Role of Heat Transfer and Thermal Conductivity in the Crystallization Behavior of Polypropylene-Containing Additives: A Phenomenological Model

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ABSTRACT: The thermal conductivity of a filler and the thermal conductivity of a composite made from that filler influence the heat-transfer process during melt processing. The heat-transfer process from the melt to the mold wall becomes an important factor in developing the skin–core morphology. These aspects were examined in this study. The thermal conductivity of polypropylene–filler composites was estimated with a standard model for various fillers such as calcium carbonate, talc, silica, wollastonite, mica, and carbon fibers. The rate of cooling under given conditions, including the melting temperature, mold wall temperature, mass of the composite, and filler content, was estimated with standard heat-transfer equations. The time to attain the crystallization temperature for polypropylene was evaluated with a regression method with differential tem-perature steps. The crystallization curves were experimentally determined for the different fillers, and from them, the induction period for the onset of crystallization was estimated. These observations were correlated with the expected trends from the aforementioned formalism. The excellent fit of the curves showed that in all these cases, the thermal conductivity of the filler and composite played a dominant role in controlling the onset of the crystallization process. However, the nucleation effects became important in the later stages after the crystallization temperature was attained. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2994–2999, 2003

Key words: poly(propylene) (PP); crystallization; thermal properties; fillers; additives

INTRODUCTION

Polymers are generally used with different types of additives, such as stabilizers, processing aids, coloring agents, and fillers. In the polymer processing industry, many types of fillers are incorporated into resins for different reasons, including improvements in the mechanical properties, color matching, surface finishing, gloss, and cost reduction.[1–3] Polypropylene (PP) has drawn considerable attention in recent years because it can be modified by additives and fillers to obtain properties that are comparable to those of engineering plastics.[4,5] These various additives are known to affect the crystallization behavior of the polymer. Studies have been reported by several groups, including our own, on the crystallization behavior of PPs containing calcium carbonate, calcium sulfate, talc, mica, and wollastonite. In most of these studies, the emphasis was placed on the nucleation, preferential growth, and so forth.[6–10] However, it is well known that the rate of cooling plays an important role in determining the crystallinity and/or morphology obtained in the final product made by melt processing.[11] Because the thermal conductivity of the filler and that of the composite containing that filler are important factors governing the heat-transfer process, we felt that a systematic investigation into the role of thermal conductivity in the crystallization of PPs containing different fillers would lead to a better understanding of these phenomena. However, until now, no work has been reported on developing the corelationships of the thermal conductivity, induction time, cooling time, crystallinity value, and so forth. Furthermore, because the crystal structure and the morphology are responsible for the properties of the final product, a knowledge and understanding of the crystallization process are important for designing the material for a given product. This article addresses these issues, and an attempt has been made to correlate the different parameters with the help of a phenomenological model described here.

PHENOMENOLOGICAL MODEL

Polymers are usually processed in industry by either injection molding or extrusion techniques. The crystallization of a polymer from the melt takes place while it cools in the mold or as it extrudes out in the cooling zone (usually a water trough). During this step, the heat from the melt has to be transferred to the surroundings. In the injection-molding and compres-

sion-molding processes (considered for simplicity), the polymer is in contact with the mold, and the heat is conducted away from the melt by the mold walls. Because the polymer (melt or solid) has a quite low thermal conductivity (ca. 0.01 W/m), the heat transfer from the central portion of the melt is much slower than that at the surface. This leads to uneven crystallization rates through the polymer, giving rise to a skin–core morphology, as indicated in Figure 1. Such morphological features have been reported previously by some authors, but they have not been correlated with the rate of heat transfer or the thermal conductivity.[12,13] The addition of fillers to the polymer leads to large changes in the thermal conductivity, giving rise to faster cooling. Therefore, this aspect is first considered in this formalism.

