Transport and Adhesion Properties of an Unlined and a Liquid-Crystalline Polymer–Lined Vinyl Ester Thermoset Exposed to Severe Environments

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ABSTRACT: The application of liquid-crystalline polymers (LCP) as lining materials for fiber-reinforced plastics was investigated. The lining consisted of one uniaxially and one biaxially oriented LCP and, for comparison, a fluorinated ethylene propylene copolymer. The lining was attached to a glass-fiber–reinforced vinyl ester thermoset. The laminates were examined with respect to their chemical resistance, transport/barrier properties, and lining/matrix adhesion behavior. The transport properties were determined by gravimetric desorption measurements and cup tests. It was shown that the LCP was suitable as a lining in organic solvent and nonoxidizing acid environments. Diffusivities, equilibrium concentrations, and transmission rates of water, methanol, toluene, and trichloroethylene were obtained in the LCP, the fluorinated ethylene propylene copolymer, and also, in the case of the vinyl ester, of hydrochloric acid. In general, the diffusivity and transmission rate in the LCP were one to several orders of magnitude lower than those of the fluorinated ethylene propylene copolymer and the vinyl ester. The reinforcement in the glass-fiber–reinforced plastic led to an increase in the water and methanol diffusivities and transmission rates, which was probably attributable to liquid capillary diffusion. The lap-shear bonding strength between the LCP and the vinyl ester was poor, but it was improved almost sixfold by a combined abrasive and oxygen plasma treatment. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 797–806, 2005

Key words: diffusion; liquid crystalline polymers (LCP); composites; fluorinated ethylene propylene copolymer (FEP); adhesion

INTRODUCTION

Glass-fiber–reinforced plastics (FRP), based on vinyl ester or polyester resins, are widely used in different process components in the chemical and the pulp and paper industries, especially in highly corrosive environments where standard stainless steel cannot be used. However, FRP materials are sensitive to certain aggressive media. In such cases, a lining made of a more chemically resistant material, such as poly(vinyl chloride) (PVC), polypropylene (PP), or a fluoropolymer, is often used. The lifetime of the lining and the FRP structure is often limited by the diffusion of the corrosive substance into and through the lining. A relatively new range of polymers that show interesting barrier properties, because of their high degree of molecular packing, are the liquid-crystalline polymers (LCP). Their gas and vapor barrier properties are known to be outstanding among all types of plastic materials and their chemical resistance is also reported to be good.[1–5] Extrusion processes for LCP film and piping have recently been developed,[6] and LCP seems to have the potential to serve as a cost-effective lining material for FRP structures.

An FRP structure with a lining is basically fabricated in two to three steps. A lining in the form of sheet or pipe is first chosen in the desired or specified grade and thickness, normally ranging from 1.5 to 5 mm. The lining is then applied on a mold and welded, if necessary. Subsequently, a resin and a fiber reinforcement are applied to the lining. This means that a certain bonding strength is required between the lining and the resin and the lining must be weldable. Furthermore, the lining has to withstand both temperature and pressure variations and the coefficients of thermal expansion of both materials have to be similar to avoid the development of internal stresses.

So far, the gas-barrier properties of LCP and blends of LCP and thermoplastics[7–9] have been mainly investigated and little is known about the diffusion and barrier properties of LCP to liquids.[10]

The purpose of this work was to assess the usefulness of LCP as a lining material for FRP, by determining the transport properties of liquid chemicals, common in FRP applications, in LCP and comparing these with the liquid-transport properties of a commercial high-performance lining [fluorinated ethylene pro-

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<p style="text-align: center;">TABLE I
Characteristics of the Uniaxially and Biaxially Oriented LCP Film of Vectra A950</p>

Characteristic	U-LCP	B-LCP
Thickness	36 μm	44 μm
Orientation	uniaxial	biaxial
Tensile strength parallel to the orientation (ASTM D882-91)	580 MPa	279 MPa
Tensile strength perpendicular to the orientation (ASTM D882-91)	35 MPa	373 MPa
Melting point	$T_{m1} = 276.5°C$, $T_{m2} = 294.5°C$	$T_{m1} = 276.5°C$, $T_{m2} = 295°C$
Density	1.394 g/cm^3	1.394 g/cm^3

pylene copolymer (FEP)]. For a more complete understanding, the liquid-transport properties of both pure and fiber-reinforced vinyl ester were also determined. Further, the bonding characteristics between the LCP and the vinyl ester resin, and how they can be enhanced, were investigated.

