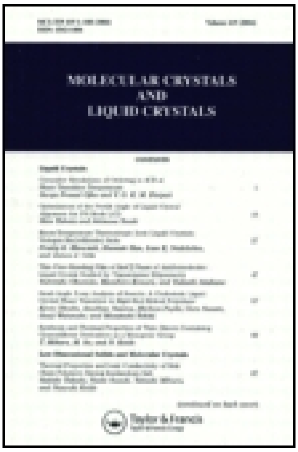

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A Study on the Elastic Properties of an Oriented Thermotropic Liquid Crystalline Polymer

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A Study on the Elastic Properties of an Oriented Thermotropic Liquid Crystalline Polymer

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Abstract The orientation and mechanical behavior of a Vectra were investigated and the results showed the different orientation manifested due to the shear stresses of the flow fields and elongational forces of the diverging dies. This flow behavior was remarkably similar to that of reinforcing fibers in the thermoplastic matrix. However, the mechanical strength of the TLCP extrudates increased in every direction as the angle of diverging dies or the rotor speed of the screw increased, which makes about contrast TLCP with fiber reinforced composites. Based on this analogy and contrast between TLCPs and FRTP, we proposed a simple composite model to explain the elastic properties of TLCP materials and analyzed the reported experimental data in the light of the proposed model. The result of such analysis illustrated well the role of structural parameters such as the aspect ratio and volume fraction of fibrillar nematic domains.

INTRODUCTION

Thermotropic liquid crystalline polymers(TLCPs) have been investigated extensively over the past two decades. Recently, in-situ composites of TLCPs have received much attention. Because of the tendency of TLCPs to form microfibers, blends of TLCP and other thermoplastic matrix have a potential to produce in-situ composites. However, it is clear from the literature that while an improvement of the mechanical properties depends largely on the formation of fine fiber-like TLCP domains in the blends, there have been relatively few morphological studies carried out on the pure TLCPs and more specifically, how the texture may be altered or correlated to the processing history.

Davies and Ward[1] applied the aggregate model to describe the mechanical anisotropy of uniaxially oriented TLCPs and Garg and Kenig[2] considered the orientation of LCP domains as the orientation of rigid rod particles such as short fibers in dilute suspension. DiBenedetto et al.[3] proposed a composite model to describe the modulus of the TLCP as it deforms in the extensional field generated during hot drawing. Meier[4] tried to produce semi-finished products with properties as good as those of glass fiber reinforced plastics by controlling the orientation of the fiber-like mixtures in the direction of flow and at an angle to the direction of flow through shear flow.

The purpose of this study is to hopefully provide some understanding of the effect of microstructure on the elastic properties of TLCPs. The experimental specimens were obtained by extruding a Vectra through sheet type dies of different diverging angles and their orientation characteristics and mechanical properties were investigated in order to develop a simple theoretical model to estimate the microstructural parameters such as the aspect ratio and volume fraction of oriented nematic domains.

EXPERIMENTAL

Materials

The TLCP used for this work was Vectra A-950 of 73mole% hydroxybenzoic acid and 27mole% 2,6-hydroxynaphthoic acid provided by the Hoechst Celanese Corp.

Sheet Preparation

Pellets of Vectra A-950 were vacuum dried at 110℃ for 24 hours and extruded through a single screw extruder(Haake Rheocord; Rheomix 600) with diverging rectangular dies of constant height. The diverging angles were varied from 0° to 45°.

Orientation Characteristics

In order to investigate the level of orientation, we examined the specimens by wide angle X-ray diffractometer of Rigaku, Geigerflex M-3A. Diffraction patterns were recorded photographically with a flat film camera and angular orientation was measured from azimuthal microdensitometer traces of the <110> equatorial reflection.

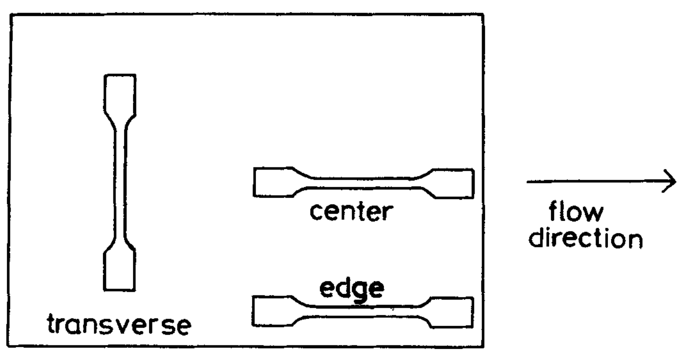

FIGURE 1. Specimens for the tensile test at the various positions.

