Effects of Heat Treatment on the Properties of Heterogeneous Cation Permeable Membranes from Blends of Poly(ether sulfone)/Sulfonated Poly(phenylene sulfide) and Phenolphthalein Poly(ether ether ketone)/Sulfonated Poly(phenylene sulfide)

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ABSTRACT: The effects of heat treatment on the properties of membranes prepared from blends of poly(ether sulfone)/sulfonated poly(phenylene sulfide) (SPPS) and phenolphthalein poly(ether ether ketone)/SPPS were studied in detail. The membranes' fundamental properties, including water content, transport number, diffusion coefficient of electrolytes, flux, and so on, changed with both treated temperature and time, whereas the ion-exchange capacity and electrical resistance remained approximately unchanged. The trends may have been due to the possible structural change resulted from the shrinking of the polymers forming the membranes. Furthermore, the membranes also retained a good physical appearance at temperatures below 220°C. Therefore, a series of heterogeneous membranes with desired conductivities and selectivities as well as proper water contents, which could satisfy different industrial purposes, such as electrodialysis, diffusional dialysis, and proton exchange, were achieved by simple heat treatment for a proper time and at a proper temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 494–499, 2005

Key words: blends; ion exchangers; membranes; poly(ether sulfones); poly(ether ketones)

INTRODUCTION

The technique for separation membrane manufacture has experienced a sharp improvement because the synthetic membrane was used half century ago, and multiroutes have been developed for different membranes due to various practical requirements.[1–3] In the procedure of these routes, heat treatment (or annealing) has frequently been used as a necessary method

for the formation of membranes or to improve the quality of the membranes, especially the latter.[3–6] For example, a heterogeneous membrane may be prepared by the dispersion of the resin powders with polymer binder and then by pressing at high temperature.[3] In addition, Amanda et al.[4] found that heat-treated poly(vinyl alcohol) ultrafiltration membranes had a higher selectivity than untreated poly(vinyl alcohol) membranes. Furthermore, for poly(ether sulfone) (PES) hollow-fiber membranes prepared by the dry–wet spinning method, a decrease in flux (*F*) and an increase in solute separation was found when they were treated at 150°C.[5] To improve quality, the temperature used may be under or above the polymer's glass-transition temperature[4–5] and even above the melting temperature.[6] The conditions mainly depend on the system considered and the outcome expected. It is not difficult to understand that when a membrane is treated by heat under the polymer glass-transition temperature, the improvement in membrane quality will be mainly caused by shrinkage of the polymer.

A polymer of PES and phenolphthalein poly(ether ether ketone) (PEEK-C) that could endure temperatures as high as 200°C had been used to prepare heterogeneous membranes of PES/sulfonated poly(phenylene sulfide) (SPPS) and PEEK-C/SPPS.[7,8] Al-

TABLE 1
Effect of Heat Treatment on the Physical Appearance of Membranes Prepared
from the PES/SPPS and PEEK-C/SPPS Blends

Heating time (h)	130°C	160°C	190°C	220°C	250°C
0	No change	No change	No change	No change	No change
2	No change	No change	No change	No change	Brittle and brown
4	No change	No change	No change	No change	Brittle and brown
6	No change	No change	No change	No change	Brittle and brown
8	No change	No change	No change	No change	Brittle and brown
10	No change	No change	No change	Little change	Brittle and brown

though the membranes were appropriate for many purposes, there were still some demands for the improvement in the membranes' properties, such as in their relatively low water content and compact membrane structure, to cater to more practical applications. As discussed in previous articles,[7,8] the membranes' properties are mainly dependent on the ion-exchange capacity (IEC) and their structure. One can expect that when the membranes are treated with heat, the properties of such membranes be naturally affected by the shrinkage of PES or PEEK-C, which acts as a binder therein. Therefore, the main purpose of this study was to investigate the effects of heat treatment on the membranes' properties. Emphasis was given on the change of both the mechanical and electrochemical properties of the membranes with the temperature and time of heat treatment.

EXPERIMENTAL

Materials

Poly(phenylene sulfide) (PPS), PES, and PEEK-C were conventional polymers and were purchased from the Chinese commercial market. Concentrated fuming sulfuric acid (98 wt %, 20% SO_3), dimethylformamide, and other chemicals were obtained commercially and were used without further purification. All of the chemicals used in the experiments were analytical grade.

