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Fabrication and Characterization of Semi-Crystalline and Amorphous Dielectric Polymer Films for Energy Storage

Hakeem Ayornu[1], **Sohail Anwar**[1], **Yash Thakur**[2]

[1]Department of Engineering, Penn State Altoona, Altoona, USA
[2]Department of Electrical Engineering and Materials Research Institute, The Pennsylvania State University, University Park, USA
Email: hakeemayornu@gmail.com

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Abstract

Dielectric polymer films are energy storage materials that are used in pulse power operations, power electronics and sustainable energy applications. This paper reviews energy storage devices with focus on dielectric film capacitors. Two prominent examples of polymer dielectrics Polyetherimide (PEI) and Poly (tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride) (THV) have been discussed. Polyetherimide (PEI) is an amorphous polymer recognized for its high-temperature capability, low dielectric loss and high dielectric strength. THV is a semi-crystalline polymer with high dielectric constant, high-temperature capability and charge-discharge efficiency. The primary focus of this paper is to introduce the reader to the fabrication procedures and characterization techniques used in research labs for processing of dielectric polymers. The fabrication and characterization process of both polymers has been discussed in detail to shed the light on experimental process in this area of research.

Keywords

Dielectric Polymer Film, Capacitor, Amorphous, Semi-Crystalline, Solution-Cast, Melt Extrusion

1. Introduction

Energy storage is an essential part of today's world, ranging from thermal, electrical and mechanical systems, to household and everyday technology. Energy storage devices, such as batteries, fuel cells, supercapacitors and capacitors are used for a variety of applications. Ragone plot (**Figure 1**) is used to show the relationship

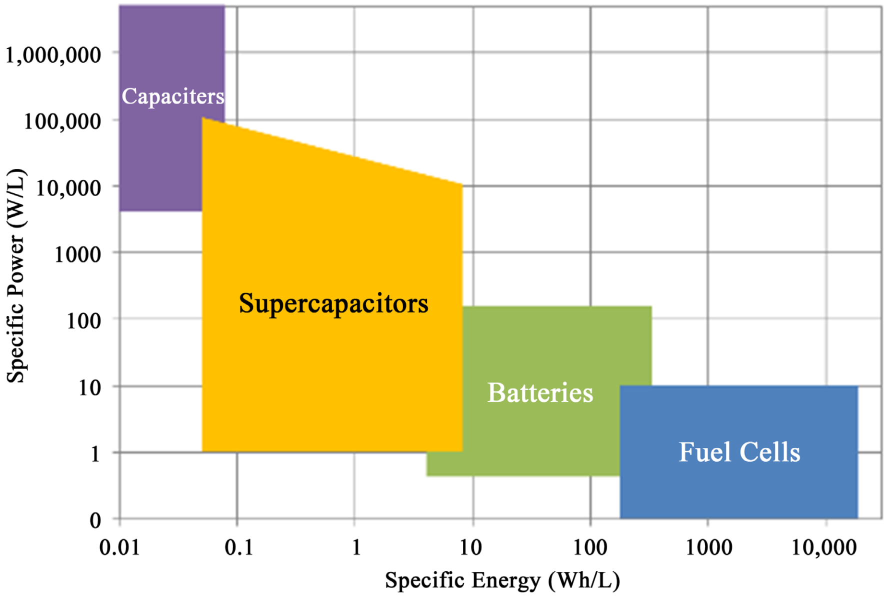

Figure 1. Ragone plot showing specific power vs specific energy of energy storage devices.

between the specific power and specific energy of energy storage devices and their design limitations [1]. Specific power (W/kg) is the rate at which the storage device discharges the energy stored per unit mass whereas specific energy (Wh/kg) is known as the amount of energy stored per unit mass of the storage device. There is a huge interest in this area to produce better energy storage devices with improved power and energy density through the design of novel materials [2].

Fuel cells possess the highest specific energy amongst energy storage devices. Fuel cells convert chemical energy into electrical energy by redox reaction between the anode and cathode [3]. Due to their high energy storage capabilities and low carbon footprint, fuel cells are used in stationary power plants, transportation systems, and portable power generation [4]. Fuel cells have many advantages and are often compared to batteries in terms of energy storage. Fuel cells are environmental friendly storage devices and have a low carbon foot print. However, they are expensive and can be dangerous because hydrogen is combustible.

