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Improved adhesion between nickel–titanium shape memory alloy and a polymer matrix via silane coupling agents

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Abstract

NiTi wires were functionalized with silane coupling agents to improve interfacial adhesion between the inorganic constituent and a host matrix for composite applications. Surface derivatization was characterized by X-ray Photoelectron Spectroscopy, and mechanical pullout tests were performed to quantify the increase in adhesion between the NiTi shape memory alloy wires and polymer matrix. Improvements of roughly 100% in the adhesion was realized as compared to unfunctionalized samples or to samples functionalized with an unreactive silane coupling agent.

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1. Introduction

The exceptional material properties exhibited by shape memory alloys (SMA) result from a reversible diffusion-less phase transformation process. Depending on the operating temperature, one of two regimes of material behavior will be displayed: shape memory effect or pseudoelasticity. The shape memory effect is exhibited when the material is in its martensitic phase and deforms in what appears to be a plastic manner; however, the deformation is completely recoverable upon heating. When loaded in the austenitic phase, pseudoelastic behavior is observed, wherein the SMA material can be stretched by up to 10% with no permanent deformation upon unloading. In addition, there is significant stress hysteresis between the loading and unloading conditions during pseudoelastic deformation, leading to exceptional damping properties. The characteristic temperatures defining the martensitic and austenitic phases are highly dependent on the SMA composition and heat treatment history. For a more complete review of the properties

and behavior of SMAs, the reader is referred to Pelton, Mantovani and Otsuka [1–3].

A great deal of attention has been paid to SMA materials as composite constituents, both as actuators and as active components. Barret [4] mimicked the low stiffness and large deformation characteristics of biological tissues using a composite comprising SMA ribbons and a low-hardness silicone matrix. They showed that when the SMA is electrically actuated, small strains within the SMA could achieve an order-of-magnitude larger strain within the composite. Researchers have also shown that by actuating SMA constituents in a composite beam, they could control the shape and tip position of the beam [5–7]. Improved tensile behavior, fatigue resistance, and damping properties have also been achieved using various shapes of SMA inclusions in a variety of different matrix materials [8–11]. Others, such as Turner [12], demonstrated that the natural frequency of a beam could be tuned using actuated SMA ribbons.

The performance of these and most other composite applications of SMA materials is heavily dependent on the quality of the SMA–matrix interface. The interface must have sufficient strength to transfer the stresses and strains from the SMA constituents to the surrounding matrix material, making the investigation of the factors affecting

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adhesion an important endeavor. Paine [13] sought to improve the adhesion of NiTi wires to a graphite/epoxy and thermoplastic matrix using four surface treatments of the wires: acid etching, hand sanding, polymer coating, and sandblasting. The subsequent fiber pullout tests showed that the sandblasted wires achieved up to a 70% increase of the debond stress over the untreated wires, while the other surface treatments yielded modest variations in the debond stress. Jonnalagadda [14] similarly showed that the debond stress of a NiTi/epoxy system could be increased by 190% by sandblasting the NiTi wires.

As the size of the SMA inclusion decreases, however, these treatments become more difficult and eventually impossible. For example, micron- and nano-sized SMA particles cannot be sandblasted, because the sand particles are on the same size scale and sometimes larger than the SMA particles. Ongoing research into SMA materials with micro- and nano-sized features is beginning to inspire the use of such materials in composites. These composites will require new techniques to improve adhesion between the SMA constituent and the matrix.

The research presented in this paper has sought to develop an adhesion-enhancing technique that can be applied to any size scale of NiTi constituent. The central concept is to attach a chemical species to the surface of NiTi covalently using a silane group such as APTS (3-acryloxypropyltrichlorosilane) or MPS (trimethoxysilylpropylmethacrylate; Fig. 1a)

