

LCP Properties Ideal for Miniaturization Trend in Electronic Industry

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Abstract

Liquid crystal polymers (LCPs) are a unique group of linear polymers that can align themselves parallel to one another to form liquid crystal phase. This alignment is "self-reinforcing," resulting in outstanding mechanical properties associated with a high degree of orientation. In the melt and under shear such as during injection molding, LCPs exhibit very low viscosity and high flow to completely fill small and intricate molds, making LCPs the favorite choice for making miniature and ultrathin parts down to 0.1 mm wall thickness with extremely short cycle time.

LCPs' unique combination of high stiffness, high temperature resistance and high flow bodes well with the growing trend of miniaturization in the electronic industry and increasing popularity of high precision molding. Applications such as connectors and sockets with high pin density have been driving the remarkable growth in LCP consumption.

Key Words: Liquid Crystal Polymer, LCP, Heat Resistance, Dimensional Stability, High Flow, Dimensional Stability, Flame Retardant, Packaging

Introduction

Liquid crystal polymers (LCP) are a family of high performance plastics, distinguished from other semi-crystalline resins by their long, rigid, rod-like molecules that are ordered even in the melt phase (Figure 1).

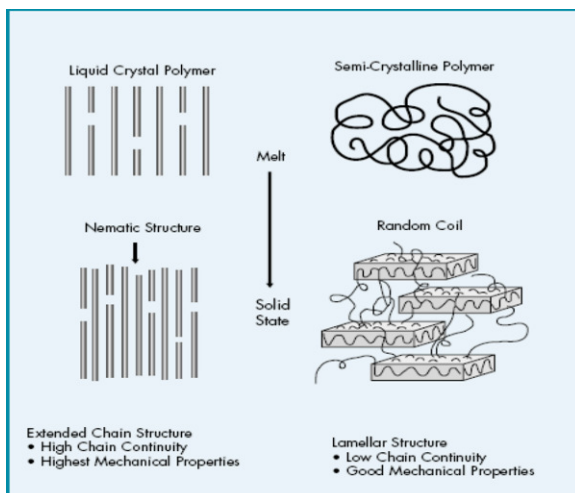


Figure 1 — Representation of structural differences between liquid crystal polymers and conventional semi-crystalline polymers.

Vectra[®] liquid crystal polymers from Ticona offer a balance of properties unmatched by most other resins. They are generally selected for a specific application or market sector based on a few key characteristics such as good flowability in molding allowing thin-walled parts, dimensional accuracy, high heat resistance, stiffness, excellent barrier properties. For instance, in molding electrical connectors, high flow in thin sections, excellent resistance to heat deflection under load, dimensional accuracy and inherent flame retardancy are the primary reasons for choosing an LCP. Key properties, such as high flow, stiffness and resistance to sterilizing radiation and sterilizing gases make LCPs extremely suitable for use in surgical instruments. A number of Vectra grades are USP Class VI compliant and meet parts of the ISO 10993 standard.

The family of Vectra resins is very easy to process in injection molding machines, providing fast cycles, high flow in thin sections and exceptional dimensional stability. Molded parts exhibit very low shrinkage and warpage and have outstanding high-temperature resistance up to 340°C.

Vectra LCPs parts have excellent dimensional stability and exceptional barrier

properties. In addition to the those advantages offered of linear thermal expansion (CLTE), high chemical stiffness, and toughness are observed in many applications. The performance of the latest Vectra grades goes beyond the requirements for thin-walled precision parts. Attributes such as an attractive surface finish with wide color versatility, good non-stick effect and resistance to cleaning agents make the materials in the Vectra portfolio good candidates for applications that have traditionally been the preserve of metal, such as cookware and bakeware.

Fillers

Glass fiber reinforced grades

Reinforcement with glass fibers increases stiffness, mechanical strength and heat resistance. At the same time, the degree of anisotropy is reduced. Vectra is available with 15%, 30%, 40% or 50% glass fiber content.

Carbon fiber reinforced grades

Reinforcement with carbon fibers gives even higher stiffness than with glass fibers. At the same time, carbon fiber reinforced compounds have a lower density than glass fiber grades with the same filler content. Carbon fiber reinforced polymers are used where the highest possible stiffness is required. It should also be noted that carbon fiber reinforced grades are to a certain extent electrically conductive.

Filler/fiber combinations

Products with various filler/fiber combinations are another important group in the Vectra portfolio. The PTFE and glass modified grades are used for low-friction and wear-resistant applications, while glass/mineral filled products are selected for components requiring both an attractive finish and improved stiffness.