Sulfonation of PPS

The sulfonation method of PPS was completely the same as described in our previous studies.[7,8] In this study, SPPS with an IEC of 2.67 mequiv/g (sulfonation degree = 0.36) was used to prepare the membranes. The particle size of the resins was about 200 mesh number, corresponding to an average particle size of less than 76 μm.

Membrane preparation and heat treatment

The membrane preparation was analogous route used in our previous investigations,[7,8] and the ratio of the binder to resin was 1:3; correspondingly, the IEC of the prepared membranes was about 2.0 mequiv/g of dry membrane

We conducted the heat treatment by putting the membranes into an oven with air circulation at the desired temperatures, including 130, 160, 190, and 220°C. At predetermined time intervals, samples were taken out and cooled in the atmosphere.

Evaluation of the membrane properties

The characteristic properties of the membranes investigated included ion exchange capacity (IEC), water content (C_R), area resistance (R_m), the diffusion coefficient (D), and F. The methods used were completely the same as those used in our previous studies,[7–10] and the experiments were conducted at room temperature, about 10°C.

The thermal behavior of the membranes was determined by thermogravimetric analysis (TGA) on a Shimadzu TGA-50H analyzer (Shimadzu Corp., Kyoto, Japan) under an air flow at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Effects of heat treatment on the physical appearance of membranes from the PES/SPPS and PEEK-C/SPPS blends

The effects of heat treatment on the PES/SPPS and PEEK-C/SPPS heterogeneous membranes was preliminarily evaluated from the physical appearance of the treated membranes, and thus, descriptions of the physical appearances of the membranes treated for different times and at different temperatures are presented in Table I. As shown in Table I, under 220°C, there were few effects on the appearance of the membranes for all of the heat treatment times. However, with increasing temperature, that is, at 250°C, serious phenomena appeared: the membranes became brown, the quality of membranes turned brittle, and most important, the electrical properties of the treated membranes underwent drastic deterioration. For instance, the IEC and the static transport number (t^+) decreased largely. Similar evidence was also observed
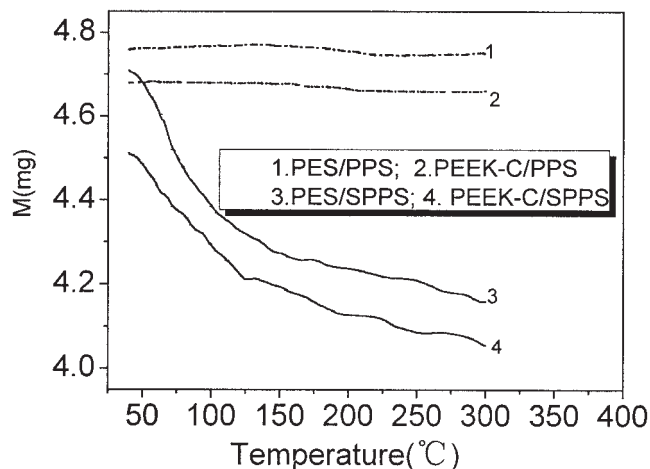
Figure 1 TGA contrasts of the PES/SPPS, PES/PPS, PEEK-C/SPPS, and PEEK-C/PPS membranes.

Figure 2 Effect of heat treatment on the IEC of the PES/SPPS membranes. T is the temperature for heat treatment.

in the results of TGA. As shown in Figure 1, there was no evidence of weight loss for the PES/PPS and PEEK-C/PPS membranes under 300°C. However, for the PES/SPPS and PEEK-C/SPPS membranes, there were three periods of weight loss. It was not difficult to understand that the loss of weight before 230°C was mainly caused by the loss of binding water in the membrane and that after that, the weight loss was mainly due to the loss of sulfuric groups.

From the viewpoint of the physical appearance of the membranes, our results suggest that appropriate conditions for such membrane treatment be a temperature of under 220°C and a time of less than 10 h. Such temperature is under the glass-transition temperature of both the PES (225°C) and PEEK-C (231°C) but higher than that of SPPS (90°C).