The thermal conductivity (K) of polymers containing fillers can be estimated by different models developed for such composites, including the simple rule of mixtures, series/parallel models, the Hashin–Schtrikman model, the Hamilton–Crosser model, and Nielsen's model.[14,15] Among these, Nielsen's model[16] is known to be most accurate in predicting the values of K. Therefore, it was used here. According to this model, the K value of a composite is given by

$$\frac{K_c}{K_p} = \frac{[1 + (A - 1)B\phi]}{(1 - \psi B\phi)} \tag{1}$$

$$\psi = \frac{1 + (1 - \phi_{max})\phi}{\phi_{max}^2} \tag{2}$$

$$B = \frac{(K_f/K_p - 1)}{(K_f/K_p + A - 1)} \tag{3}$$

where ϕ is the filler concentration (volume fraction); A and B are parameters; ϕ_{max} is the maximum filler packing for a given geometry; and the subscripts c, f, and p give the corresponding values for the composite, filler, and polymer, respectively. The coefficient A depends on the geometry and orientation of the filler particles. Nielsen provided values of A for a wide range of common filler types. For spherical filler par-
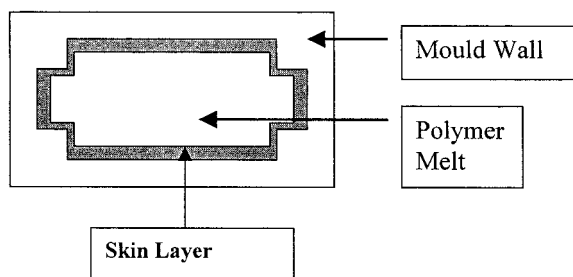
TABLE I
Reported Standard Values for K and C_p for Different Fillers[21–24]

Filler type	K (W/mK)	C_p (cal/g.°C)	Φ_{max}
Wollastonite	0.824	0.24	0.62
Silica	1.49	0.19	0.70
Glass fiber	1.17	0.197	0.42
Talc	2.09	0.203	0.45
Mica	2.5	0.207	0.38
Calcium carbonate	2.7	0.21	0.80
Carbon fiber	7	0.2	0.40

ticles, A is 2.5. The values used for the parameters A and ϕ_{max} in Nielsen's equation are 2.5 and 0.637, respectively. The values of K, the specific heat (C_p), and ϕ_{max} for the fillers used are indicated in Table I. PP by itself has K and C_p values of 0.23 W/mK and 0.427 cal/g °C, respectively.[17] The K value for each of the compositions was estimated with these values in eqs. (1)–(3). These are indicated in Tables II and III.

The rate of cooling of a molten composite can be estimated as follows. Initially, when the melt comes in contact with the external mold wall surface, the heat is transferred according to the Fourier equation for unsteady heat transfer in one dimension (x). A heat balance for the object being cooled then gives the amount of heat transferred in the time interval (Δt) as follows:

$$\frac{\Delta Q}{\Delta t} = \left[\frac{KA_1\Delta T}{\Delta x}\right]$$

$$\Delta Q = (mC_p\Delta T) \tag{4}$$

where ΔT is the temperature difference between the melt and the external medium, A_1 is the cross-section area, Δx is the thickness of the sample, and m is the mass. It is assumed that the heat, once transferred to the wall, is rapidly conducted away (the metal being

TABLE II
Dependence of the Induction Period on the K Values of PP with Fillers at 10 wt %

Composition (10 wt %)	K[a] (W/mK)	Induction period[b] (s)
Pure PP	0.23	263
PP + wollastonite	0.263	191
PP + glass fiber	0.271	183
PP + silica	0.277	138
PP + talc	0.285	135
PP + mica	0.286	140
PP + calcium carbonate	0.286	130
PP + carbon fiber	0.292	108

[a] Estimated from eqs. (1)–(3).
[b] Samples isothermally crystallized at 115°C from the starting melt at 200°C.

Figure 1 Schematic diagram of polymer melt cooling in the mold with the formation of a skin layer.

TABLE III
Variation of K and Skin-Layer Thickness in PP with ϕ

Composition (wt %)	K^a (W/mK)	Skin-layer thickness^b (mm)
PP with		
5% TC	0.253	0.38
10% TC	0.285	0.41
20% TC	0.345	0.44
30% TC	0.436	0.54
40% TC	0.573	0.57
PP with		
5% CC	0.257	0.41
10% CC	0.286	0.48
20% CC	0.354	0.56
30% CC	0.454	0.58
40% CC	0.612	0.64

TC = talc; CC = calcium carbonate.
^{a} Estimated from Nielsen's model with eqs. (1)–(3).
^{b} Data reported for injection-molded 3-mm-thick samples (refs. 12 and 13).