Mineral filled grades

The mineral filled grades typically have high impact strength and elongation at break relative to the glass fiber reinforced grades. In addition, they provide an attractive surface finish and good flow properties. Mineral filled Vectra products are available with 40% filler content.

Graphite filled grades

Graphite flake provides some added lubricity and exceptionally good hydrolytic stability and chemical resistance.

by Vectra, other properties such as its low coefficient *Specialty grades*

Modification with electrically conductive carbon black makes the following products particularly suitable for antistatic applications.

Physical Properties

The properties of Vectra® LCP are influenced to a high degree by its liquid crystal structure. The rod shaped molecules are oriented in the flow direction during injection molding or extrusion and are rod shaped, even in the melt phase. Due to the highly ordered nature of liquid crystal polymers, mechanical properties, shrinkage and other part characteristics depend on the flow pattern in the part. During mold filling, the molecules are oriented in the flow direction. In the finished part, these molecules are ultimately aligned on the surface where they form a skin that is highly oriented in the flow direction. The skin makes up 15-30% of the part's total thickness. This molecular orientation causes a self-reinforcement effect giving exceptional flexural and impact strength as well as good tensile performance. Relative strength values increase as a direct correlation with decrease in wall thickness. (Figures 2 and 3)

The level of properties depends primarily on the type of filler or reinforcement used. Glass fibers impart increased stiffness, tensile strength and heat deflection temperature. Carbon fibers give the highest stiffness. The addition of mineral fillers improves stiffness and provides increased toughness and a smoother surface compared with glass fiber reinforcement. Graphite improves elongation at break and provides added lubricity. PTFE modified grades have excellent sliding and wear properties. The impact strength of unfilled Vectra polymers is reduced by the addition of fillers and reinforcing materials but is still high.

As the wall, film or sheet thickness decreases, the highly oriented outer layer accounts for a higher proportion of the total wall thickness (skin/core effect).

This higher percentage of highly oriented surface layer, in general, results in greater strength and modulus in thinner sections.

The excellent flow properties of Vectra make it possible to fill extremely fine structures and so produce very thin-walled parts.