Effects of heat treatment on the IEC and water content of the PES/SPPS membranes

Sufficient IEC and proper moisture content values are important for such membranes from the viewpoint of practical purposes. As shown in Figure 2, the IEC of the membranes kept approximately unchanged after heat treatment under temperature 220°C, despite what the treatment time was. This suggests that the sulfonic groups were stable under this temperature. The facts were confirmed by TGA, as shown in Figure 1.

As discussed in our previous articles,[7,8] the water content was mainly determined by both IEC values and the structures of the membranes. Thus, with the same IEC, the water content of the membranes will mainly depend on the structure. Due to the heat treatment, the binder tend to shrink and condense the membrane structure. This will give rise to a decrease in the water content. As shown in Figure 3, for all the temperatures concerned, the water content decreased
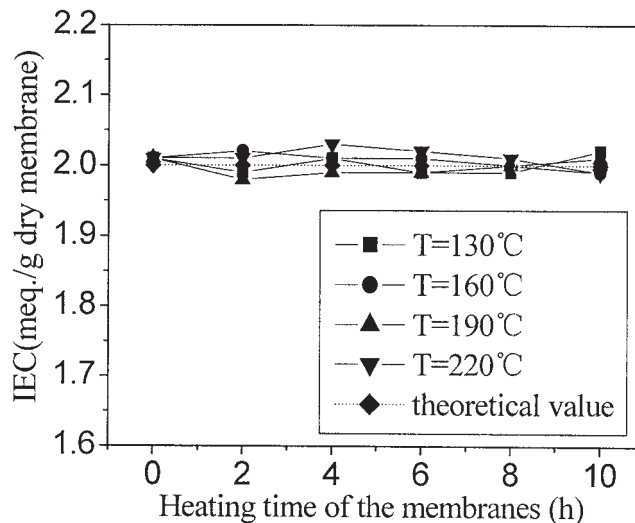
with heat-treatment time at the initial 2h and then kept approximately unchanged. The maximum degree of decrease in the water content was 25%, that is, water content decreases from an original value of 1.87 to a final value of 1.40 at 220°C. These facts indicated that the higher temperature was, the higher shrinking degree of the membranes' binder was; that is, the lower water content (C_R) is. As far as the treatment time was concerned, there was a limited affect on the shrinkage, that is, on the water content. Therefore, by controlling both the temperature and the time of the treatment, we reasonably acquired a series of membranes to satisfy with different industrial demands with desired water content but without changing the IEC values.
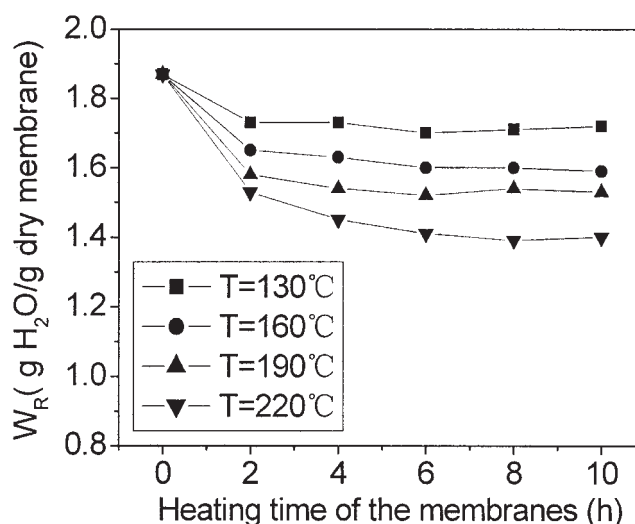

Figure 3 Effect of heat treatment on the water content of the PES/SPPS membranes.