Mechanical Properties

The tensile properties were measured at room temperature in an Instron tensile testing machine with a cross head speed of 10mm/min. The tensile specimens were prepared by punching out of the sheet at different positions as illustrated schematically in Fig.1.

RESULTS AND DISCUSSIONS

Characteristics of Orientation and Mechanical Behaviors

As pointed out in the introduction, one of the objectives of the present work was to obtain some insight into the nature of the morphological texture oriented as a result of processing history. Fig.2 shows WAXS patterns for the extruded samples through a die of diverging angle of 45°(die temperature = 270℃, screw speed = 120rpm). To complete 3-dimensional structural characterization, the structure was examined with the microtomed sections through the thickness and width as indicated at the center of the figure. The results showed that in the outer skin layers, the TLCP fibrils were oriented in the direction of flow and the degree of orientation improved toward the edge. In the middle layer, the molecules are oriented at angles to the direction of flow and the orientation directions changed smoothly from the parallel in the edge to the perpendicular in the center compared to the flow direction(Fig.2).

This perpendicular orientation at the center resulted from the tensile hoop stress generated by the diverging flow. Similar orientation behaviors were also observed by several others[4,5] and the aim of these studies was to confirm that these flow

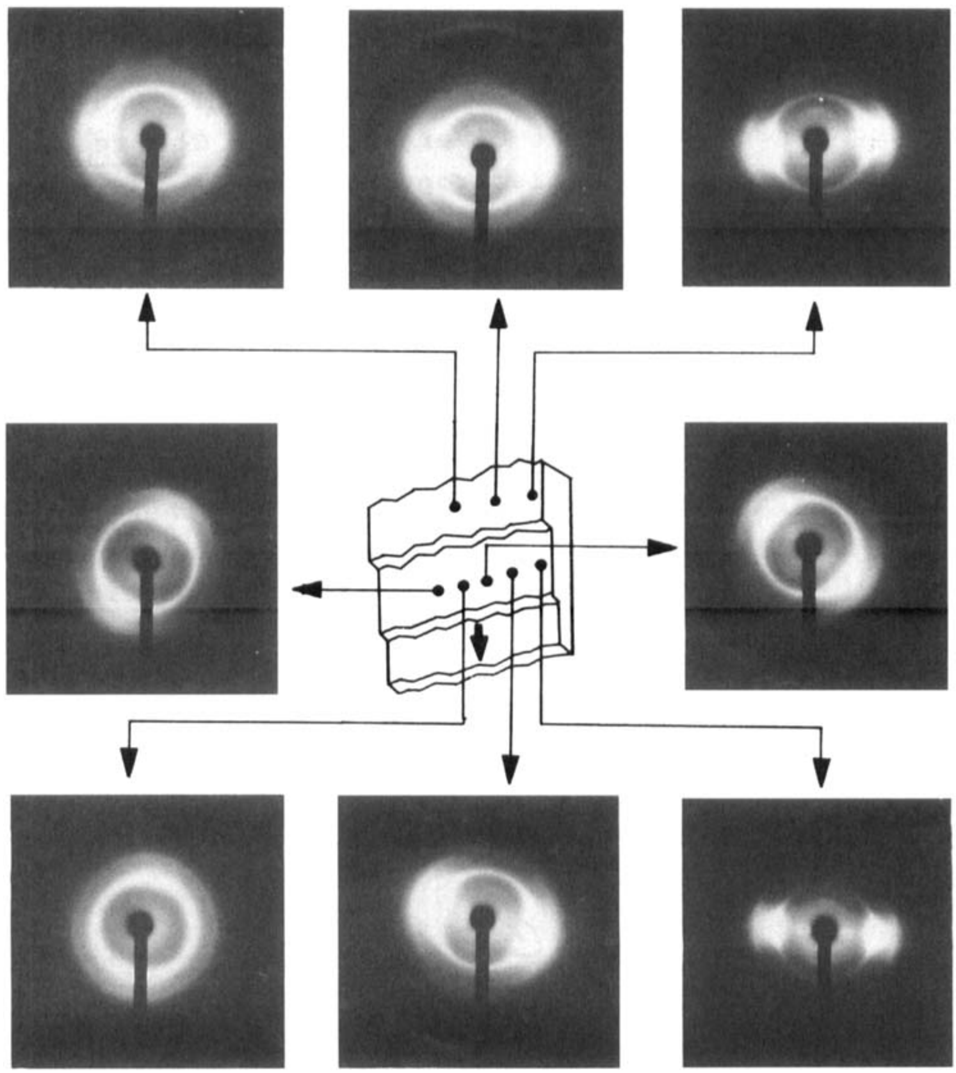

FIGURE 2. WAXS patterns for the microtomed samples of the extruded sheets at different positions indicated at the center of the figure

behaviors of the neat TLCP through diverging channels are remarkably similar to the orientation of glass fibers in the thermoplastic matrix. This analogy between TLCPs and fiber reinforced thermoplastic composites(FRTP) will be the basis of the next simple theoretical model. Figs.3-5 show the stress-strain curves of the TLCP extruded through three different diverging dies. The results showed a prominent anisotropy. Generally the edge specimens exhibited higher stiffness and strength than the other two specimens. The variation of these mechanical properties on the positions of the extruded plaques seems to be a direct consequence of the oriented structure. It should be recalled that the cross section of the tensile specimens was composed of layered structures and depending on the position, the direction of orientation changed in the layers and the degree of orientation improved toward the edge. This high level of orientation in the edge specimens leads to higher mechanical properties.

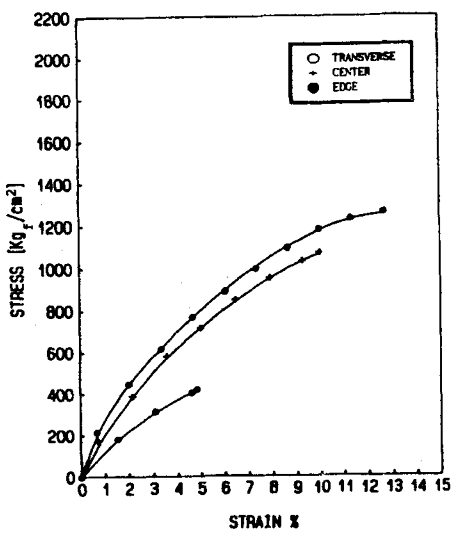

FIGURE 3. Stress-Strain curves of the LCP extruded sheet(Div. Angle=0°, Die Temp.=270℃, Rotor Speed=120rpm).

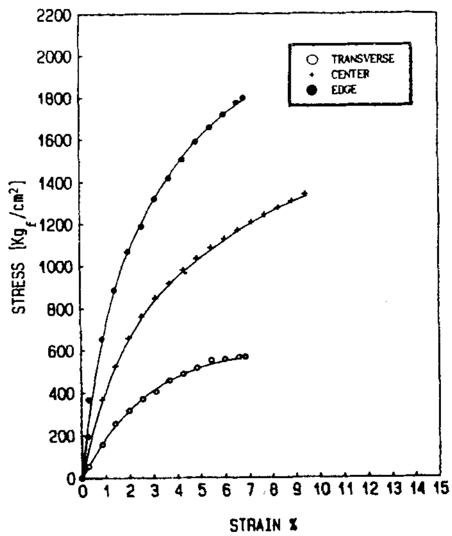

FIGURE 4. Stress-strain curves of the LCP extruded sheet(Div. Angle=30°, Die Temp.=270℃, Rotor Speed=120rpm).

