



CHARACTERISTICS OF ELECTROSPUN CARBON NANOTUBE-POLYMER COMPOSITES

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ABSTRACT

For the past three years, the Army has been investigating a nanofiber production technique: *electrospinning*, for numerous military applications. It has been known since the turn of the century that electrically charged liquids can produce fine fiber. This fiber spinning technique was first patented in 1934.¹ However, as a method of producing sub-micron fiber, electrospinning has seen little commercial application beyond limited filter manufacturing. Electrospun fibers naturally assemble into membrane structures, and this is an entirely new way to manufacture high surface area membranes for all types of applications. One interesting new application might be conductive membrane coatings for lightweight, flexible photovoltaic film patches as wearable solar power cells.² These would require thin, flexible, highly conductive electrode materials. In this work, the use of carbon nanotubes to boost the conductivity of organic polymers has been investigated. Carbon nanotubes were dispersed in a mixed polymer solution. The electrospun product is a network of organic polymer fibers encapsulating carbon nanotubes. Processing characteristics of electrospun polymer solutions has been examined with respect to the orientation and dispersion of the nanotubes within the fibers and the impact of nanotubes upon measured conductivity of a fiber mat of conductive polymer.

INTRODUCTION

Over the past 50 years, electrospinning of fibers from solutions of dissolved polymers has been extensively studied, patented, and even commercialized. Fibers of diameters ranging from 10 μm to 0.1 μm have been reported.³ The smallest fibers reported to date are 20 nm.⁴ This is the approximate size of carbon nanotubes,⁵ and we have undertaken to imbed individual carbon nanotubes within electrospun organic fibers in an effort to orient carbon nanotubes, and to increase the conductivity of organic nanofibers.

Organic nanofibers were prepared by electrospinning blends of conductive poly(aniline) with non-conductive polyurethane (PU). Poly(aniline) in its conductive state has been very difficult to process in the past,⁶ but recent advances in the synthesis of conductive poly(aniline) have overcome this problem.⁷

We have used a form of poly(aniline) for this study: a conductive polyaniline-sulfonated polystyrene complex (PANI-SPS), which is a template-synthesized form of polyaniline (PANI) that produces a complex between the two polymers, PANI, and the

strong acid polyelectrolyte, sulfonated polystyrene (SPS). The polyelectrolyte is presumed to provide the ionic doping of the templated PANI in the complex, and aids in keeping the PANI soluble and processable in all of its conductive forms.

Additionally, we blended two forms of carbon nanotubes (CNT) into thermoplastic elastomeric polyurethanes for processing into nanotube-containing nanofibers. The two forms are 1) plasma enhanced chemical vapor deposition prepared carbon nanotubes, pCNTs; and 2) furnace chemical vapor deposition prepared carbon nanotubes (fCNTs). The pCNTs are straighter and have relatively shorter lengths (1-5 μ m long) compared to the twisted and coiled form of fCNTs with lengths of 5-10 μ m.

EXPERIMENTAL

Materials

Polyurethane thermoplastic elastomers were dissolved in dimethylformamide (DMF) solvent. One type of polyurethane, Pellethane 70A, is a polytetramethylene glycol ether, supplied by The Dow Chemical Company. Pellethane was chosen because it is a good fiber forming polymer and is found to produce large well defined fibers when electrospun out of dilute solution. The other type of thermoplastic polyurethane was Estane 80A, supplied by BF Goodrich. Estane blends more readily with PANI-SPS, but forms smaller diameter fibers that are less well-defined, depending upon the additives used during electrospinning.

Poly(aniline)-SPS was prepared by enzyme catalyzed polymerization of aniline in aqueous solution in the presence of poly(sodium 4-styrenesulfonate) of a molecular weight of 70K Daltons in one case, and 1M Daltons in another case, according to the procedure of Liu et.al.⁶ This produced a polymer complex containing a 1:1 molar ratio of PANI to SPS.

Carbon nanotubes were grown by plasma-enhanced hot filament chemical vapor deposition of acetylene gas on polycrystalline Ni-coated silica at 660°C, producing carbon nanotubes of 100nm diameter and 1-5 μ m in length, according to the procedure of Ren, et.al.⁸ Carbon nanotubes were also prepared by a furnace synthesis technique involving the use of matrix dispersed iron catalysts of 20-50nm particle size in a tube furnace at 750°C. Tubes of 5-10 μ m lengths were grown for two-hour periods during the decomposition of flowing acetylene and ammonia gases. The structural differences between these types of carbon nanotubes are shown in Figures 1 and 2.