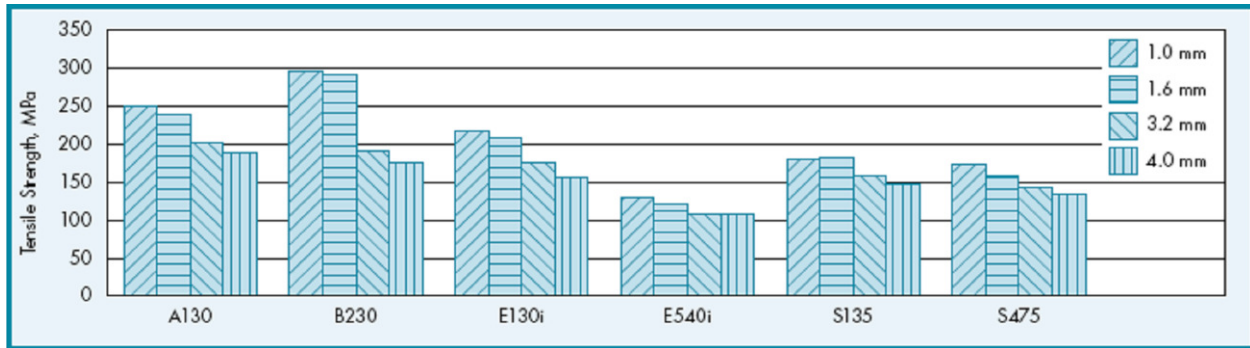


Figure 2 — Tensile strength vs. wall thickness of Vectra® LCP

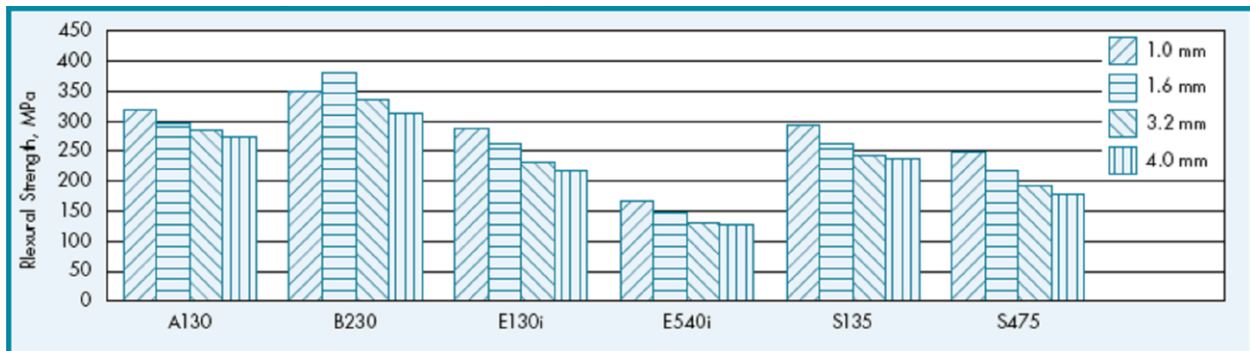


Figure 3 — Flexural strength vs. wall thickness of Vectra® LCP.

Behavior under short-term mechanical stress

The tensile stress-strain curves shown in Figure 4 are representative of the Vectra product line. Vectra A130 and E130i are 30% glass filled resin, S135 is a 35% glass fiber reinforced resins, Vectra A230D-3 and B230 are 30% carbon fiber reinforced resins, Vectra A430 is a 25% PTFE filled resin, Vectra E540i and S540 are 40% mineral filled resins, and Vectra S471i is a 45% glass/mineral filled resin.

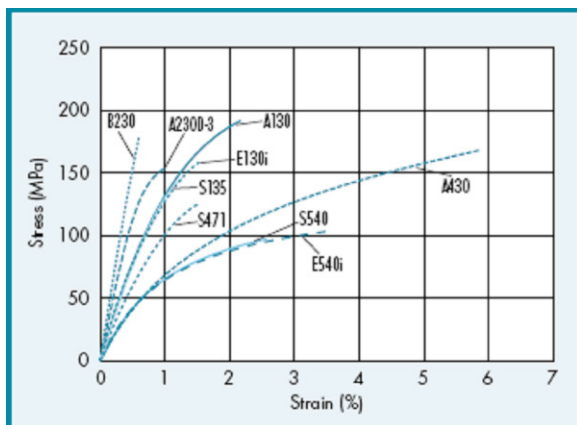


Figure 4 — Stress strain curves, tensile test at 23 degrees Celsius.

As with any thermoplastic, the stiffness and strength of the Vectra decreases with increasing

temperature. Figs 5 show the influence of temperature on the stress strain curves of Vectra E130i.

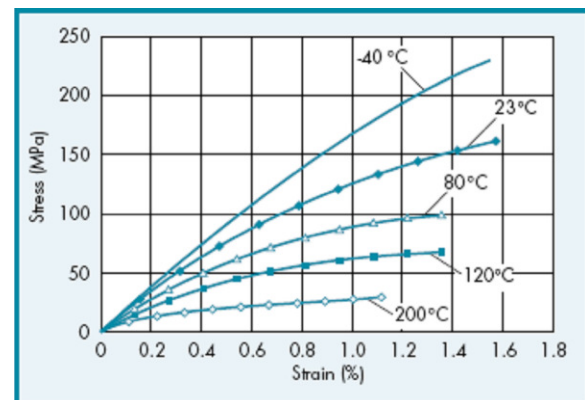


Figure 5 — Influence of temperature on stress strain behavior, tensile test, Vectra® E130i.

Behavior under long-term mechanical stress

Vectra has good creep resistance. Figure 6 shows the tensile creep modulus of Vectra E130i at 23°C and 120°C for various stress levels. The maximum exposure time was 1000 hours for E130i. The stress levels were chosen to be 30% of the short-term failure stress and none of the samples failed testing. No sign of creep rupture – a common form of failure – was observed at stress levels below 30%.

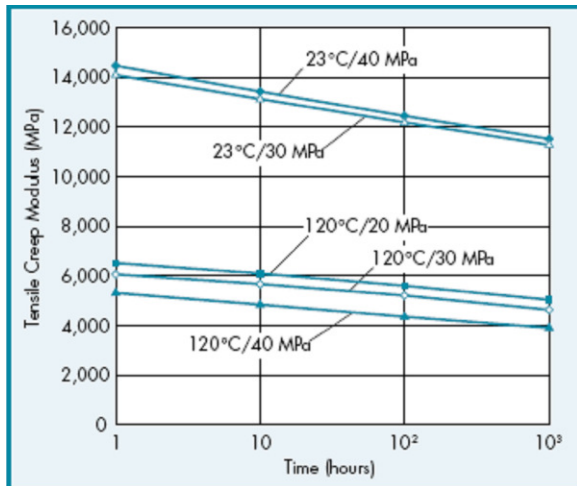


Figure 6 — Tensile creep modulus, Vectra® E130i.