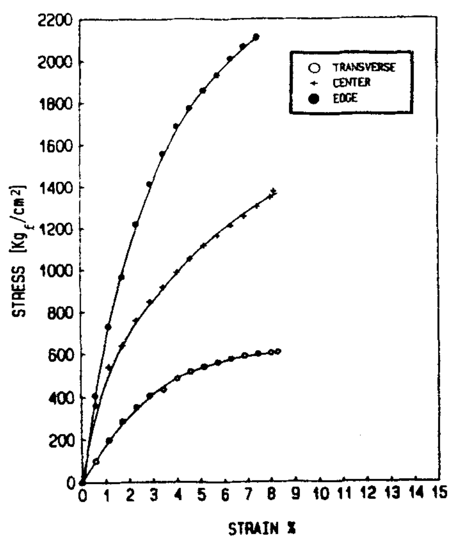

FIGURE 5. Stress-strain curves of the LCP extruded sheet(Div. Angle=45°, Die Temp.=270℃, Rotor Speed=120rpm).

Fig.6 shows the tensile strength as a function of diverging angles. For the three samples, the tensile strength increased significantly with the diverging angles. We also observed the same tendency with the screw speeds as shown in Fig.7. One important point to note is that in case of FRTP, the enhanced properties in one direction usually imply the property decrease in the other direction since the total amounts of fibers are constant. However, in case of TLCPs, the mechanical properties increased for all the three different directions. Another point to make about contrast TLCPs with FRTP is that TLCPs exhibited higher stiffness with higher elongation at break(see Fig.3) since this trend reverses and higher stiffness usually means lower elongation at break in the FRTP.

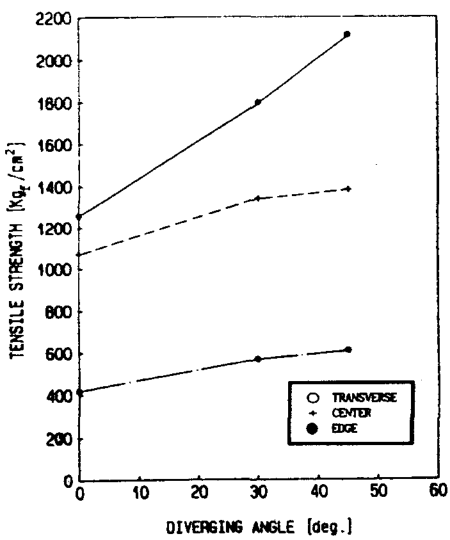

FIGURE 6. Tensile strength vs. diverging angle of the LCP extruded sheet(Die Temp.=270℃, Rotor Speed=120rpm).

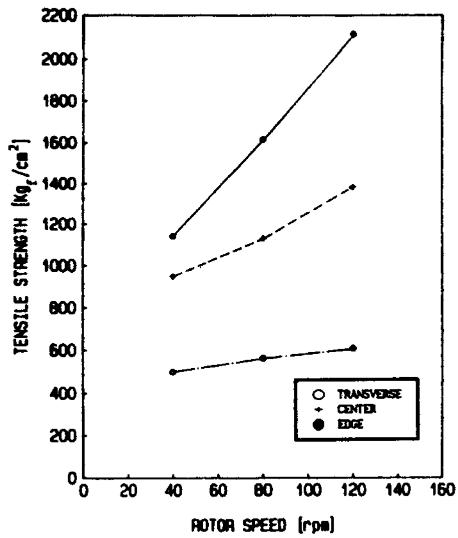

FIGURE 7. Tensile strength vs. rotor speed of the LCP extruded sheet(Die Temp. =270℃, Div. Angle=45°)

THEORETICAL MODELING

In order to explain the mechanical properties of TLCPs, we propose a simple composite model based on the following structural features of TLCPs. A common view of the structure of TLCPs is that of randomly oriented micrometer or semimicrometer size domains of highly ordered molecules surrounded by boundaries of the less order. Each domain possesses structural homogeneity and uniformity, and the size and shape of domains are sensitive to processing conditions. On the other hand, the matrix(boundary) has nearly isotropic properties so that rapid relaxation will maintain amorphous mass at the temperature range considered.

In this model, the ordered nematic domains assumed to be polyhedric and their aspect ratio changes depending on the processing conditions. Contrary to the conventional glass fiber filled thermoplastics, the aspect ratio of the nematic domains tends to increase with increasing orientation since the domains elongate by slippage of the oriented molecules past one another. Another important point to be considered in modeling TLCPs is that the fibrillar nematic organization of TLCP improves under the flow field as a result of simultaneous rotation and elongation of the domains and the total amount of fibrillar nematic domains increases with the orientation. To a first approximation, we assumed a linear increase of the nematic contents with orientation.