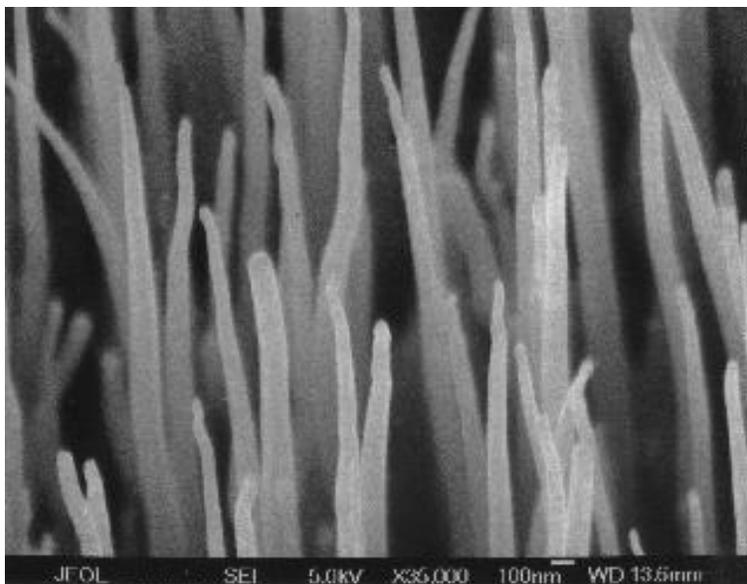


Figure 1. SEM of plasma prepared carbon nanotubes.

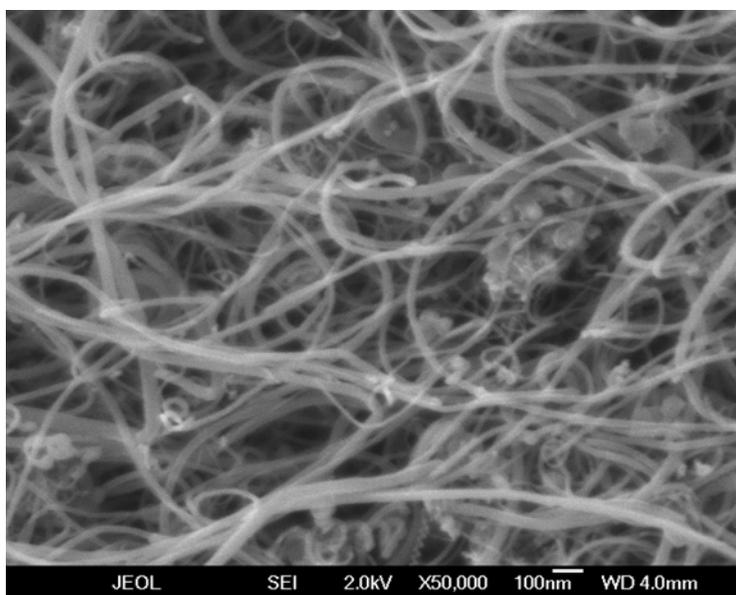


Figure 2. SEM of furnace synthesized carbon nanotubes.

Sample Preparation

Complexed PANI-SPS is water-soluble and can be blended with the selected polyurethanes at limited concentrations of in a common solvent, DMF. Solution concentrations of 1% PANI-SPS in 10%Estane were prepared in 90%DMF with and without carbon nanotubes. Additional solutions of Pellethane in DMF were prepared

with and without carbon nanotubes for a study of the method of nanotube incorporation within a separate polyurethane.

The solutions containing 10-20% solid in DMF were electrospun from filled Pasteur pipettes held horizontally and fitted over a positive electrode lead charged to 15kV from a current limited DC power supply. The droplet of polymer solution at the tip of the pipette formed a spray of fine, positively charged fiber that quickly dried and collected in a continuous network onto a grounded metal target in a manner described by numerous authors.^{9,10} Figure 3 shows the electrospinning of a polymer solution containing furnace-grown carbon nanotubes.