1000 times better as a conductor than the polymer). The cooling curve (the temperature at any given time) was generated with a Δt value of 1 min. Equation (4) was used for estimating the temperature difference for the initial step, which gave the temperature attained by the melt after Δt, which was then subsequently used for the next step and so on. The values of K and C_p were those estimated for that type of filler and composition with the Nielsen model, which was described previously.

To estimate the induction time for the onset of crystallization, we assumed that the melt had to reach the temperature at which maximum crystallization was observed for that polymer. Therefore, a line through this temperature was drawn parallel to the time axis on the cooling curve, and the common points gave the induction times for crystallization for that composition. The nucleation effects were not taken into consideration, but they are discussed later in the article.

EXPERIMENTAL

PP (Indothane, SM 85N, MFI 8-12, IPCL, India) was made into a fine powder form by the precipitation of its solution followed by thorough washing with acetone and drying for 24 h *in vacuo*; this yielded the pure form of the PP powder. To study the crystallization behavior of PP filled with different types of fillers (e.g., wollastonite, silica, glass fiber, talc, calcium carbonate, mica, and carbon fiber), we mixed the additive, available in a particulate form, in a desired quantity with PP powder in an agate pestle and mortar and thoroughly ground the mixture for 30 min. The samples were subjected to isothermal melt crystallization on the hot stage of a polarizing microscope (melting temperature = 200°C, crystallization temperature = 115°C). The crystallization behavior was investi-

gated by the continuous recording of the growth of spherulites and the intensity of transmitted light in the cross-polar mode of the optical polarizing microscope (Leitz, Germany) coupled to an image analyzer system (VIDPRO32, Leading Edge, Australia). The details of these experiments have been described elsewhere.[18–20] Care was taken to avoid any loss of time in the transfer of the sample from the hot plate to the microscope stage. From the isothermal crystallization curve, the induction period, crystallization half-time, growth rate, and so forth were evaluated.

RESULTS AND DISCUSSION

The cooling curves for PP melts containing different fillers (10%), for which K values were estimated with the aforementioned phenomenological model, are shown in Figure 2. The melting temperature was assumed to be 200°C, the mold wall temperature was 25°C, the specimen thickness was 3 mm, the cross-section area was 1 cm^2, and Δt was 1 min. The K and C_p values in Table I were used in eq. (4) for the calculations with the same unit system. The density of PP was taken to be 0.95 g/cm^3. The higher thermal conductivity of the filler produced faster cooling, as expected from the model. The induction time, estimated with the method outlined earlier in this article, is shown in Figure 3 (10% filler concentration). The time required for the melt to attain the temperature for the onset of crystallization decreased with an increase in the thermal conductivity of the filler present in the composite. Therefore, we expected that the induction period for the crystallization would also depend on the thermal properties of the filler.