Effects of heat treatment on R_m of the PES/SPPS membranes

The effect of heat treatment on R_m of the membranes prepared from PES/SPPS blends is shown in Figure 4. R_m remained approximately unchanged with changes in both treatment temperature and time. The trend was almost the same as that of the IEC changes shown in Figure 2. Superficially speaking, the membrane R_m should have increased after heat treatment due to water loss, as shown in Figure 3. Another factor possibly existed to counter condensing effects on R_m. As we know, a heterogeneous exchange membrane can be considered by a three-phase model to be a gel phase with a relatively uniform distribution of ionogenic groups (SPPS occupation), an intergel phase with an electroneutral solution filling the interstices between the elements of the gel phase, and an inert phase with hydrophobic polymer (PES occupation).[11–12] When the membranes are exposed to heat treatment, the shrinkage of the membranes may lead to a volumetrical decrease in intergel phase, as proven in Figure 3. This tends to give rise to a corresponding increase in membrane R_m. However, on the other hand, shrinkage of the membranes may also tend to decrease the volumetric ratio of the inert phase occupied by PES, causing the activity points to become closer to each other, which should improve the continuity of the activity points and thus reduce R_m. Colligating these two reverse effects caused by binder shrinkage; the integrative result was that R_m remained approximately unchanged after the heat treatment process. This is very important for ion-exchange membranes, especially for electrodialysis purposes.

Effects of heat treatment on t^+ of the PES/SPPS membranes

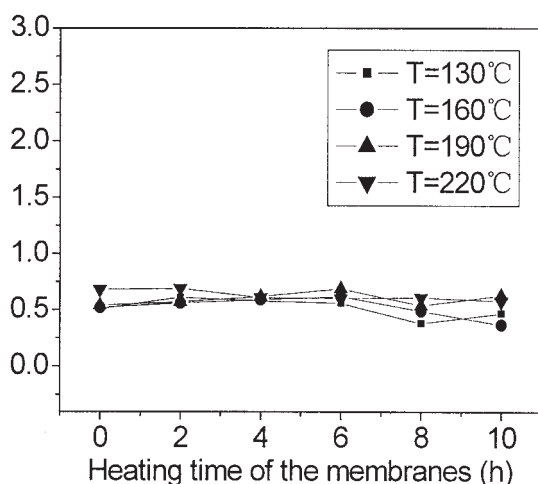The permselectivity of the treated membranes at different temperatures and times was characterized by

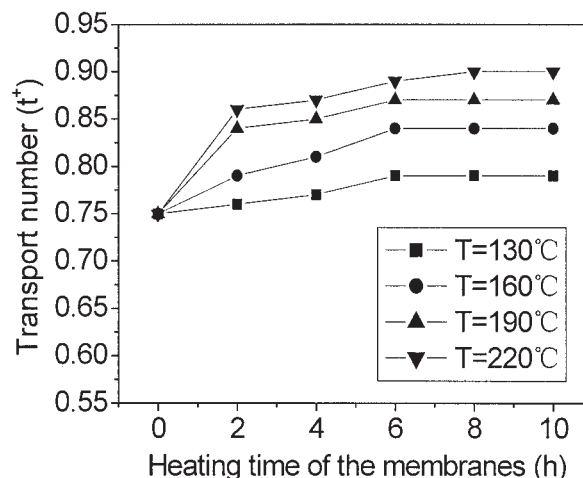**Figure 5** Effect of heat treatment on t^+ of the PES/SPPS membranes.

Figure 4 Effect of heat treatment on the IEC of R_m of the PES/SPPS membranes.

the measurement of the concentration membrane potential between $0.2M/0.1M$ KCl solutions. The t^+ values of the cations (potassium ions) were calculated on the bases of these potentials and are shown in Figure 5. Obviously, t^+ increased with temperature of heat treatment. At temperatures of 130 and 160°C, t^+ slightly increased during the first 4 h and then attained a plateau value, whereas at temperatures of 190 and 220°C, the increase trends occurred in the first 2 h. This suggests that the higher the temperature for heat treatment was, the faster t^+ approached a stable value (i.e., the faster the membrane structures approached stability).

Theoretically speaking, t^+ or selectivity is related to the ratio of IEC to water content, that is, fixed-group concentration, and is not directly related the single water content or IEC.[7,8,13] The fixed-group concentration calculated from IEC and water content at different heating times and temperatures is shown in Figure 6. Obviously, the fixed-group concentration increased with temperature and time of the heat treatment, permitting the same order for selectivity, based on which trend in t^+ was understood.

To summarize, by the simple process of heat treatment, membranes with desired t^+ values were obtained just through the adjustment of the temperature and time of the treatment.