Batteries also produce and store electrical energy via redox reduction between the anode and cathode. In batteries, the energy conversion and storage occur in the same compartment, while in fuel cells the anode and cathode are charge-transfer media and the energy is stored in a tank [5]. Batteries are classified as primary or secondary based on their capability to recharge [6]. Primary batteries are non-rechargeable in which the electrochemical reaction is irreversible, and often discarded after they are discharged. Secondary batteries are rechargeable after the cell is discharged, an externally applied electrical energy forces a reversal of the electrochemical process where the reactants are returned to their original form [7] [8]. Batteries have several advantages over other energy storage devices, and they are portable and widely used in electronic devices. Primary batteries are often inexpensive but once discharged, they have to be disposed properly or recycled. Secondary batteries lose some of their energy storage capacity after several use cycles [6].

Supercapacitors are also known as electrochemical capacitors or ultra-capacitors. Supercapacitors possess low specific energy compared to batteries, but they have a higher specific power [9]. Electrochemical capacitors use electrodes to transfer electric potential to electrolytes and store energy using double layer and pseudo capacitance via faradaic charge transfer [9] [10] [11] [12]. Electrochemical capacitors are classified as symmetric and asymmetric. Symmetric electrochemical capacitors use the same material for the positive and negative electrodes, while asymmetric capacitors use different materials for the positive and negative electrodes [10]. Electrochemical capacitors are used in transportation, utility and large consumer electronics that require quick discharge of stored energy.

Capacitors possess the highest specific power compared to the other energy storage devices but the lowest specific energy. Capacitors are key components in electrical and electronic systems. They are often used in applications that require pulsed power systems, power electronics, medical devices, filters, switch mode power supplies, and inverter in hybrid electric vehicles [13]-[20]. These applications often require capacitors with high energy density, low loss, high efficiency and operating temperature [21]. A capacitor consists of two metallic conducting plates separated by an insulating material. An insulator prevents the flow of electrons through the medium. A dielectric material is an electrical insulator that can be polarized by an applied electric field, thereby storing the energy electrostatically and releasing it by depolarization [22].

There are three types of capacitor technologies: ceramic, polymeric film, and electrolytic capacitors. Ceramic capacitors possess moderate energy density and high power density. They are used in low-voltage dc control circuits for blocking, buffering, by pass, coupling low frequency filtering, tuning, and timing. Polymer films are inexpensive and have great capacitive properties compared to the other materials. Polymer films possess high reactive power, high energy density and power density. They are often used in dc and ac applications involving high-power electronics pulse-duty circuits, high-frequency filtering, continuous ac operation and high-frequency inverter. Electrolytic capacitors possess moderate energy and power density with high losses. They are used in high-voltage applications mainly for dc applications involving filtering, rectified circuits, pulse circuits and commutation circuits [13]. **Table 1** below summarizes the dielectric properties of state of the art materials used for polymer film capacitors.

Polymer films are the focus of our studies because they show potential for high energy density, high dielectric constant and high-temperature applications. Polymer film capacitors are preferred for use in high-voltage pulsed power applications such as ac filtering because of their high dielectric breakdown strength [14]. They undergo degradation failure where the capacitor performance degrades slowly rather than abruptly [15]. This is important in systems that are

Table 1. Summary of dielectric properties of polymers used for capacitors.

Properties	BOPP	PEI	THV	PEEK	PI	PC	PTFE	PVDF-CTFE
Film Type	Semi-crystalline	Amorphous	Semi-crystalline	Semi-crystalline	Amorphous	Amorphous	Semi-crystalline	Semi-crystalline
Max use Temperature (˚C)	90	200	220	150	300	130	260	125
Energy Density at break down strength (J/cm^3)	5	1.3	6.84	2.6	1.3	3.7	2.1	17
Dielectric Constant at 1 kHz (K)	2.2	3.2	4.5	3.2	3.3	3.0	2.1	10
Dielectric Loss at 1 kHz (10^{-3})	0.2	2	0.5	4	2	1.3	0.5	50
Breakdown strength (MV/m)	720	300	600	430	300	530	300	620
Tensile Strength (ksi)	4.9	14	3.5	17.4	10.5	9.5	3	7.5

required to run constantly, graceful degradation allows the capacitor to perform at lower levels until it is replaced. Metalized film capacitors with metal electrodes are capable of a self-clearing, a process that repairs the breakdown losses that occurs in the polymer films [16].