In this figure, a segregation process is apparent, whereby the large agglomerates of fCNTs are left in the pipette and not carried to the tip during fiber spinning. In this process, we have observed that individual, well-dispersed nanotubes emit first from the pipette within the fiber structure, followed later in the spinning by the larger agglomerates of tangled nanotubes.

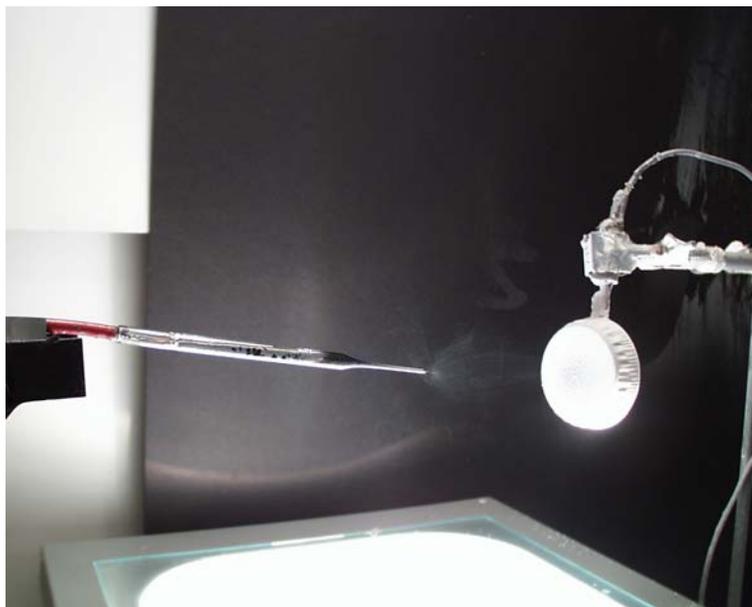


Figure 3. Electrospinning of a DMF/Pellethane/fCNT solution from a wire-charged Pasteur pipette to a grounded aluminum target.

Transmission electron microscope (TEM) grids and scanning electron microscope (SEM) stubs placed on the target were covered with dry polymer fiber network for examination. Nanofiber mats of 0.1 mm thickness were removed from 5 cm² area metal targets and tested in a TA Instruments dielectric analyzer (DEA) for dielectric conductivity measurements.

The following electrospun and dried polymer fiber compositions were studied:

TABLE I.

Polymer Nanofiber Compositions

<u>Polyurethane Type</u>	<u>PANI Type</u>	<u>Carbon Nanotube Type</u>
Estane (80%)	PANI-SPS70K (20%)	none
Estane (75%)	PANI-SPS1M (15%)	fCNT (10%)
Pellethane (90%)	none	fCNT (10%)
Pellethane (99.997%)	none	pCNT (0.003%)

Estane blended well with PANI-SPS in a DMF solvent while Pellethane did not. The two types of carbon nanotubes were blended with the polyurethanes in DMF at ratios of 10% polymer, 10% nanotubes, and 80% DMF to produce a spinning solution.

Furnace carbon nanotubes, fCNTs, were dispersed into the polymer solutions by addition of the tangled mass of material directly to a scintillation vial solution containing 90% DMF, 10% dissolved polymer, followed by high shear mixing with a 1cm diameter blade on a Dremmel Tool operating at 10,000 rpm for 2 minutes. This thick solution blackened quickly with dispersed nanotubes, but many were found to remain tangled within clusters after this mixing condition.

Plasma carbon nanotubes, pCNTs, were dispersed very differently. These nanotubes are prepared by growth from a nickel-coated silica substrate and produce a mat of uniformly long and straight nanotubes anchored to the glass substrate, as shown in Figure 4. The pCNT-covered substrate was immersed in DMF while the nanotubes were scraped off the top surface of the substrate with a sharp blade, dispersing the release nanotubes directly into the DMF solution. In the case of the shorter plasma nanotubes, solvent dispersion was apparently higher by visual examination, and few agglomerates could be detected by eye. This nanotube-containing solution was added to the polymer/DMF solution and electrospun into fiber mats.