The results of experiments on the isothermal crystallization kinetics, carried out at 120°C, are depicted in Figure 4 for PPs containing different additives (10%). The onset of crystallization was found to depend on the type of additive. From these curves, the induction time was deduced from the time at which the onset of crystallization was observed, and it was compared with the expected value of the cooling time, which was determined for each composition with the aforementioned theory. Figure 5 compares these values with those estimated from the melt cooling curves described earlier in this article. We have depicted the data in normalized scales with respect to the original PP to avoid any errors arising from sample-to-sample variations and PP grades, which may be different from those reported in the literature. Figure 5 shows that the overall trend for the experimentally observed data follows the same trend expected from the theory. There was some difference in the actual values: the experimentally noted induction time in some cases was lower than that expected from thermal conduction. This might be due to nucleation effects, which
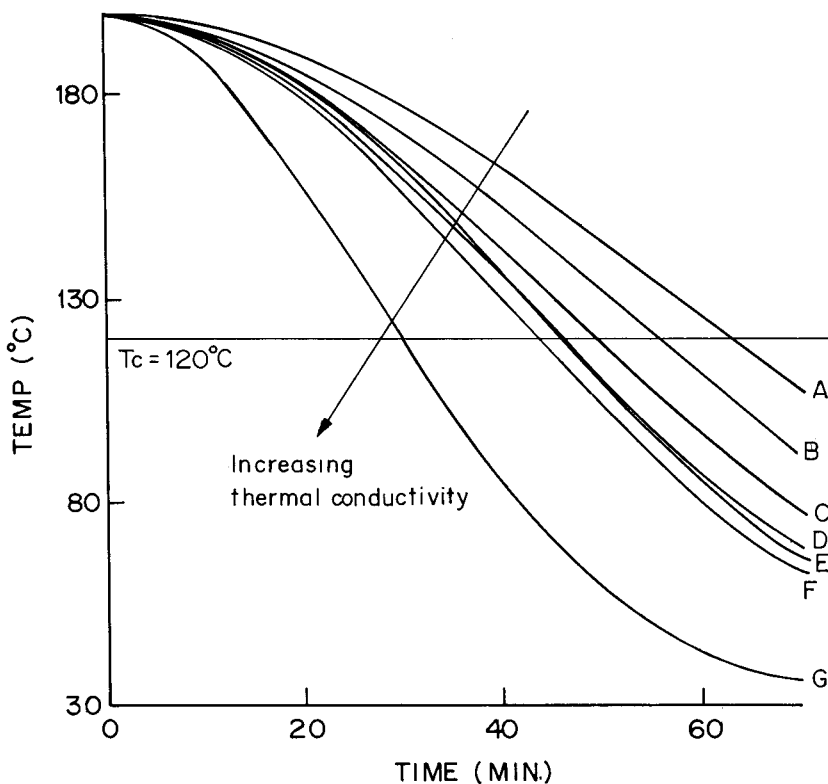
Figure 2 Effect of the thermal conductivity of the additive in the polymer melt on its cooling rate: (A) pure PP, (B) PP with wollastonite, (C) PP with silica, (D) PP with talc, (E) PP with mica, (F) PP with calcium carbonate, and (G) PP with carbon fiber. The filler concentration was 10 wt % in all cases.
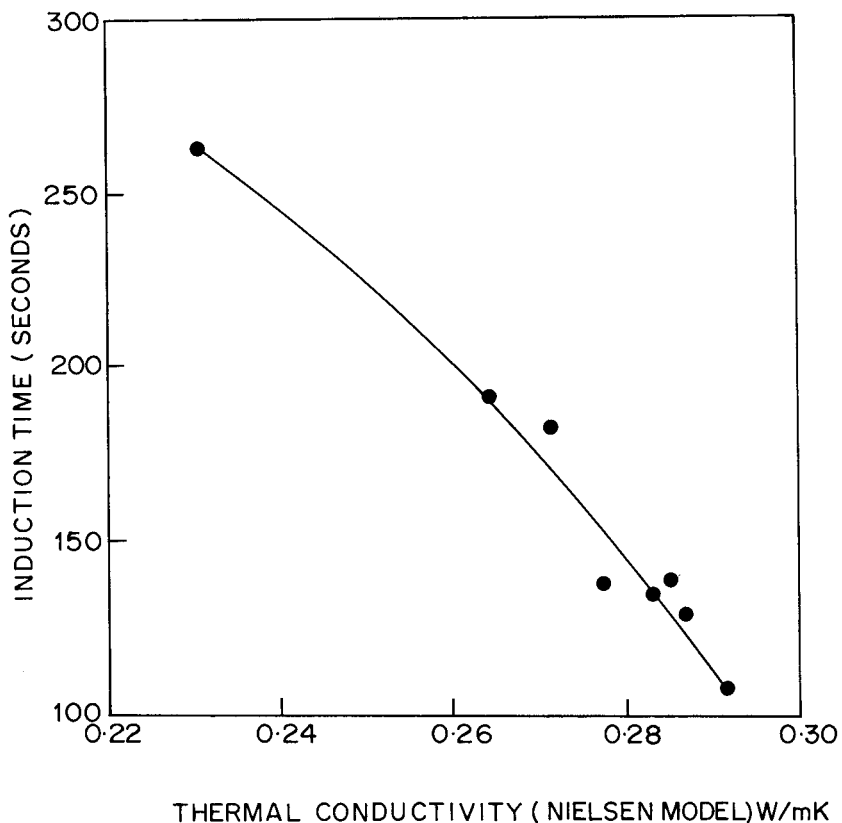