Biaxial oriented polypropylene (BOPP) is the current state of the art high-energy-density material for polymer film capacitor, with a break down strength > 700 MV/m. But BOPP has a low dielectric constant of ~2.2 which limits the energy density, and low working temperature of 90˚C limits its use in high-temperature applications. The high-temperature applications often require an additional cooling system for effective thermal management within the capacitors in the electrical system that adds to the overall weight. The high-temperature polymer films can reduce the need for this extra cooling system, therefore, it is important to develop high-temperature polymers for future applications. Here, we will discuss two classes of polymers, and explain in detail the fabrication and characterization techniques used to develop these polymers in the research labs.

Polymers are chains of monomers chemically bonded together, which can be characterized by morphology and structure. Polymers are considered to be either amorphous or semi-crystalline, but they can never be completely one or the other. The glass transition temperature (T_g) or glass-rubber transition, is the temperature above which the polymer is rubbery and can be elongated and below which the polymer behaves as glass. Thermal analysis of amorphous polymers shows only a glass transition temperature, whereas crystalline polymers also exhibit a crystalline melting temperature. Semi-crystalline polymers exhibit a melting transition temperature (T_m), a glass transition temperature (T_g), and crystalline order, as shown by X-ray and electron scattering. The fraction of the crystalline material is determined by X-ray diffraction, heat of fusion, and density measurements. Major structural units of semi-crystalline polymers are the platelet-like crystallites, or lamellae [17].

In this study two polymer films were fabricated and characterized for their use as capacitors. PEI also known as ULTEM, is a member of the polyimide family, a group of polymers provided by General Electric [18]. PEI is an amorphous polymer with great electrical, mechanical and thermal properties which make it desirable for use as a dielectric material in capacitors [18] [19]. THV is a semi-crystalline polymer with high dielectric constant and high charge-discharge efficiency, and melting temperature [19] [23]. THV can be modified with different compositions of TFE/HFP/VDF by weight; in this study THV with high TFE (tetrafluoroethylene) content will be used. Polymer films can be readily scaled for large industrial production. Film fabrication techniques include solution casting, melt extrusion, which will be reviewed in this study. Other film process techniques such as stretching and annealing have been used to process polymer films.

2. Experimental Section

In this study, a solution cast method is used to process PEI resins to film. In a solution-cast method polymer resin or powder is dissolved in a miscible solvent to prepare a solution. PEI resins are soluble and can be dissolved in partially halogenated aliphatic liquids such as methylene chloride and chloroform as are certain dipolar aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC) and N-methylpyrrolidone (NMP) [18]. A melt extrusion involves the melting and pressing of the polymer resin into a film. The melt extrusion method is used to process the THV resins.

PEI can be processed into film using a solution-cast method or a melt extrusion [22]. For the solution cast method used in this study, PEI is dissolved in dimethyl formamide (DMF), a polar solvent used in this study. **Figure 2(a)** A 2%wt PEI and DMF solution **Figure 2(b)** is used to make the PEI films. PEI resins weighed at 0.2 grams are dissolved using 9.8 grams of DMF. A magnetic stir bar is cleaned with ethanol and placed into the mixture to stir the solution. The solution is heated and stirred on a hot plate at 30˚C for 12 hours with the magnetic stir bar. The PEI resins are completely dissolved into the solution. The PEI solution is filtered using a nylon acrodic syringe filter to remove impurities in the solution. The filtered solution is transferred evenly using the syringe to a