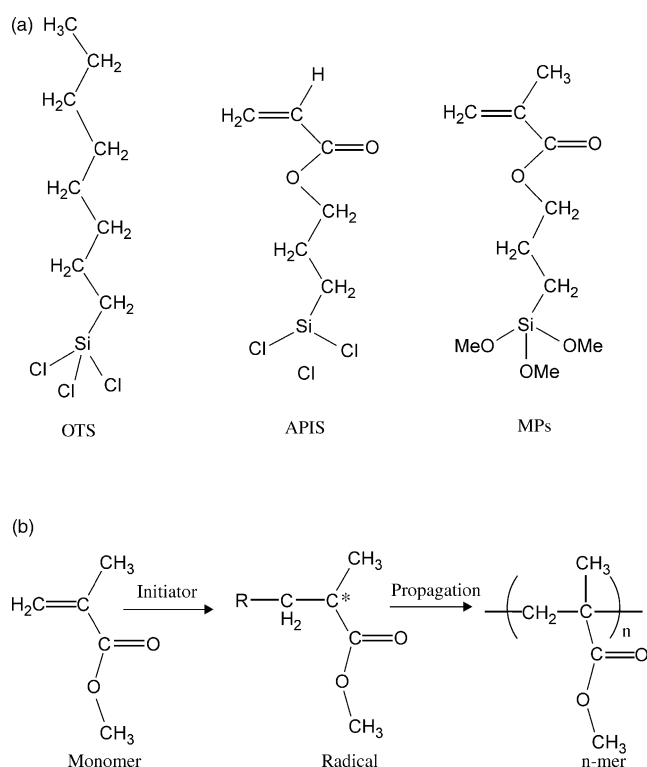


Fig. 1. (a) Chemical structures of APTS, MPS, and OTS silane-coupling agents; and (b) polymerization of methyl methacrylate monomer. The free-radical (dot) in the middle image represents an unstable species that will propagate the chain growth relatively quickly.

that will be integrated into the polymerization of the matrix material, resulting in a chemical bond between the NiTi and the matrix. Silane coupling agents have long been used for modifying surfaces in order to change the nature of interfacial interactions [15]. Fig. 1 illustrates the basic idea: a bridging species (the silane) is able to attach itself to both a metal oxide surface (through a silicon-chlorine or silicon-methoxy bond) and the propagating polymer chain. Free radical polymerization is used to accomplish the covalent attachment between the dissimilar species. An initiator, triggered by UV radiation or heat, begins the polymerization by either being exposed to UV radiation or heat. The polymerization will propagate essentially until the monomer is nearly depleted.

The system studied comprises NiTi wires treated with various silane groups embedded in poly(methylmethacrylate) (PMMA), commonly known as Plexiglas. The silanes APTS and MPS have the correct chemical functionality at their ends to facilitate the proposed idea. One end of the molecule contains a silane group, which is known to react with metal oxide surfaces [15], while the other portion has the same (as in MPS) or similar (as in APTS) structure to that of the monomer. Thus, when the surface that is covered with the silane molecule is exposed to a polymerizing solution of the methacrylate monomer, there is a strong likelihood that some of the growing chains will interact with the surface adduct, giving rise to a direct attachment of the host matrix to the substrate.

In addition to these silanes, OTS (*n*-octyltrichlorosilane; Fig. 1a) was used as a control to test whether the adhesion enhancements were due to chemical binding rather than entanglement. As can be observed in Fig. 1a, OTS does not have a structure that would allow it to be incorporated into the polymer backbone during polymerization. All samples and testing were done with macroscale samples for proof-of-principle purposes.

2. Experimental techniques

2.1. Sample preparation

All reagents were used as received. Black oxide-coated NiTi wire (0.03 inch diameter, Nitinol Devices and Components, $A_f = 80^\circ\text{C}$) was etched (20 min. sonication in conc. H₂SO₄) degreased (hexanes, isopropyl alcohol and ultrapure H₂O [Millipore]; 20 min. sonication in each solvent), and exposed to a base/acid sequence to enhance the concentration of surface hydroxides (20 min. sonication in 1 M NaOH, 5 min. sonication conc. H₂SO₄).

A portion of the cleaned wires was immersed in an 8 mM solution of APTS (United Chemicals), OTS (United Chemicals) or MPS (Sigma-Aldrich) in dry toluene for at least 6 h at room temperature. Due to similarity of the chemistry of the methyl methacrylate monomer and the APTS and MPS coupling agents, it was expected that

the end that was functionally similar to that of the monomer would be incorporated into the polymerization of the PMMA. The OTS molecule, however, was not expected to interact with the polymerizing methyl methacrylate. The treated wires were washed (3×20 min. in dry toluene), then stored under dry nitrogen until further use.