Effects of heat treatment on D of the PES/SPPS membranes

D values of the membranes with different heat treatment times and temperatures are shown in Figure 7. Interestingly, D underwent different change trends with different treatment temperatures. For example, at 130°C, D of the membranes first decreased and then flattened. Although at the other temperatures, such as
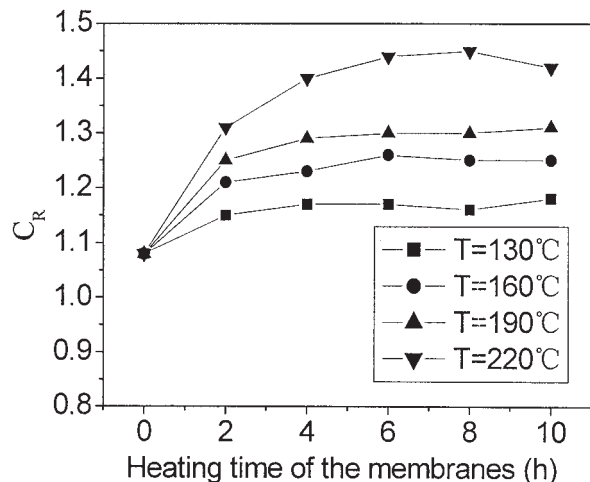
Figure 6 Effect of heat treatment on the fixed-group concentration of the PES/SPPS membranes.
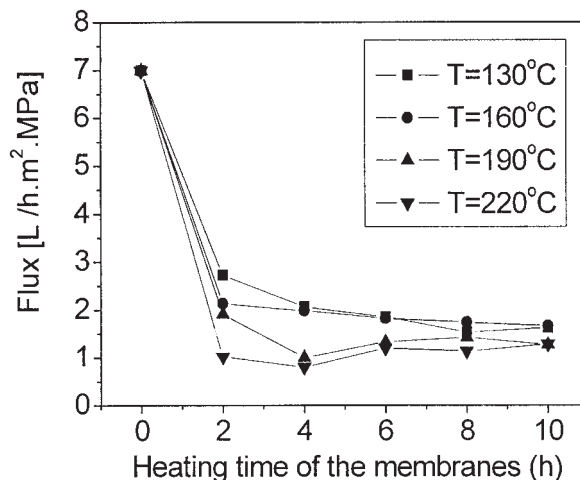

Figure 8 Effect of heat treatment on F of the PES/SPPS membranes.

160, 190, and 220°C, with an increase in the treatment time, D underwent a curve of first decrease and then increase. Also, the higher temperature of treatment was, the earlier the turning point appeared.

As discussed previously, the physical structure of an ion-exchange membrane was considered from the viewpoint of a three-phase membrane model, where the membrane consists of a hydrophobic polymer zone (inert phase), an active exchange zone (gel phase), and an interstitial zone (intergel phase containing an electroneutral solution). Unlike t^+, which is dependent on counterion diffusion occurring mainly through the active region, where it moves by a hopping mechanism and has a greater mobility than that in the interstitial zone due to the dragging mechanism,[12] D is, in fact, dependent on the co-ion diffusion occurring mainly
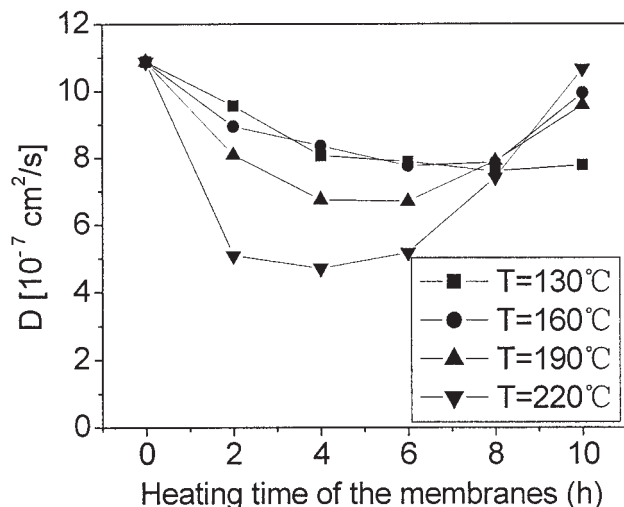
through the interstitial zone and inert phase. Therefore, when the temperature increases or the heat treatment time is elongated, the intergel phase with the electroneutral solution filling the interstices between the elements of the gel phase decreases due to the shrinkage of polymers, and this thus leads to a corresponding decrease in D or the transport of co-ions. However, there exists another possibility: when the membrane is exposed to heat treatment, the active points in the gel phase and those isolated by the inert polymer PES become more intimate and compact due to the shrinking of the inert phase, and counterion transport is enhanced, and co-ion diffusion is thus simultaneously enhanced. This explained the experimental fact that with high-temperature treatment, D first decreased (due to the reduction in the intergel phase) and then increased (due to a reduction in the inert phase, the counterions sped up the transport and simultaneously carried the corresponding co-ions).

