is not an amorphous, flexible, coil polymer. There is evidence that its local structure is smectic-like[31] and Russell *et al.*[32] have found that the small angle neutron scattering pattern indicates that the polymer adopts a rigid local conformation rather than a flexible coil conformation. The mechanism of interdiffusion of the polyamic acid (perhaps partly imidized) into such an ordered material is quite unknown, particularly since PMDA–ODA films that are cured on a rigid substrate show a high degree of biaxial orientation in the plane of the film[33]. The molecular weight between entanglements decreases and the radius of gyration increases with increasing chain stiffness in coil polymers, so the results presented here tend to suggest that the diffusion distance required for strength retention may approach the radius of gyration and/or perhaps even the end-to-end distance of the chain for a stiffer polymer. In this context it is worth noting that the contour length of a PMDA–ODA of 30 000 molecular weight is about 130 nm, a value very similar to the diffusion distances measured when T_1 was 150°C.

These experiments have interesting implications in the information that they give on the failure mode, at a molecular level, of this unusually tough, high temperature polymer. The diffusion distance for complete strength retention can be considered as a load transfer length and is surprisingly high value, shown by these experiments, might explain the origin of the flexibility that causes the high ductility.

It is worth comparing the size of the crack opening displacement that can be estimated from the fracture surfaces with that expected from the peel strength and mechanical properties of the material. From the fracture surfaces it would appear that the crack opening displacement δ was about 3 μm for the 150/400 specimen. The yield stress of PMDA–ODA is about 120 MPa[34] but the material on the fracture surface shows evidence of considerable voiding, so 80 MPa is a reasonable estimate for an average yield stress σ_0 of the plastic zone. As

$$G = \sigma_0 \delta$$

a failure energy of about 250 J m^{-2} would be expected. If there was no plastic deformation within the bulk of the sample this would correspond to a peel strength, for a T peel test of 125 N m^{-1}. It seems likely, therefore, that a considerable portion of the peel energy of this sample, which had a peel strength greater than 300 N m^{-1}, went into plastic deformation in the bending of the peeled strip. This point will be considered in greater detail in a later publication.

CONCLUSIONS

The main conclusion of this work is that the adhesion of PMDA–ODA to itself is controlled primarily by the diffusion of the precursor polyamic acid into a cured polyimide layer. This interdiffusion is in turn controlled by the cure temperatures of the two layers with good adhesion resulting from a low cure temperature of the first layer. A high cure temperature of the second layer also has beneficial effects on the adhesion. A surprisingly large diffusion distance, at least 200 nm, is required for full bond strength and this suggests that the 'stress transfer distance' in this material at high strains must be equivalently large.

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