Under the above simplifying assumptions, the volumetric content of nematic domains could be estimated using reported experimental data at the following two extreme cases. When the nematic zones are perfectly oriented(Hermans orientation function , F=1), the longitudinal modulus can be obtained by a rule of mixture(continuous fiber case)

$$E_L=E_MV_M+E_NV_N \quad (1)$$

when LCP fibrils formed a continuous phase, the rule of mixture would be the appropriate model. In the equation (1), E_L, E_M and E_N are the moduli of the composite, matrix and nematic domains, and V_M and V_N are the corresponding volume fractions. In the case of TLCPs, E_M and V_M are very small compared to E_N and V_N respectively and their product can be neglected. The hypothetical modulus of E_N can be equated from the experimental longitudinal modulus deduced from changes in the meridional X-ray scattering as a function of stress. Taking E_N=150GPa, a value of V_N=0.80 was obtained using the limiting longitudinal moduli of the composite E_L calculated from the Chung's experimental literature data.[6,7]

In the case of the lower bound($F \rightarrow 0$), the modulus of the composite could be calculated using the Halpin-Tsai equation[8,9](particulate filler case; ℓ /d=1) and equated to the experimental limiting value to obtain V_N.

$$\frac{E_L}{E_M} = \frac{1 + \xi\eta V_N}{1 - \eta V_N}$$

where

$$\eta = \frac{\dfrac{E_N}{E_M} - 1}{\dfrac{E_N}{E_M} + \xi} \qquad (2)$$

The quantity ξ is equal to $2(\ell/d)$, where (ℓ/d) is the length-to-diameter ratio of the polyhedric liquid crystal domain. The quantity V_N is the volume fraction of the oriented liquid crystalline domains and E_L is the longitudinal modulus of the composite, namely TLCPs. E_M and E_N are the moduli of the matrix and nematic domains, respectively. The quantity V_N at F=0 was estimated as 0.46. Using these two limiting values for V_N, the orientation dependency was determined as

$$V_N = 0.34F + 0.46 \qquad (3)$$

This equation indicates that the fibrillar nematic domians varies in the range 0.46-0.80 depending on the orientation. This range seems to be reasonable since the maximum volume fraction of perfectly aligned fibrils is 0.82.[10]

ANALYSIS OF EXPERIMENTAL LITERATURE DATA

The reduced longitudinal modulus was calculated using equations(2) and (3), and the results are presented as a function of F for various aspect ratios in Fig.8. The predicted E_L/E_M shows a strong dependence on the aspect ratio and the orientation parameter in the range considered. These aspect ratios were used in conjunction

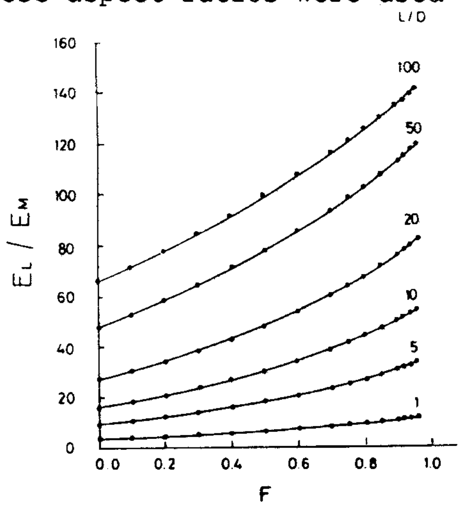

FIGURE 8. Reduced longitudinal modulus (E_L/E_M) vs. Hermans orientation function with various aspect ratio of nematic domains calculated using the relation V_N=0.46+0.34F.