Figure 3 Variation of the induction time derived from the cooling curves with respect to the thermal conductivity of PPs filled with different fillers at 10 wt %.
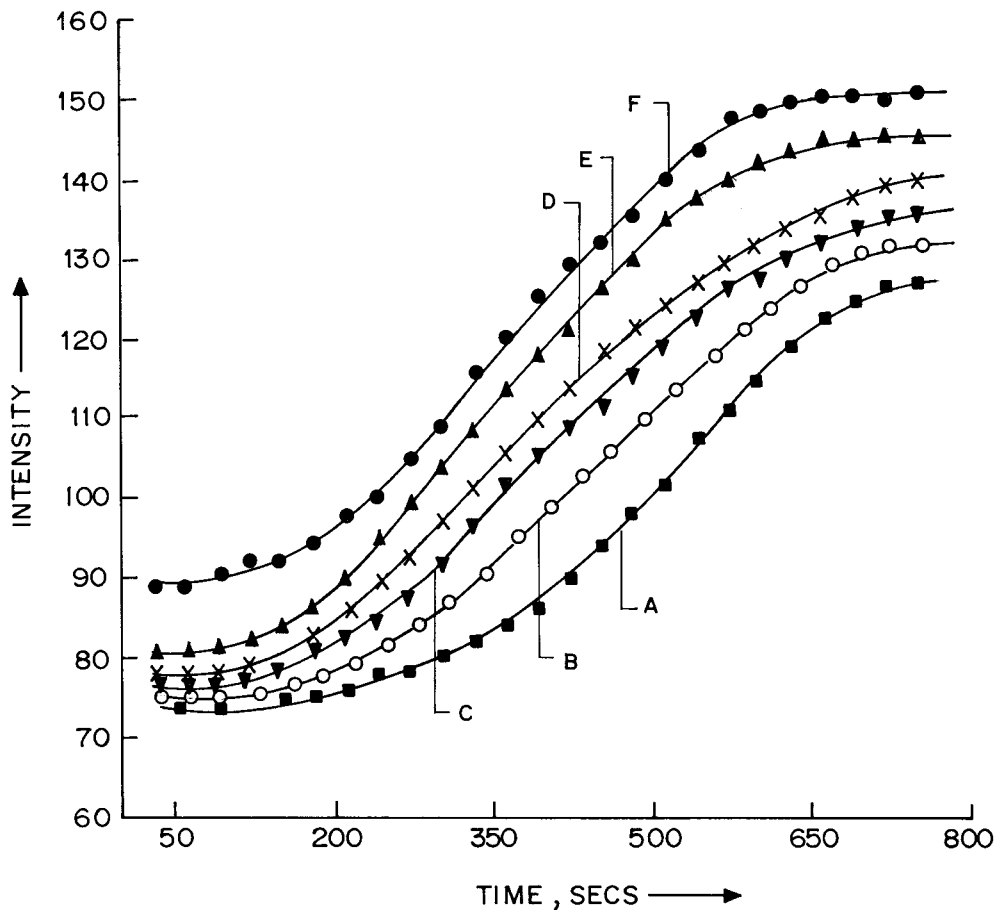
Figure 4 Isothermal crystallization curves for PPs containing fillers (10 wt %): (A) pure PP, (B) PP with silica, (C) PP with talc, (D) PP with calcium carbonate, (E) PP with mica, and (F) PP with carbon fiber.

depended on the filler–polymer interaction, the nucleating efficiency of the filler particle, and so forth.

The rate of cooling of the melt has a profound effect on the morphology that develops in semicrystalline polymers during processing. For example, during the