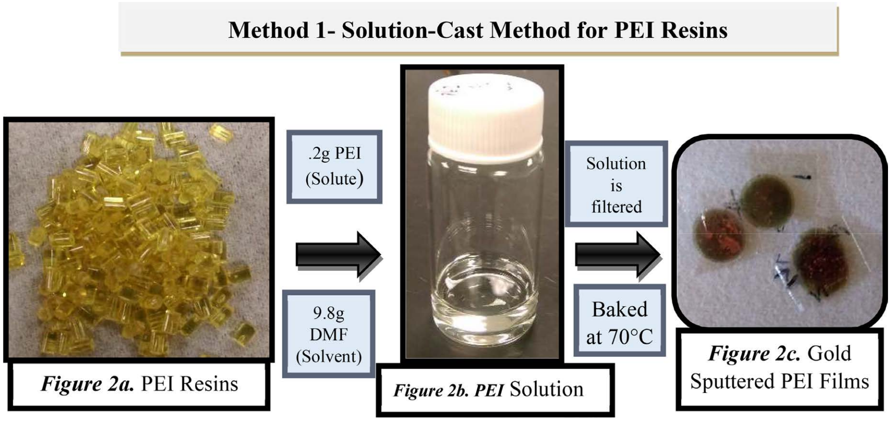

Figure 2a. PEI Resins

Figure 2b. PEI Solution

Figure 2c. Gold Sputtered PEI Films

Figure 2. Solution cast method for PEI resins.

glass plate and oven heated at 70˚C for 12 hours to reduce the DMF content of the solution. Once solution is baked, the film is air cooled and peeled off the glass plate.

THV resins with TFE/HFP/VDF-76/13/11 by weight are processed into film using a melt-extrusion process described here. THV's semi-crystalline structure makes it difficult to dissolve. The melt-extrusion method is used by industry to process polymers to film. A HAAKE Minilab with 18 mm twin screw extruder Figure 3(b) is used to melt 10 grams of THV resins Figure 3(a). The THV is melted at 250˚C for 20 minutes in the HAAKE Minilab. The melted THV is removed from the twin screw. The THV is placed into Teflon and pressed at 300˚C between the hot plates. The starting pressure between the plates is 700 psi for five minutes. The pressure between the plates is increased to 1000, 1500, and 2000 psi at 5 min intervals. It is then air cooled for 1 hour, and water cooled for 15 - 30 mins. The melt extrusion process is much faster than the solution cast method.

In order to characterize the processed films (Figure 2(c) & Figure 3(c)) they are prepared for characterization. The processed films are metalized using a sputter machine. The films are placed between shadow masks. Sputtering to create contacts for characterization contacts is done by using conductive metals such aluminum and gold. The metalized spot determines conductive area of the film. Gold spots about 6 mm in diameter are sputtered on both sides of the film by placing it in the sputter chamber of an Emitech K550A. Using an Agilent 4294A precision impedance analyzer, the dielectric loss of the films is measured using a sweep log from 100 Hz to 1 MHz frequency as shown in Figure 4.

3. Results and Discussion

A capacitor's ability to store charge is determined by its capacitance C. A materials's capacitance is governed by Equation (1) where ε = permittivity, A is the contact area, and d the thickness of the material.

$$C = \frac{\varepsilon * A}{d} \tag{1}$$

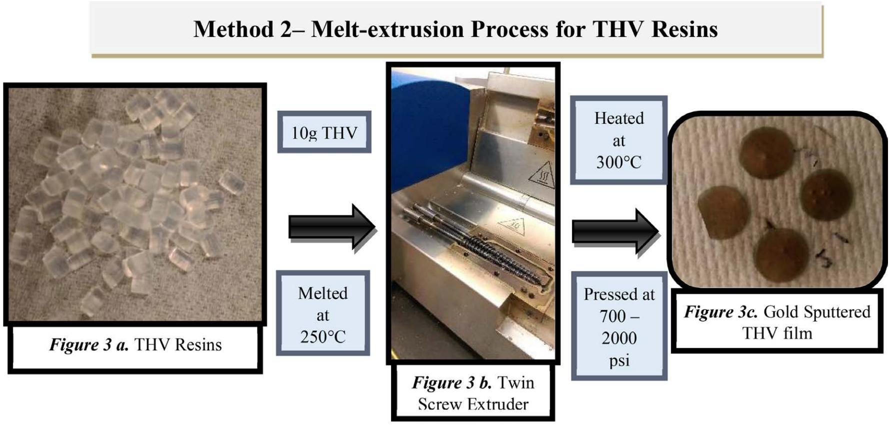

Figure 3. Melt-extrusion process for THV resins.