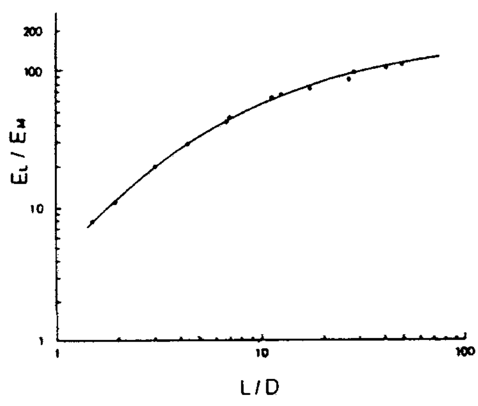

FIGURE 9. Effects of LC domain aspect ratios on the longitudinal stiffness of unidirectionally oriented LCP rods.

with the experimentally determined moduli from Chung's work in an attempt to characterize the related structure. To achieve a good fit with the experimental value of E_L/E_M, an appropriate value of the aspect ratio was determined as shown in Fig.9. In this calculation, we took the advantage of the Halpin-Tsai equation, which covers the particulate as well as fiber reinforced cases. Fig.10 shows the aspect ratio of nematic domains as a function of Hermans orientation function F. The aspect ratio increases gradually at low orientation(F<0.87) and when the orientation parameter approaches unity, it increases rapidly. The aspect ratio ranged from 1 to 70 with a steep change at an aspect ratio of about 5. These results suggest that the mechanical behavior of TLCP materials may be described either as particle reinforced composites(low orientation) or as fiber reinforced composites(high orientation).

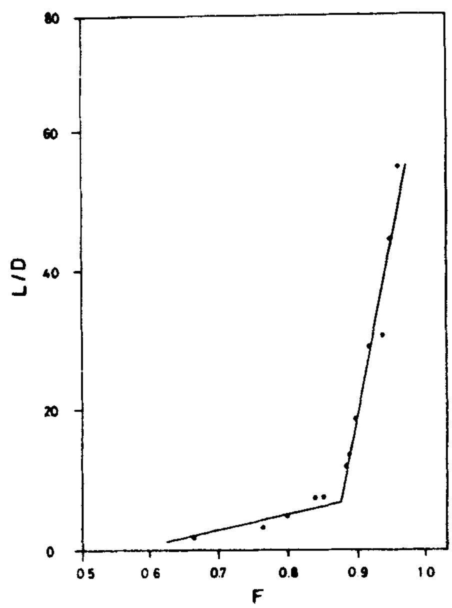

FIGURE 10. Aspect ratio of nematic domains as a function of Hermans orientation function F.

As was mentioned earlier, the longitudinal stiffness of unidirectionally oriented TLCPs is highly dependent on the aspect ratio of the nematic domains(Fig.9). Fig.11 shows the experimental and calculated reduced modulus as a function of the orientation parameter. A good fit means that this model describes the elastic properties of TLCP materials well and the values of the model parameters such as the aspect ratio and V_N are reasonable. It is also interesting to note that these structural parameters are highly dependent upon the orientation. For example, the degree of orientation of 0.8 or so is no longer sufficient to achieve ultra high modulus. The longitudinal modulus for the material considered in this model apparently depends on $F^{7.4}$ (Fig.11).

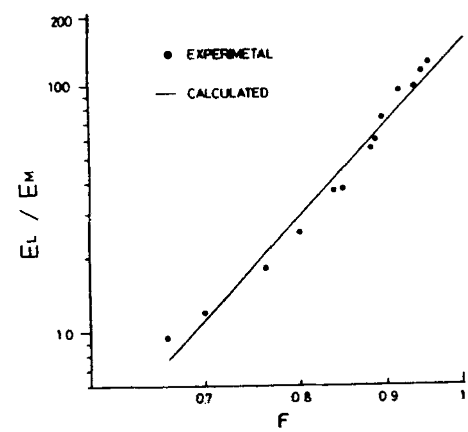

FIGURE 11. Reduced longitudinal modulus (E_L/E_M) vs. Hermans orientation function F with various aspect rartio of nematic domains.

This in-situ formation of the fiber-like domains potentially provides a degree of control over fiber aspect ratio and fiber content that is not achievable with conventional reinforcing fibers.

CONCLUSION

Orientation characteristics and their effect on the mechanical properties of a TLCP were investigated and a simple theoretical model for predicting the elastic properties of TLCP materials was presented and discussed. According to the experimental results we assumed in this model that the volume fraction and aspect ratio of fibrillar nematic domain increase with the degree of orientation. The analysis of reported experimental data by using this model showed that the volume fraction of oriented nematic domains for the TLCP Vectra varies from 0.46 to 0.80 and the aspect ratio ranges from 1 to 70 depending on the orientation. These calculated values seem to be reasonable and accord with intuitive expectations for the TLCP materials.

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