Seven different liquid media, representing typical chemical environments, were chosen. The transport of deionized water was investigated at 80°C to show the barrier properties toward a small polar molecule of LCP in the vicinity of its glass-transition temperature. The transport properties of the hydrogen bonding and polar organic solvent (methanol), the aromatic solvent (toluene), and the chlorinated solvent (trichloroethylene) were first studied at 35°C to provide a comparison with previous work on methanol/LCP.[10] The diffusion of toluene, however, was very slow and the temperature in the toluene experiments was therefore increased to 60°C. Experiments with concentrated hydrochloric acid were also run at 35°C (acidic, nonoxidizing environment). The exposure to an acidic oxidizing environment (concentrated sulfuric acid) was conducted at 25°C, given that a certain degradation of the LCP material was already expected at this temperature. In an alkaline environment, a caustic soda solution, the analysis was run at 60°C to provide a comparison with selective etching experiments in Hedmark et al.[11]

EXPERIMENTAL

Materials

Three samples of the liquid-crystalline polymer Vectra A950 were studied, one uniaxially and one biaxially oriented film and injection-molded plates. Vectra A950 is a copolymer of *p*-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid and is produced by Ticona GmbH (Kelsterbach, Germany). The uniaxially oriented film (U-LCP) was produced by Ticona GmbH/ USA. The biaxially oriented film (B-LCP) was kindly provided by Superex Polymer Inc. (Waltham, MA).[5] The characteristics of the films are presented in Table I. The injection-molded plates (I-LCP), with a thickness of 1 mm, were produced using a Battenfield BA 500 CDK (temperature on the injection side 295°C, injection speed 80 cm/s, pressure 180 MPa, cycle time

18 s) at Möllers Verktygsmakeri (Munsö, Sweden). A bisphenol-A epoxy-based vinyl ester resin of the Atlac 430 type, supplied by DSM Composite Resins (Zwolle, Netherlands), was chosen as FRP matrix material. A formulation of 100 mL resin, 0.5 mL 1% cobalt solution, and 1.0 mL methyl ethyl ketone peroxide (Butanox M-50) was used. Clear castings and hand laid-up laminates, with different glass fiber contents, were made using chopped-strand mats (CSM) of E-glass fiber followed by postcuring at 100°C for 8 h. A fluorinated ethylene propylene copolymer (FEP, melting point 259.1°C, density 2.126 g cm^{-3}) was provided by Symalit AG (Lenzburg, Switzerland). Deionized water, toluene (99.5% purity grade, $\rho_{toluene} = 864-868$ kg m^{-3}; Kebo Laboratory, Uppsala, Sweden), methanol (99.0% purity grade, $\rho_{methanol} = 791-793$ kg m^{-3}; Merck Eurolab AS, Oslo, Norway), trichloroethylene (TCE, 99.0% purity grade, $\rho_{TCE} = 1460$ kg m^{-3}; Alcro Parti AB, Stockholm, Sweden), hydrochloric acid ($\rho_{HCl} = 1180$ kg m^{-3}; Prolabo/Merck Eurolab), sulfuric acid (98% purity grade; $\rho_{H2SO4} = 1840$ kg m^{-3}; Merck Eurolab), caustic soda (97% purity grade; Merck Eurolab), chromosulfuric acid ($H_2SO_4 > 92\%$, $CrO_3 > 1.3\%$; Merck Eurolab), and potassium permanganate (99.0% purity grade; Merck Eurolab) were used.

Sorption and desorption measurements

The barrier properties, such as diffusion, sorption, and transmission rate coefficients, were gravimetrically determined by sorption and desorption studies on at least duplicate specimens. The mass increase was determined by intermittently weighing the surface-dried samples using a Sartorius MC 210P balance (Precision Weighing Balances, Bradford, MA), with an accuracy of 0.01 mg. The desorption experiments were performed by placing the samples in an "air-conditioned" oven and measuring the weight using the same balance. The following environments were chosen: deionized water at 80°C, HCl 35 wt % at 35°C, methanol at 35°C, toluene at 60°C, and TCE at 35°C. The diffusivities and transmission rates were calculated from the desorption data, taking into account the initial thickness of the specimens.
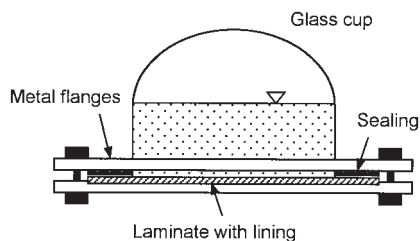
Figure 1 Experimental setup of the cup experiments.