Damping

The unique structural characteristics of Vectra have an extremely favorable effect on its damping characteristics (Figures 7). Generally speaking, materials with high modulus, such as metals, have low damping (internal loss) characteristics and low modulus materials, such as rubbers, have high damping characteristics. Vectra, however, exhibits high damping characteristics despite its high modulus (Figure 8). This is due to the unique morphology of liquid crystal polymers.

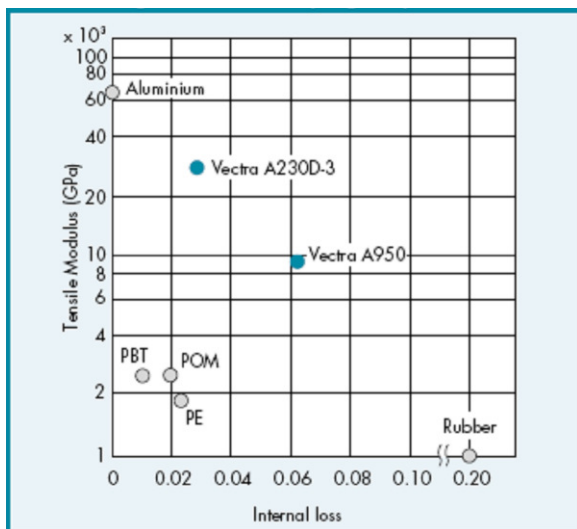


Figure 7 — The damping properties of various materials.

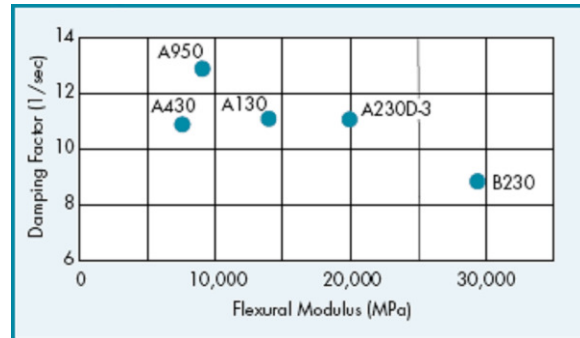


Figure 8 — Vibration characteristics of different Vectra® grades.

Deflection temperature under load

The deflection temperature under load (DTUL/HDT) measured at 1.8 MPa (HDT/A) for Vectra grades ranges from 120°C for an unreinforced, low-temperature product to 340°C for the glass fiber reinforced high heat products (Figure 9).

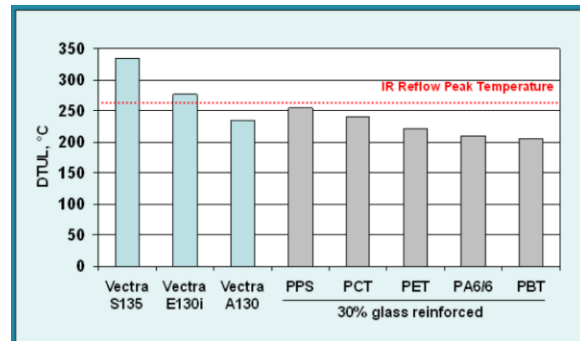


Figure 9 — Deflection temperature under load, degrees Celsius at 180 MPa (264 psi).

Coefficient of linear thermal expansion

One of the advantages of Vectra is its exceptionally low coefficient of linear thermal expansion (CLTE) in comparison with other thermoplastics. The expansion coefficient change only slightly and almost linearly. The coefficient of expansion, like most properties of Vectra, displays marked anisotropy. It is much lower in the flow direction than the cross-flow direction. With very high orientation in the flow direction, the expansion coefficient may even be negative, especially for carbon fiber reinforced grades.

The expansion coefficient of Vectra can be varied within certain limits and matched to the expansion coefficient of glass, steel, ceramic, or glass fiber/ epoxy substrates. Figure 10 compares the expansion coefficients of various engineering materials. When composite structures of Vectra and other materials are heated, no thermally induced stresses occur because the thermal expansion coefficients are similar. Electrical components for

(SMD or surface mounted devices) should have expansion coefficients closely in line with those of the circuit board substrate (usually FR 4 epoxy plastic/glass fiber) to avoid mechanical stresses at the soldering points as a result of thermal loading. Vectra is therefore a good material for composite structures, particularly for surface mount technology (SMT).