Based on Equation (1) for capacitance, reducing the thickness of the material increases the capacitance, polymer films with thickness in the nm - µm range make them favorable and can also increase the energy density of the film capacitors. With advanced production technologies, free-standing ultrathin polymeric capacitor film with thickness down to 0.5 µm can be manufactured at large scale with low cost [23]. The film thickness is measured using a Heidenhain ND287 digital micrometer. The thickness of the PEI films ranged from 7 - 15 µm, the thickness of the THV ranged from 30 - 50 nm. The uniformity in film thickness can be further improved by enhancing the fabrication methods used. The dielectric loss of THV and PEI from 1 kHz to 1 MHz are presented in **Figure 4** and **Figure 5** respectively.

The materials permittivity is determined by equation (2), where k is the materials dielectric constant and ε_o, is the vacuum of permittivity, $\varepsilon_o = 8.85 \times 10^{-12}$ F/m. The dielectric constant (k) of the films is calculated by rewriting Equation (1) to Equation (3).

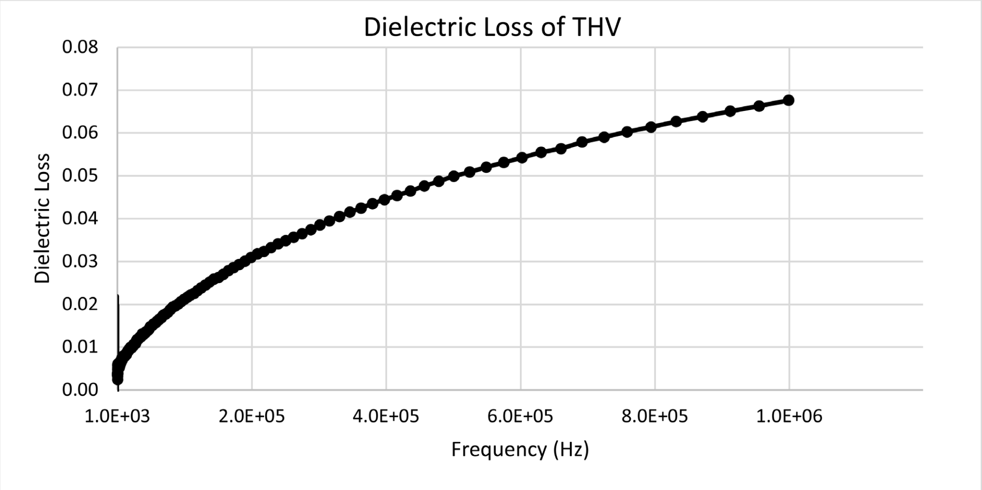

Figure 4. Dielectric loss of THV polymer film from 1 kHz to 1 MHz.

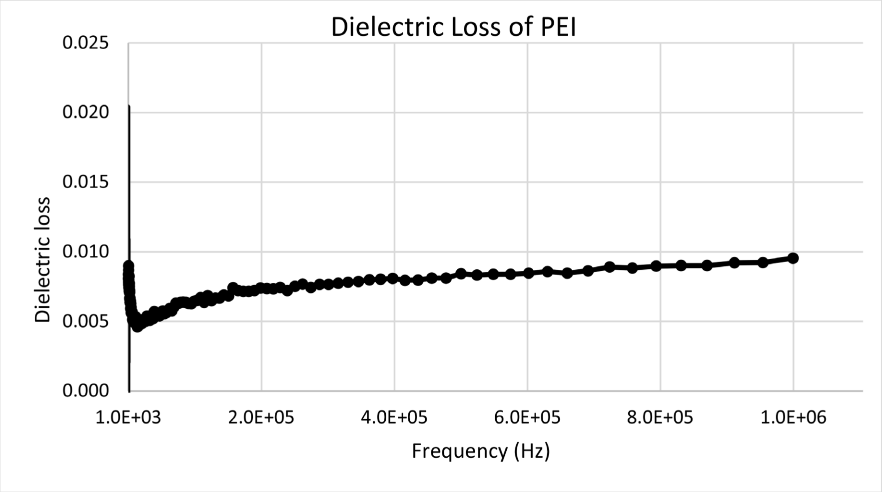

Figure 5. Dielectric loss of PEI polymer film from 1 kHz to 1 MHz.