Chemical stability

Duplicate specimens of U-LCP, B-LCP, and I-LCP were exposed to the same chemicals used in the sorption experiments and to caustic soda 10 wt % at 60°C and sulfuric acid 98 wt % at 25°C for certain time intervals after drying at 80°C. After exposure, the specimens were washed with deionized water and acetone in an ultrasonic bath and dried to constant weight at 80°C. The etching rate was calculated according to

$$\frac{dL}{dt} = \frac{m(t) - m_0}{m_0} \frac{L}{2t} \tag{1}$$

where L is the initial thickness of the specimen, m_0 is the initial weight, and $m(t)$ is the weight at time t.

Transmission rate measurements

The rates of transmission of different chemicals through glass-fiber–reinforced laminates and clear castings with a lining of LCP film or FEP were determined in a cup test by intermittently measuring the weight loss (Sartorius LP1200S, accuracy 1 mg; Fig. 1). The cups were placed in an "air-conditioned" oven at selected temperatures (water, 80°C; methanol, 35°C; toluene, 60°C; TCE, 35°C; HCl, 35°C). Duplicate determinations were carried out. The mass loss of the cup was corrected for the mass loss attributed to liquid permeating through the sealing, and the transmission rate Q was calculated according to eq. (2) by fitting the data points by the least-squares method.

$$Q = \frac{(m_C - m_S)l}{tA} \tag{2}$$

where m_C is the mass loss of the cup, m_S is the mass loss through the sealing, l is the thickness of the laminate, t is time, and A is the exposure area.

Bonding strength between LCP and the vinyl ester

The bonding strength between LCP and the vinyl ester was determined by a lap-shear test. Two test bars, cut from injection-molded plates ($1 \times 15 \times 50$ mm), were

bonded with the vinyl ester (overlapping area 20×15 mm) and the bonding strength was measured at room temperature using an Instron 5558 (Canton, MA) tensile testing machine (crosshead speed: 1 mm/min). The influence of the following surface treatments of the LCP on the bonding strength was examined: solvent treatment with acetone, abrasive treatment with sandpaper of mesh P320 and P500, chemical treatment with chromosulfuric acid (20 and 30 min), chemical treatment with potassium permanganate (0.7 g $KMnO_4$ per 100 mL solution of two parts sulfuric acid and one part dry phosphoric acid, 30 min), chemical treatment with chlorosulfonic acid (10 s), chemical treatment with sulfuric acid (5 min), combinations of mechanical and chemical treatment, application of adhesive polymers [EMA OE5614 from DuPont (Wilmington, DE); Primachor 3440 from Dow Chemical (Midland, MI)], and plasma treatment (oxygen flow 50 mL/min, 200 W, pressure 27 Pa, 10 min). A minimum of five specimens was tested for each treatment.

THEORY

Diffusion into a plate is described by Fick's second law[12]:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[D(C) \frac{\partial C}{\partial x} \right] \tag{3}$$

where D is the concentration-dependent diffusion coefficient, x is the distance, and C is the penetrant concentration in the polymer. The concentration-dependent diffusivity was calculated from desorption measurements. Only half the plate was considered, the inner boundary coordinate being described as an isolated point. The surface concentration was assumed to be zero during desorption. The concentration-dependent diffusivity $D(C)$[13] was expressed as

$$D(C) = D_{C0}e^{\alpha_D C} \tag{4}$$

where D_{C0} is the zero concentration diffusivity and α_D is the "plasticization power." Equations (3) and (4) are solved using a multistep backward implicit method described by Edsberg and Wedin[14] and by Hedenqvist et al.[15,16] The average transmission rate $\bar{Q}$ is defined as

$$\bar{Q} = \bar{D}S \tag{5}$$

where $\bar{D}$ is the average diffusion coefficient and S is the sorption coefficient. The average diffusion coefficient is calculated according to

$$\bar{D} = \frac{1}{C_{max}} \int_0^{C_{max}} D_{C0}e^{\alpha_D C} \, dC \tag{6}$$

TABLE II
Degradation/Etching Rate of Different LCP samples
Exposed to Sulfuric Acid and Caustic Soda Solution

	I-LCP (μm/min)	U-LCP (μm/min)	B-LCP (μm/min)
H_2SO_4, 98 wt %, 25°C	0.8	0.8	0.9
NaOH, 10 wt %, 60°C	0.0013	0.0003	0.0004

where C_{max} is the saturation concentration.

For comparison, the concentration-independent diffusion coefficient was derived from the time needed to reach 50% of the saturation concentration, $t_{0.5}$, according to[17]

$$D_{0.5} = \frac{0.04919}{\dfrac{t_{0.5}}{l^2}} \tag{7}$$

where l is the thickness of the plate.