Effects of heat treatment on F of the PES/SPPS membranes

It is certain that the shrinkage of the binder should have been reflected in the F values of the membranes. As shown in Figure 8, for the treated membranes at the investigated temperatures, F decreased drastically during the first 2 h and then remained approximately unchanged. Furthermore, the higher the treatment temperature was, the sharper the decrease in F was. The results were consistent with the water content change as discussed earlier and also showed consistency with the heated PES hollow-fiber membranes prepared by the dry–wet spinning method.[5] Therefore, we concluded that the membrane structure became condensed after heat treatment.

Figure 7 Effect of heat treatment on D of the PES/SPPS membranes.

TABLE II
Effect of Heat Treatment on the PEEK-C/SPPS Membranes

Temperature (°C)	Time (h)	IEC (mequiv/g)	W_R (g of H_2O/g of dry membrane)	t^+	D (10^{-7} cm^2/s)	R_m (Ω cm^2)	F [L/(hm^2 MPa)]
160	0	2.01	1.71	0.70	16.72	0.40	5.40
	2	1.98	1.54	0.73	15.35	0.43	1.51
	4	2.01	1.50	0.74	15.35	0.52	1.00
	6	1.99	1.50	0.74	15.36	0.61	1.05
	8	2.02	1.50	0.75	15.30	0.52	1.00
	10	2.00	1.47	0.75	15.23	0.43	1.12
190	0	2.01	1.71	0.70	16.72	0.32	5.40
	2	2.00	1.49	0.78	14.09	0.39	1.02
	4	2.02	1.47	0.80	12.98	0.43	0.60
	6	2.03	1.46	0.80	13.29	0.41	0.95
	8	2.00	1.46	0.79	13.66	0.30	1.07
	10	1.99	1.45	0.79	17.66	0.54	1.22
220	0	2.01	1.71	0.70	16.72	0.46	5.40
	2	2.02	1.47	0.80	10.66	0.48	0.70
	4	2.03	1.36	0.81	9.68	0.63	0.43
	6	1.99	1.32	0.82	10.72	0.42	0.68
	8	2.00	1.27	0.82	12.55	0.50	0.70
	10	2.03	1.27	0.82	18.22	0.61	1.02

Effects of heat treatment on the properties of the PEEK-C/SPPS membranes

As a comparison, the effects of the heat treatment of heterogeneous membranes prepared from PEEK-C/ SPPS (i.e., PEEK-C in place of PES) were also investigated. The characteristics of these membranes before and after heat treatments are shown in Table II. Obviously, the fundamental conclusions of the PES/SPPS membranes were well applicable to the PEEK-C/SPPS membranes: the IEC and R_m remained approximately unchanged with treatment; the water content and t^+ first decreased and then reached plateaus. The reasons may have been the same and are not discussed here. Therefore, the improvements in membrane performance with heat treatment can be applied to all membranes prepared from the polymers of polysulfone and polyketone or their blends with other polymers.

CONCLUSIONS

By the rational adoption of the shrinking properties of the polymers of polyketone or polysulfone, a simple but efficient method for conveniently adjusting the properties of heterogeneous cation permeable membranes made from phase inversion was initiated. Special examples were conducted on the membranes made from PES/SPPS and PEEK-C/SPPS blends. As expected, some of the fundamental membrane properties, such as water content, transport number, diffusional coefficient of electrolyte, and pure water flux

were easily and conveniently adjusted with different heat-treatment conditions, with the IEC and the electrical resistance remaining approximately unchanged. This method may provide a very flexible means for adjusting the properties of heterogeneous membranes such as PES/SPPS and PEEK-C/SPPS, which were discussed in detail in our previous articles,[7,8] and thus enlarge the application field for such cation-exchange membranes.

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