The polymerization of methyl methacrylate (Sigma-Aldrich) was done via a free-radical mechanism using approximately 0.5 wt.% of the initiator azobis-isopropionitrile (AIBN), benzoyl peroxide (BPO), or BPO/benzoin (Sigma-Aldrich). Both the treated and untreated wires were immersed in the polymer solution, then cured by either exposing the solution to longwave UV light (at least 8 h in ambient conditions, or under a partial vacuum of roughly 200 Torr), or heating at 55 °C for 7 h in ambient conditions.

2.2. Surface characterization

The surfaces of the treated and untreated wires were characterized with X-ray Photoelectron Spectroscopy (XPS; Philips 5400 ESCA). The binding energies associated with the individual components of the surface species were identified using the NIST XPS database [16] and the ESCA handbook [17].

2.3. Mechanical testing

Adhesion between the NiTi wire and the PMMA matrix was quantified by a tensile pullout test. The increase in adhesion was determined by the increase in applied force required to induce wire slip within the matrix divided by the length of wire embedded within the polymer.

The samples are constrained in such a way that no compressive stress is applied to the matrix that would otherwise affect the measured adhesion strength. A specially designed sample holder compatible with the testing apparatus was machined from a 1 inch NPS stainless steel pipe nipple and pipe cap. Fig. 2 shows the testing device with a cut-away image of the pipe cap. Initially, the sample bottle sits in the device unsupported. As the lip of the bottle

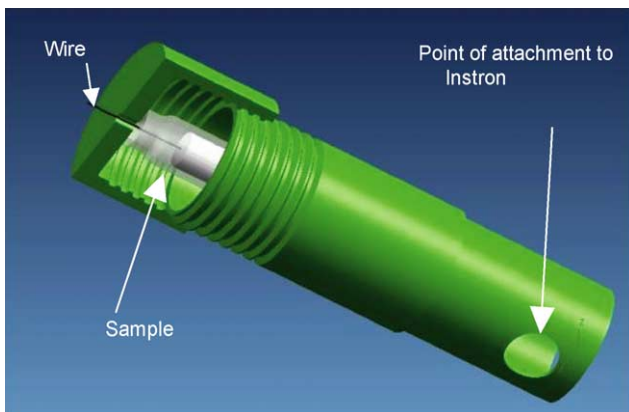


Fig. 2. Testing apparatus for pullout samples.

comes in contact with the pipe cap tensile stress is applied to the wire. This apparatus facilitates testing of the wire/PMMA interface without applying any compressive stress to the sample. This loading method relies on the friction between the sample bottle and the PMMA to constrain the sample and does not compress the PMMA.

All tests were conducted on an Instron 5566 testing device with a constant crosshead speed of 0.2 mm/s. In order to capture the high rate of change of loading immediately surrounding the initial slippage of the wire–matrix interface, the data acquisition rate was specified at every Newton increment.

To account for the variations in the embedded length of the NiTi wire, the loading data resulting from each pullout test were normalized by the length of the embedded wire. It was confirmed that the applied loads did not approach the level needed to induce permanent plastic deformation in the NiTi wires based on a simple tension test; however, in some cases the load was sufficient to induce martensitic twin rearrangement.

3. Results

Fig. 3 shows a schematic diagram of the normalized load vs. deflection curve of a typical pullout sample. In some cases, the PMMA sample slipped at the PMMA/sample bottle interface, and this slip corresponded to the first small peak in the schematic curve. An elbow was often observed in the loading data of the functionalized samples, corresponding to the yield stress of the martensitic wires. The maximum value achieved in the loading data is regarded as the maximum adhesion strength of the sample.