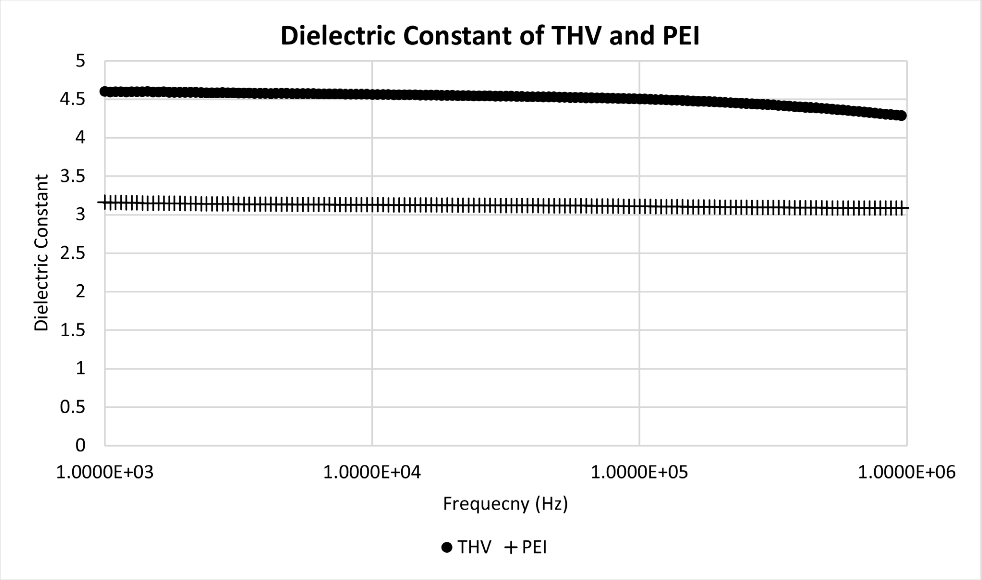

Figure 6. Dielectric constant of THV and PEI polymer films from 1 kHz to 1 MHz.

$$\varepsilon = k * \varepsilon_o \tag{2}$$

$$k = \frac{C * d}{\varepsilon_o * A} \tag{3}$$

The dielectric constant of the films over 1 kHz to 1 MHz is presented in **Figure 6**. PEI has a dielectric constant of 3.2, while the dielectric constant of THV is 4.5, which is higher than state-of-the-art dielectric BOPP.

In Ref. [3] PEI was tested for use in high-temperature applications. It was found that the PEI is suitable for use in applications with a maximum use temperature of 200˚C. In [4] THV polymers with varying TFE contents were studied under different tests. The melting temperature of the THV is above 220˚C [23]. Thus it makes them suitable for high-temperature applications.

Energy density of a dielectric material is defined by Equation (4). Where ε_o is the permittivity of free space, k is the material's dielectric constant, and E is the breakdown strength of the dielectric material.

$$U_E = \frac{1}{2} \times K\varepsilon_o \times E^2 \tag{4}$$

Various government agencies have been seeking dielectric materials that can offer a high energy density > 20 J/cm^3 and operating temperatures at 200˚C for pulsed power and power conditioning application [7]. A dielectric material's energy density can be increased by increasing the breakdown strength. PEI has an energy density of 3.5 J/cm^3 and THV has an energy density of 4.65 J/cm^3.

4. Conclusion

This paper reviewed four major energy storage devices, fuel cells, batteries, supercapacitors and capacitors. Among the energy storage devices reviewed, capacitors possess the highest specific power and they are preferred in high-pulsed power applications. The search for innovative materials with high power density, high energy density and high-temperature capacities is of utmost interest in this field. The two categories of polymers—an amorphous and semi-crystalline polymer—were fabricated and characterized for their use in capacitor applications. The amorphous polymer film was fabricated with a solution-cast method while the semi-crystalline polymer film was fabricated with a melt extrusion method.

There has been a growing interest by researchers in this community to improve the dielectric properties of the polymer films by introducing nanocomposites during the film fabrication process, which is likely to be a future trend in this area.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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