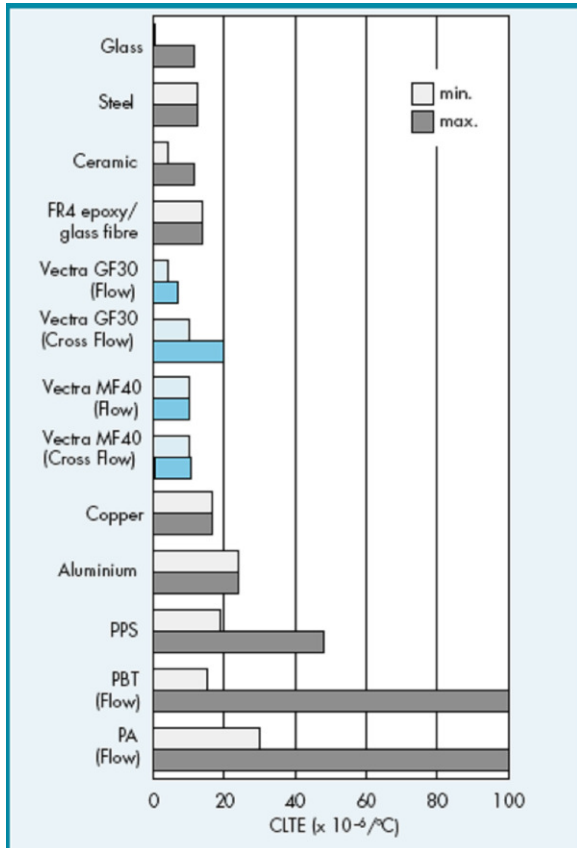


Figure 10 — Coefficient of linear thermal expansion of selected engineering materials.

Soldering resistance

Parts molded from Vectra LCPs are suitable for applications requiring vapor phase (wave) and infrared (reflow / SMD / through-hole) soldering. They are dimensionally stable and have extremely low thermal expansion coefficients at soldering temperatures. Vectra LCPs' exceptionally low moisture absorption has a positive effect on dimensional stability, minimizing dimensional changes and warpage.

Experience has shown that Vectra A130 is resistant to soldering temperatures up to 240°C. Above this temperature, parts can soften or distort due to the proximity of the melting point (280°C). Vectra E130i, with its much higher melting point (335°C), is able to withstand short-term soldering temperatures of up to 300°C. The introduction of

high-temperature grades such as Vectra S135 (melting point 350°C) significantly extends the possible processing window.

The melting point is, however, only one criterion for assessing the suitability of Vectra grades for exposure to soldering operations. Another important consideration is heat deflection temperature under load. It is necessary to decide on a case by case basis whether to use HDT/A or resistance to other loads such as HDT/B or C as the basis. In making this decision, loads due to internal pressure in the component (e.g. from trapped inert gas) or other mechanical effects, such as clamps, must be taken into account.

As a result of the increased use of lead-free soldering, temperature peaks in the soldering operation have risen to 270°C. It should be noted that Vectra Ei and S grades are suitable for such soldering operations, provided that they have been correctly processed.

Thermodynamics, heat of fusion

Figure 11 shows the specific heat C_p of Vectra LCPs as a function of temperature compared to PPS and PBT. Vectra LCPs have a significantly lower specific heat than semi-crystalline thermoplastics. The curves are more like those for amorphous thermoplastics. This is attributed to the liquid crystalline structure of Vectra. With LCPs, the transition from the solid to the melt phase is associated with a relatively small change in the state of order since the melt maintains the high orientation of the solid.

Because of the high order of the melt state and the ability to solidify with minimal change in structure, the transition energy during melting or freezing of Vectra is one to two orders of magnitude less than that of semi-crystalline thermoplastics (Figure 12).

In designing the optimum of injection molding machinery and parts, it is essential to know how much heat must be supplied or removed during processing. With Vectra, less heat has to be removed and the melt freezes rapidly. This means that much faster cycles are possible than with semi-crystalline materials, so thus permitting lower-cost production of parts. The thermal conductivity λ of unreinforced Vectra is in the same range as that for semi-crystalline polymers. Thermal conductivity is dependent both on the base polymer and the type as well as the use of fillers and reinforcements (Figure 13).