Fig. 4 is a compilation of XPS data illustrating the carbon and oxygen content for treated and untreated surfaces (observed values tabulated in Table 1). Fig. 4a and b indicates the presence of some surface contaminants on the untreated wires. The O1s peak positions for the untreated

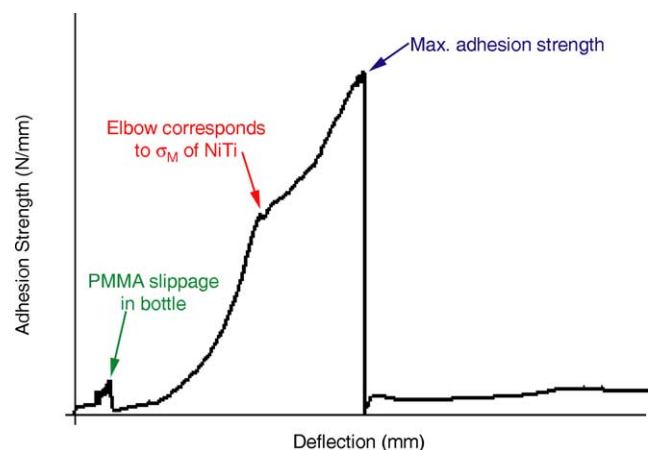


Fig. 3. Schematic diagram of adhesion strength as a function of applied load. σ_M corresponds to the point where the applied stress is sufficient to induce martensitic twin rearrangement.

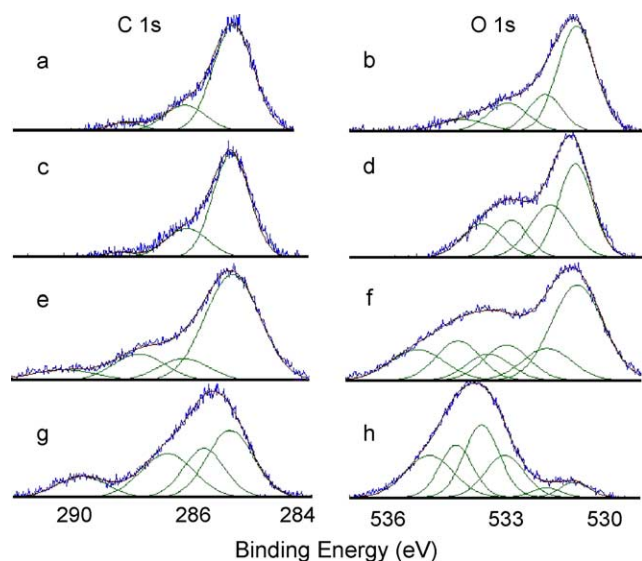


Fig. 4. XPS multiplex peaks for surface-modified NiTi wires. Graphs are associated with (a,b) untreated, (c,d) OTS-, (e,f) MPS- and (g,h) APTS-treated samples. Peak positions associated with each species present are tabulated in Table 1.

wires indicate the presence of oxygen predominantly in the form of TiO_2 . Fig. 4c and d shows spectra for OTS-treated wires. Here, the peaks associated with oxygen bound to silicon can be seen (Si–O–Si and Si–O–Ti), confirming the presence of surface-bound OTS. Fig. 4e and f shows the spectra for MPS-treated wires. The O1s spectrum confirms the presence of surface-bound MPS. It shows the presence of both the silicon-bound oxygen, and the oxygen incorporated into the surface adduct itself (Fig. 1a).

Fig. 4g and h shows the spectra for APTS-treated wires. There is a clear difference between the O1s spectra of APTS and that of MPS, even though they are very similar chemically. It is believed that the large discrepancy between

Table 1
XPS binding energy data (eV)

	Bare	OTS	MPS	APTS
Carbon	BE (eV) (a)	BE (eV) (c)	BE (eV) (e)	BE (eV) (g)
Aliphatic	285.0	285.0	285.0 and 286.0 ^A	285.0 and 285.7 ^A
Ester	286.6 ^B	286.4 ^B	287.0	286.8 ^C
Carbonyl	288.3 ^B	288.4 ^B	288.8	289.2 ^C
Oxygen	BE (eV) (b)	BE (eV) (d)	BE (eV) (f)	BE (eV) (h)
TiO_2	530.1	530.1	530.1	530.1
Si–OH	NA	530.9	530.9	531.0
Ti–OH	531.1	NA	NA	NA
Ti–O–Si	NA	532.0	531.7	532.2
Si–O–Si	NA	532.9	532.7	532.9
Water	532.8	NA	NA	NA
Carbonyl	532.0 ^B	NA	532.0	533.6 ^C
Ester	533.4 ^A	NA	533.6	534.4 ^C

^A Polymer backbone aliphatic carbon.