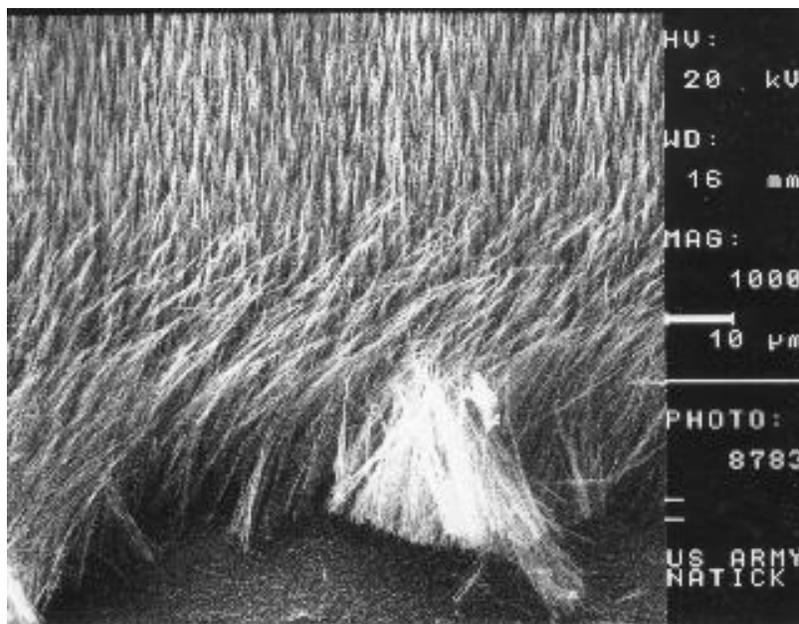


Figure 4. Appearance of pCNTs as attached to the nickel-coated silica substrate.

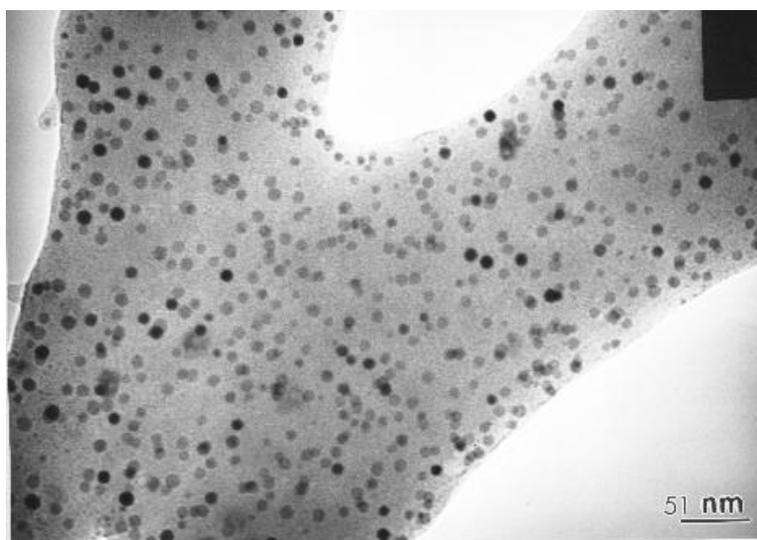


Figure 5. TEM image of electrospun fiber containing 80% Estane, 20% PANI-SPS(70K).

RESULTS

The electrospun fiber mats of polyurethane blended with PANI consisted of webs of interconnected fibers of varying diameters, ranging from 100-800nm in size. Figure 5 shows a TEM micrograph of the electrospun Estane/PANI-SPS blend. There are small

10nm sized dark spots in the fiber. This appears to be nanophase-segregated PANI-SPS regions within the polyurethane fiber

The goal of this work was to increase the conductivity of the electrospun nonconductive polyurethane fiber mats. To examine the conductivity of PANI/SPS in blended form, Estane and PANI-SPS blends were prepared over a wide range of PANI-SPS concentration and electrospun to determine the effect of concentration upon conductivity. Dielectric relaxation measurements were taken as a function of increasing temperature between parallel plates in the DEA fixture. A plot of ionic conductivity of the 0.1 mm fiber mats at a frequency of 100kHz at 55°C shows a steady increase in conductivity with PANI concentration up to a ratio of 1:1 Estane to PANI-SPS. Beyond 50%, the PANI-SPS becomes the major phase in the blend and overall conductivity jumps by an order of magnitude higher than the conductivity of 100% Estane. Addition of 10% fCNT to a polymer mixture of 80% Estane and 20% PANI/SPS shows a further increase in conductivity, up to 2.5 orders of magnitude higher than the conductive polymer blend with no nanotubes present.