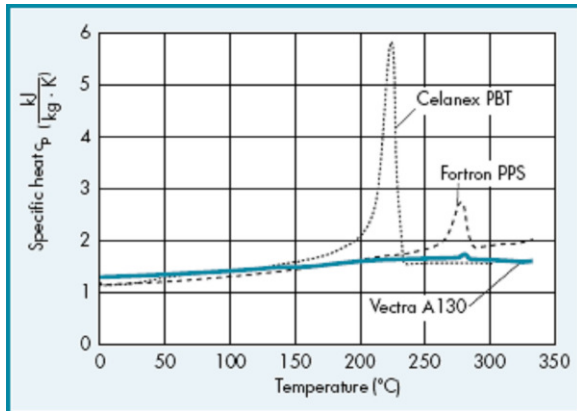


Figure 11 — Specific heat.

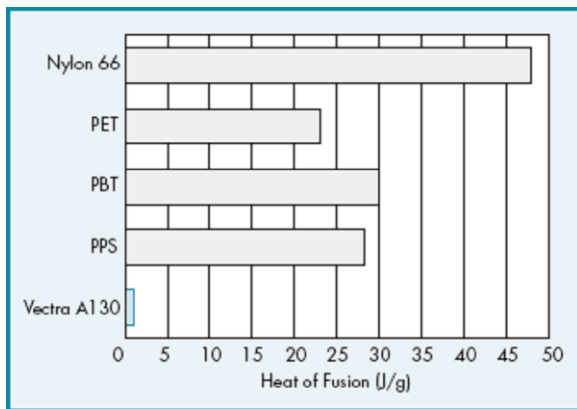


Figure 12 — Relative phase transition energy.

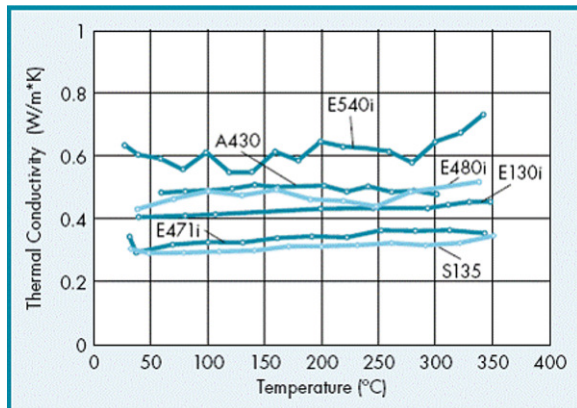


Figure 13 — Thermal conductivity.

Electrical properties

Vectra LCPs exhibit good electrical properties (see enclosed product information). The electrical characteristics combined with easy processing, dimensional stability, heat resistance and mechanical integrity make Vectra LCPs a good choice for electronic components, especially surface mounted devices (SMD). Vectra grades are also available with low to moderate electrical conductivity (Table 1). These products are good candidates for

antistatic applications and electromagnetic shielding (EMI).

Table 1 — Vectra® LCP conductive grades.

	Vectra A2300-3 Carbon fiber	Vectra A700 Carbon black	Vectra A725 Graphite/ carbon black
Volume Resistivity* ($\Omega \cdot m$)	10^0	10^3	10^1
Surface Resistivity (Ω)	10^1	10^5	10^4
* Measured on molded plaques painted with conductive silver			

There has so far been no common industry standard for determining the dielectric properties of materials. Several test methods were therefore evaluated. In the method finally selected (IEC 250), round test specimens with a diameter of 10 mm were punched out of 0.4 mm thick injection molded plaques and then metallized on both sides by gold vapor deposition. The plating helps eliminate possible fault sources such as surface unevenness. A rough surface tends to lead to lower relative permittivity (DC) values and higher dissipation factors ($\tan \delta$) due to poor contact. The relative permittivity values determined by the method used here therefore tend to be relatively higher and the $\tan \delta$ values lower than values measured on unplated specimens (see enclosed table). On the other hand, they are more realistic, since antennae or parts for shielding applications are normally also metallized. When selecting materials on the basis of relative permittivity (DC) and $\tan \delta$ values, it is therefore essential to take into account the specific test method used to determine the dielectric characteristics.

Tables 2 and 3 give the relative permittivity values and dissipation factors at various frequencies for some selected Vectra grades used in antennae and shielding applications.

Table 2 — Electrical properties of as-molded/unplated Vectra® LCP.