injection molding of PP, there is a faster cooling rate near the mold walls due to rapid heat transfer than in the central portion of the melt. This leads to uneven crystallization rates, and a skin–core morphology is known to present in final products, especially thick-
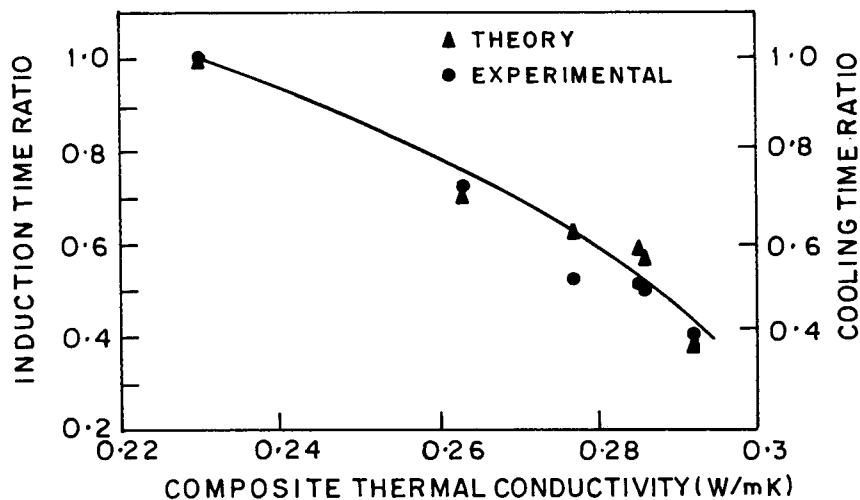

Figure 5 Comparison of experimental data and theoretically estimated values for the induction time of crystallization with the thermal conductivity of the PP composite. The solid line has been drawn only as a guide.
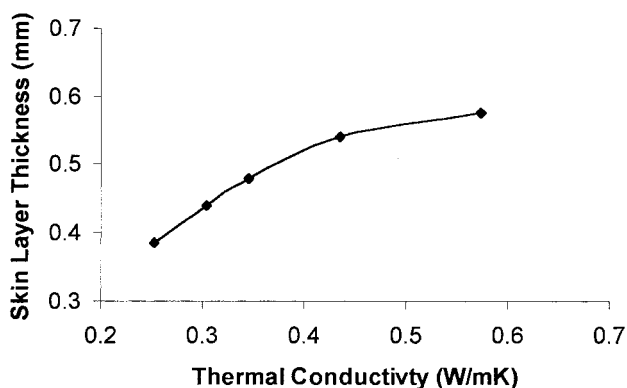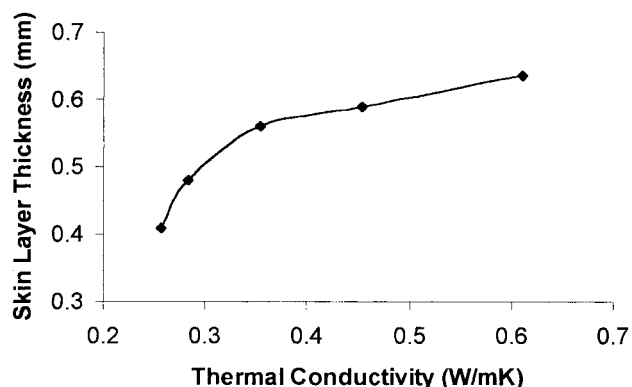
Figure 6 Variation of the skin-layer thickness of injection-molded PPs containing different amounts of fillers: calcium carbonate (top) and talc (bottom). The data are plotted directly in terms of the composite thermal conductivity estimated from Nielsen's equation.

walled items (see Fig. 1). To determine the effect of a faster cooling rate on the crystallization process of PPs containing additives, we compiled data for the skin-layer thickness of injection-molded samples of PP with calcium carbonate and talc in Figure 6. The skin-layer thickness depended on the amount of the additive present in each PP sample. These data were redrawn in terms of the thermal conductivity of PP containing a filler, which was estimated with Nielsen's model (see Table I). This graph clearly indicates the importance of the thermal conductivity of a composite on its crystallization process and the morphology developed in the PP samples containing additives. This can be associated with the fact that a high thermal conductivity filler content leads to better heat transfer and a faster cooling rate, which, in turn, produces greater skin-layer thickness than that of the original polymer.

CONCLUSIONS

The crystallization behavior of polymers is dependent on the heat-transfer process from the melt to the surroundings (e.g., quenched air and mold walls). A phenomenological model has been developed for estimating the cooling rate for any given polymer with known K and C_p values. The addition of fillers to the polymer leads to an increase in the thermal conductivity of the composite, and so faster cooling is expected for such systems. The role of the thermal conductivity of the filler/additive in the crystallization behavior of PP has clearly been presented in this article. The experimental results for PPs containing different types of fillers clearly support the aforementioned hypothesis. Also, the reported data on the skin-layer thickness for injection-molded PPs containing talc and calcium carbonate can be understood in terms of this model.

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