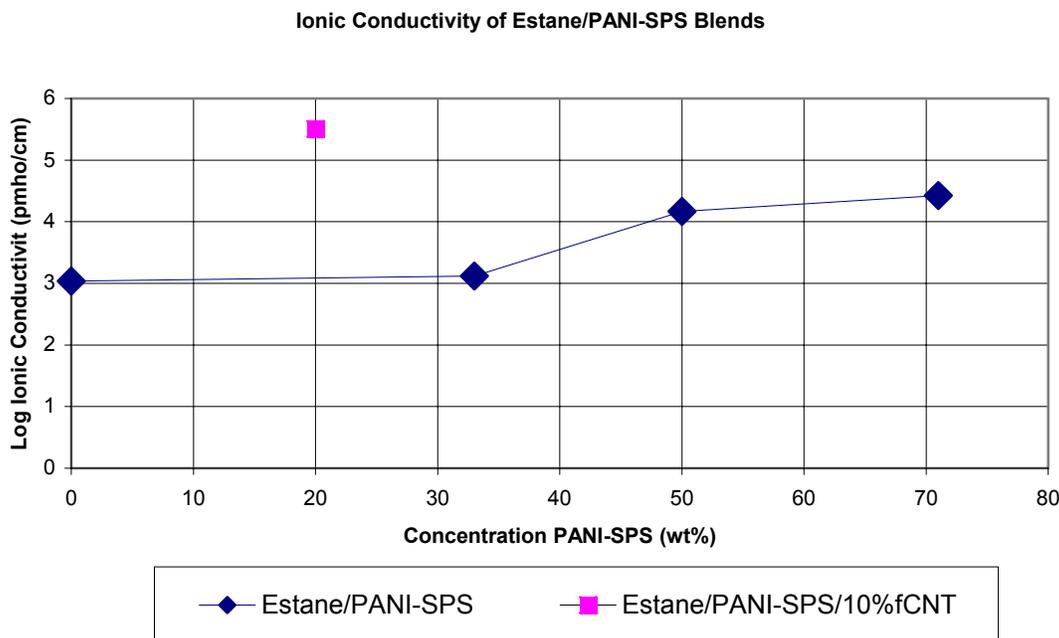


Figure 6. Plot of Log ionic conductivity of electrospun fiber mats of Estane/PANI-SPS70k blend compositions at 55°C.

Based upon the observations of PANI phase segregation and the concentration threshold behavior of the polyurethane/PANI-SPS blends, the possibility of “bridging” the PANI phases with carbon nanotubes, or generally boosting the conductivity of the blends with this highly conductive form of carbon was investigated.

Of the two forms of carbon nanotubes investigated for this purpose, the short plasma CNTs might be able to serve as bridges between the microphase separated PANI, since the individual tubes are synthesized in well separated form to assist in full nanotube dispersion within the phase segregated blend. The longer, more flexible loops of furnace synthesized CNTs would be expected to perform as long nanowires within the nanofiber structure, increasing the overall content of conductive nanofibers in the fiber mat. In order for this type of function to work within the fiber mat of low conductivity organic fibers, we would strive for an architecture that would achieve excellent dispersion of plasma nanotube bridges, while we would require high concentrations of furnace nanotube wires to meet a given percolation threshold for through-thickness conductivity of the mat. Our initial mixtures of polymers with nanotubes have produced some of these desired features.

To start, we examined a simple mixture of Pellethane with carbon nanotubes to observe the distribution of the two types of nanotubes within this polyurethane. Pellethane was chosen for this because it produces well formed fibers easily, even when mixed with solid particles such as CNTs. The Pellethane fiber mat containing 0.003% pCNTs are shown in Figure 7. This TEM micrograph shows a plasma CNT encased within a Pellethane fiber. The pCNT appears to have an articulated surface structure along the length of the tube. Dark spots of 50nm nickel are also apparent in this image.



Figure 7. TEM of electrospun Pellethane fibers containing 0.003% pCNT.