Relative Permittivity	1 MHz	10 MHz	100 MHz	1 GHz	2 GHz
A130	3.7	3.2	3.5	3.2	—
A430	3.1	2.8	—	—	—
E130i	3.3	3.2	3.2	3.1	—
E471i	3.8	3.7	—	—	—
E820i	3.6	—	—	—	—
S135	3.5	3.4	—	—	—
Dielectric Loss Tangent					
A130	0.018	0.008	0.007	0.006	—
A430	0.016	0.008	—	—	—
E130i	0.025	0.02	0.01	0.008	—
E471i	0.031	0.007	—	—	—
E820i	0.03	—	—	—	—
S135	0.009	0.023	—	—	—

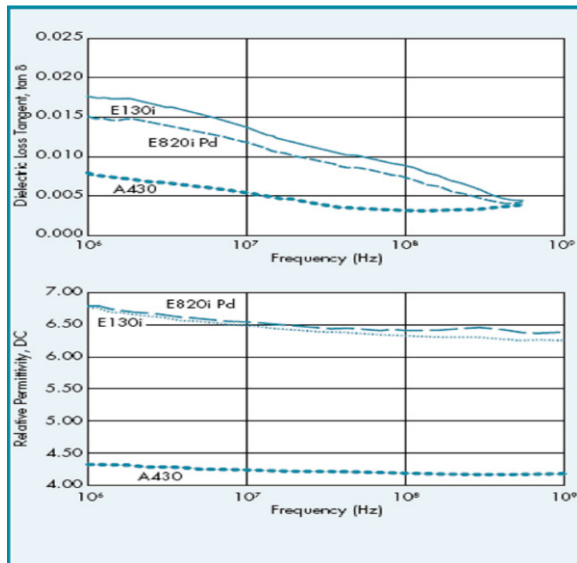
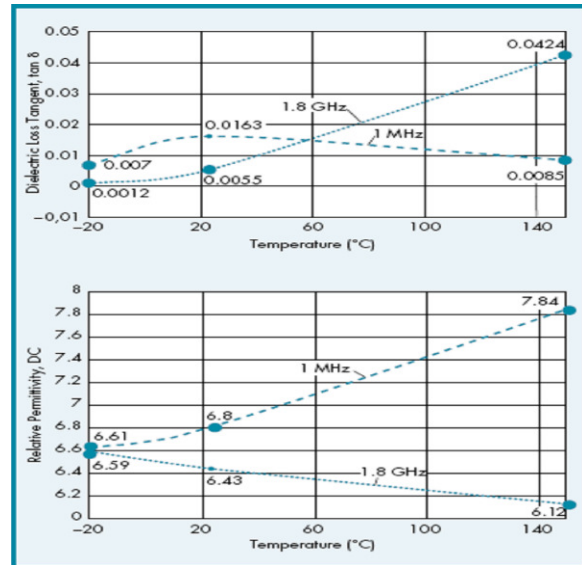
Table 3 — Electrical properties of gold-plated Vectra[®] LCP.

Relative Permittivity	1 MHz	10 MHz	100 MHz	1 GHz	1.8 GHz
A130	5.18	5.05	5.00	5.01	5.00
A430	4.34	4.25	4.20	4.19	4.23
E130i	6.77	6.49	6.33	6.26	6.29
E820i	7.19	6.92	6.79	6.74	6.79
E820i Pd	6.79	6.54	6.42	6.39	6.43
Dielectric Loss Tangent					
A130	0.014	0.009	0.006	0.006	0.006
A430	0.009	0.006	0.003	0.004	0.005
E130i	0.019	0.015	0.010	0.004	0.004
E820i	0.016	0.014	0.009	0.004	0.006
E820i Pd	0.016	0.013	0.008	0.003	0.005

Figure 14 shows the relative permittivity and dissipation factors of some characteristic Vectra grades as a function of frequency. The temperature dependency of these values can be seen in Figure 15 for the E820i Pd grade specially developed for plating.

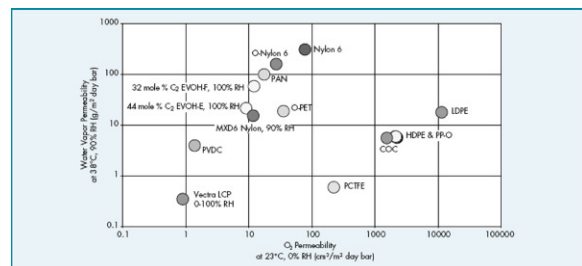
The tests were carried out by COMTECH Labor für Kunststoffe GmbH Munich on a Hewlett Packard HP 4291A RF impedance analyzer in the 1 MHz to 1.8 GHz range.

Underwriters Laboratories (UL) has evaluated the majority of Vectra grades. They report measurements of flammability, arc resistance, hot wire ignition, high current arc ignition, high voltage tracking rates and comparative tracking index. The data is reported on the UL “yellow card”. Many Vectra products allow the use of 50% regrind while continuing to maintain the UL rating.