^B Surface contamination.

^C Polymeric species.

the surface coverage of the APTS compared to the other derivatizing agents is due to an acid-catalyzed polymerization through the acrylate group (Fig. 1a). Hydrochloric acid is a by-product of the derivatization using the trichlorosilanes, and therefore is assumed to play a role in the additional surface coverage of APTS. This phenomenon is not observed with MPS, which has methanol as a by-product.

In order to characterize the effect of the NiTi wire surface functionalization on adhesion, fiber pullout tests were performed in a manner similar to that reported by Paine [13] and Jonnalagadda [14] on the polymerized NiTi/PMMA composite. These tests measure the force required to induce slippage between the fiber and matrix material by constraining the matrix, pulling out the fiber, and correlating the maximum pullout force with the maximum adhesion strength. Most of the tests performed in this manner follow a very similar path to that illustrated in Fig. 3, with the exception that the observation of martensitic twin rearrangement (σ_M) did not appear in all tests (particularly those with low maximum adhesion strength).

Figs. 5 and 6 are compilations of all the pullout data, showing the various levels of adhesion improvement depending on polymerization conditions. Fig. 5 illustrates the adhesion improvement over unfunctionalized control samples under various initiator and curing conditions. These data were collected on samples prepared with APTS as the derivatizing agent. The BPO initiator and the BPO/Benzoin initiator produced a smaller increase in adhesion than any of the AIBN-initiated samples. This is believed to be due to

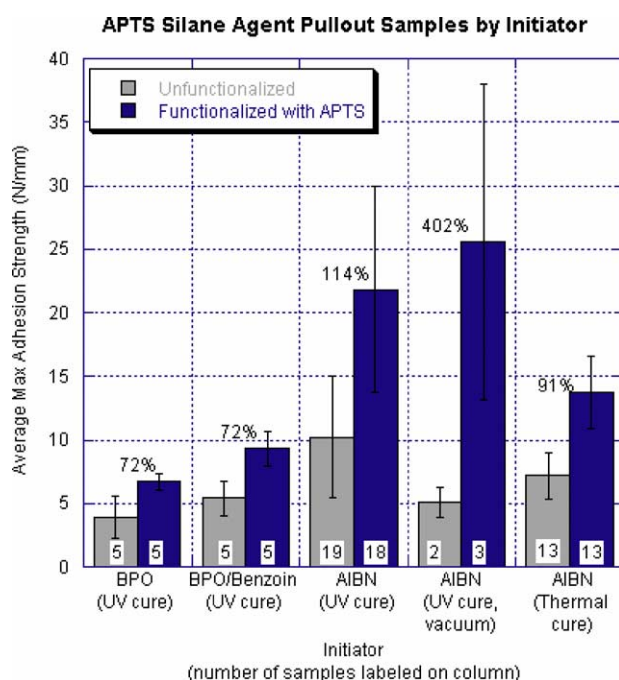


Fig. 5. Compilation of pullout results for APTS and UV- and thermally-cured host. The percentage value represents the relative increase in applied force required to remove the embedded wire. The number located at the base of each column represents the number of samples associated with that data point.

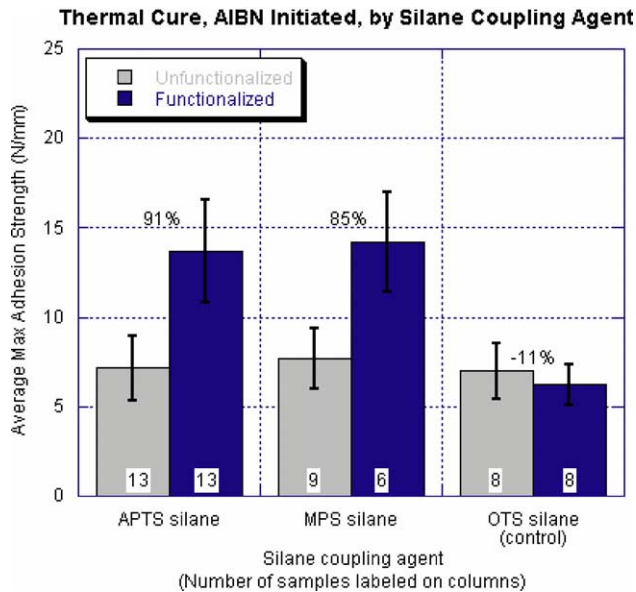


Fig. 6. Direct comparison of functional group interaction between MPS and OTS silane-coupling agents and host matrix. The number located at the base of each column represents the number of samples associated with that data point.