TEM imaging is useful to determine the positions of the nanotubes within the organic fibers. Figure 8 shows a cluster of fNCTs in an Estane/PANI-SPS electrospun mixture. There is a range of nanotube diameters present, and articulated structure is apparent along the length of both the wide and narrow nanotubes within this cluster. The

Estane/PANI-SPS blend can also be seen in this micrograph, but the polymer and the nanotubes cannot be viewed as separate, discrete fibers.



Figure 8. TEM of electrospun mixture of bamboo structured fCNTs in Estane/PANI-SPS(1M).

In order to more easily view the position of the nanotubes with respect to electrospun organic fibers, a sample of Pellethane/10%fCNT was examined by TEM. The Pellethane produces a more distinct fiber than the Estane/PANI-SPS blends, and in Figure 9 we see a fNCT embedded along a $2\mu\text{m}$ section within an electrospun Pellethane fiber.

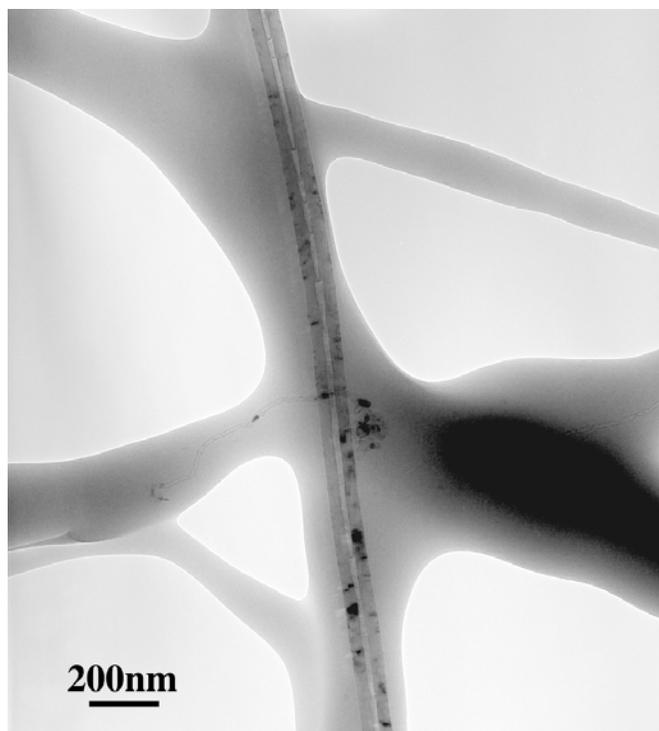


Figure 9. TEM of electrospun fCNTs in Pellethane.

CONCLUSIONS

Blends of PANI-SPS in Estane showed a distinct nanophase segregation of the PANI-SPS from Estane, for both PANI-SPS(70K) and PANI-SPS(1M). Conductivity of the electrospun mats of Estane/PANI-SPS indicated that when PANI-SPS was the minor phase in the phase separated structure, very little of the PANI conductivity could translate through the structure. Once the PANI-SPS became the major phase, a large increase in conductivity was observed. Further addition of a small concentration (10%) of carbon nanotubes to the moderately conductive polymer blend enhanced the conductivity of the fiber mat by over 200 times.

Electron micrographs of furnace synthesized nanotubes in Estane/PANI-SPS electrospun fibers show that it is difficult to pull apart all of the individual nanotubes from the furnace-prepared clusters and fully disperse them into an electrospun fiber mat. Electrospinning itself causes some segregation of clusters from individual nanotubes. These individual nanotubes can be found both in clusters within the electrospun fiber mat and within individual organic electrospun nanofibers. An advantage of plasma synthesized carbon nanotubes for electrospinning appears to be the ready dispersion of the as-synthesized separated carpet of nanotubes. Due to the need for improved dispersion of furnace nanotubes and the need for greater plasma nanotube yields, we have not yet achieved the best blend compositions of the nanotubes with conductive polymers. The potential of both types of nanotubes has still not been fully realized for this application. However, preliminary dielectric measurements indicate that CNTs can boost

the overall conductivity of organic nanofiber “electrodes” for the purpose of conducting photocurrent from photovoltaic cells.

Future work will be focusing upon new dispersion techniques to disentangle furnace nanotubes and the blending of new forms of PANI and plasma nanotubes to enable a higher concentration of PANI, to ensure better blending of the PANI with the fiber-forming polymer carrier, and to provide good contact between the PANI and the carbon nanotubes.

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