**Figure 14** — Relative permittivity/dielectric loss tangent vs. temperature for Vectra[®], gold plated.**Figure 15** — Relative permittivity/dielectric loss tangent vs. temperature, Vectra[®] E820iPd, gold plated.

Permeability to gases and vapors

Vectra has extremely low permeability to gases and water vapor. Figure 16 shows the superior performance of unfilled Vectra polymers compared with conventional barrier materials such as ethylene vinyl alcohol copolymer (EVOH), polyvinylidene chloride (PVDC), MXD6 (a copolyamide of meta-xylenediamine and adipic acid), and PCTFE (polychlorotrifluoroethylene). The greater impermeability of Vectra makes it possible to use thinner barrier layers in coextruded structures. In the production of liquid crystalline monolayer film, the problem of fibrillation must be addressed. This anisotropy can be overcome by post-extrusion techniques such as biaxial orientation. The water permeability of Vectra is shown in Table 16.

**Figure 16** — Permeability of various polymer films (thickness 25 µm).

Radiation resistance

Vectra has excellent resistance to gamma radiation. Table 4 shows the effect of Cobalt 60 radiation on the mechanical properties of Vectra A950.

Table 4 — Cobalt 60 radiation Vectra® A950 (percent retention of properties).

Radiation Dose	25 Mrads	100 Mrads	250 Mrads	500 Mrads
Tensile strength ⁽¹⁾	97	95	95	95
Tensile modulus ⁽¹⁾	100	100	106	106
Break elongation ⁽¹⁾	81	81	79	79
Flexural strength ⁽²⁾	101	102	102	102
Flexural modulus ⁽²⁾	108	108	116	125
HDT @ 1.82 MPa ⁽²⁾	100	100	100	94
⁽¹⁾ ASTM D638 ⁽²⁾ ASTM D790 ⁽³⁾ ASTM D648				

Conclusion

LCPs lend themselves to a variety of electrical and electronic applications because of their high temperature stability, low mold shrinkage, and excellent dimensional stability. The high-flow polymers are easily molded into intricate parts, such as electrical connectors with high pin densities, with little or no flash. Moreover, thin-walled components made from LCPs are exceptionally strong and stiff because of the self-reinforcing nature of the polymer.

With the move to Pb-free soldering, LCP (liquid crystal polymer) became the primary material for premolded air-cavity packaging. This thermoplastic can withstand assembly temperatures well beyond the abilities of polyester, polyethersulfone, and other engineering polymers. Only LCP and PEEK (polyetheretherketone) can tolerate 260°C or more without melting or distorting, and PEEK is more expensive, more difficult to bond, and much harder to mold in thin cross-sections than LCP. Not only has LCP begun displacing more expensive ceramic packaging – equivalent LCP packages typically cost about 40% less – but it is also replacing less-expensive EMC in high performance applications, such as those that call for high power density and high frequencies.

Manufacturing with LCP differs from other packaging processes. LCP packages are injection molded around lead frame inserts, often at mold cycle times under 10s. This method lends itself to high-efficiency approaches, such as a continuous process that molds strips of metal lead frames in multi-cavity molds. Alternatively, conductor patterns can be placed on LCP after molding by such automated processes as laser direct structuring, in which a laser draws a circuit pattern on a platable LCP that is then metalized in an electroless plating bath.

Once a die is attached and wire bonded, the air-cavity package can be sealed with a metal, ceramic, glass, or plastic lid. Sealing often involves an adhesive such as epoxy, although heat, laser, or other means can be used. LCP works well in premolded LCP packaging because many grades of

this polymer withstand temperatures above 300°C. It is inherently flame retardant and meets UL 94V-0 flammability criteria without the addition of halogen, phosphorous, or other flame retardants. And, as a thermoplastic, it is recyclable.

LCP has 10 times the water vapor barrier of epoxy and absorbs just 0.02% moisture, so it can create near-hermetic packaging. It has excellent dimensional stability in molding and creates precision parts having flat surfaces right out of the mold, without rework. It also has good electrical properties: for instance, it has a low dissipation factor and its dielectric constant is 3 to 4, compared to 9 to 13 for ceramic.

For advanced packaging designs, LCP offers greater functionality and flexibility than ceramic. While ceramic packages can be shaped in two dimensions, they have trouble with three-dimensional shapes or complex contours. Injection molded LCP does not, and thus lets many elements – connectors, inductors, and other structures normally placed on boards – be integrated into complex packages. This will reduce demand for board space and lower component, processing, and assembly costs.

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