the relatively large amount of water in BPO, which would react with the silanes while in solution, rendering them unreactive with the metal hydroxides located at the substrate surface. In addition to the initiators investigated, two curing conditions were also explored in conjunction with the AIBN initiator. No significant difference in the overall enhancement of adhesion relative to an untreated wire was found between the UV cured and thermally cured samples. The sample set that was cured under vacuum showed the highest overall improvement, but due to difficulty in sample processing, the data set was small.

Fig. 6 summarizes the pullout results for the thermally-cured polymer host and AIBN initiator, with the silane agents APTS, MPS and OTS. These data illustrate the direct chemical interaction of the surface functional groups with the host matrix. The APTS and MPS show a similar level of improvement in adhesion, while the OTS exhibited no statistical difference between the modified and control samples. Thus, these data provide evidence that chemical binding to the matrix rather than polymer chain entanglement is the cause of the increased adhesion.

4. Discussion

Composites rely on the interfacial adhesion between the inclusion and matrix materials. Of significant concern to the design of composites is debond failure, whereby the applied loading conditions cause the inclusion/matrix interface to slip. By improving the interface between the inclusion and the matrix, the overall strength of the composite can be

improved, which can increase the lifetime before failure and the versatility of composite applications.

It has been shown that the interfacial adhesion strength of a composite material has a significant impact on the method of crack propagation through the composite. Ray [18] and Dong [19] concluded that the fracture behavior of a fiber-reinforced composite is strongly dependent on the strength of the interfacial adhesion. With extremely strong interfacial adhesion, a propagating crack that encounters the matrix/fiber interface would continue to propagate through the fiber, leading to catastrophic failure of the composite. With a slightly weaker adhesive strength, the incident crack would propagate along the fiber's axis and debond the fiber, which dissipates energy more effectively and could slow or arrest crack propagation, preventing catastrophic failure [20]. Consequently, the goal of examining the interfacial adhesion is not simply to improve the adhesive strength, but to devise an adhesion-enhancing technique that will enable a composite to be designed with control over the strength of the fiber/matrix interface. The strength of the interface should be large enough to allow the composite to operate under normal conditions without damaging the composite, while not being so large that progressive damage in the form of crack propagation occurs so quickly that it cannot be detected to prevent catastrophic failure. Although the research presented has not sought to optimize the controllability of the maximum adhesion strength, it has shown that a range of adhesion strengths can be achieved. Further experimentation with the wire-functionalizing reaction time and the local density of the surface adduct could provide enough information to tailor a composite material with specific maximum adhesion strength.

The experiments described above examined the effects of surface functionalization on the adhesion properties of macro-scale samples. Composites involving micro- and nano-sized constituents, however, would also benefit from this surface functionalization technique, because this method is independent of the size scale of the substrate. In addition, the modification of the surface chemistry of the NiTi wires does not change the surface topology of the constituent, unlike a method such as sandblasting, which is inherently destructive. Chemically functionalizing the surface preserves the size and shape of the NiTi constituent, leading to more uniformity in the composite inclusions. Although the specific silane coupling agents used in this study have been applied only to NiTi inclusions and PMMA as a matrix material, this research sets the framework for a methodology to exert control over the interfacial adhesion between any polymer and oxide-coated inclusion.

5. Conclusions

Techniques such as mechanical roughening, while quite effective on the macroscale for enhancing adhesion between constituent phases in a composite material, become

unusable at small scales. The method described in this paper utilizes techniques involving silane-coupling agents to improve adhesion between the NiTi wire and the host matrix by roughly 100% relative to an untreated wire. By varying the method of initiation and conditions of polymerization, a range of adhesion strengths can be achieved. This technique allows for adhesion control on essentially any size scale. Although the chemistry contained in this report has only been applied to PMMA as a matrix material, it establishes a methodology to improve the interfacial adhesion between any polymer and an oxide-coated alloy such as NiTi.

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