RESULTS AND DISCUSSION

Sorption and desorption measurements

The LCP deteriorated in strong oxidizing environments (H_2SO_4, 98 wt %) and in alkaline environments (NaOH, 10 wt %) (see Table II), but it did not lose mass in a nonoxidizing acidic environment (HCl, 35%). It was also unaffected in the different solvents, where only a small initial weight loss of about 0.02% was observed. These results agree with those from previous studies, where it was found that LCP was suitable for use in organic solvents and nonoxidizing acidic environments.[7,18]

Transport coefficients for deionized water, methanol, toluene, and TCE were obtained for the LCP, the vinyl ester, and the FEP, as well as hydrochloric acid transport coefficients in the vinyl ester (Table III). Figure 2 illustrates the methanol desorption curves of LCP, FEP, and the vinyl ester and the fits obtained using eqs. (3)–(6). An attempt was made to use the numerical method [eqs. (3)–(6)] on the LCP data, but the scatter in data, because of the very low liquid uptake, meant that it was more effective to obtain diffusivities by the half-time method. Little was lost by doing so because the only advantage of the numerical procedure is that it takes into account concentration-dependent diffusivities, something that can be neglected for LCP.

In general, the diffusion coefficients and the transmission rates in the LCP material were several orders of magnitude lower than those in the vinyl ester and, although to a lesser degree, they were also lower than those in FEP (Table III). Among the solvents studied, deionized water had the highest diffusivity ($\sim 10^{-9}$ cm^2/s) and transmission rate ($\sim 10^{-12}$ g cm/cm^2 s) in LCP. The diffusivities and transmission rates of the organic solvents were on the order of 10^{-11} to 10^{-12} cm^2/s and 10^{-13} to 10^{-14} g cm/cm^2 s, respectively. Transport coefficients for hydrochloric acid in LCP and FEP could not be determined because the strong scatter in the data made the evaluation unreliable. In the literature, the gas-barrier properties of LCP and its blends have so far been mainly investigated, and only a few of these studies present data that can be com-

TABLE III
Transport Coefficients in the Vinyl Ester, FEP, and LCP of Different Liquids

Environment	Polymer	D_{C0} (cm^2/s) $\times 10^{-9}$ [a]	α_D	$\bar{D}$ (cm^2/s) $\times 10^{-9}$ [a]	C (g liquid/ 100 g polymer)	$\bar{Q}$ (g cm/cm^2 s) $\times 10^{-12}$ [a]
H_2O, 80°C	Vinyl ester	117 ± 8	56.11 ± 14.9	178 ± 8	1.52 ± 0.02	3250 ± 70
	FEP	538 ± 366	$2.54 \times 10^4 \pm 1.9 \times 10^{-4}$	538 ± 367	0.02 ± 0.01	17.3 ± 24.0
	U-LPC[b]			0.867 ± 0.232	0.12 ± 0.02	1.52 ± 0.64
	B-LCP			2.30 ± 1.87	0.16 ± 0.02	2.05 ± 0.79
	I-LCP			3.93 ± 2.14	0.10 ± 0.02	7.21 ± 3.89
Methanol, 35°C	Vinyl ester	0.948 ± 0.173	35.50 ± 2.4	34.7 ± 2.4	15.32 ± 0.04	6040 ± 400
	FEP	2.04 ± 0.14	$1.1 \times 10^4 \pm 0.64 \times 10^4$	12.8 ± 4.9	0.02 ± 0.002	6.79 ± 3.22
	U-LCP			0.0035 ± 0.0004	0.17 ± 0.02	0.0083 ± 0.0018
	B-LCP			0.0017 ± 0.0005	0.24 ± 0.02	0.0055 ± 0.0021
Toluene, 60°C	FEP	2.55 ± 0.06	347.0 ± 7.1	5.70 ± 0.01	0.42 ± 0.003	50.3 ± 0.4
	U-LCP			0.0067 ± 0.0024	0.11 ± 0.02	0.010 ± 0.0054
	B-LCP			0.0053 ± 0.0021	0.10 ± 0.001	0.0074 ± 0.0029
TCE, 35°C	FEP	0.841 ± 0.001	9.03 ± 7.31	0.883 ± 0.035	1.06 ± 0	20.0 ± 1.0
	U-LCP			0.0540 ± 0.029	0.10 ± 0.02	0.072 ± 0.026
	B-LCP			0.0723 ± 0.0076	0.09 ± 0.04	0.0950 ± 0.034
HCl, 35°C	Vinylester[c]			1.65 ± 0.12	2.26 ± 0.08	44.9 ± 1.5

[a] The values given should be multiplied by this factor.
[b] Transport properties of this and all of the LCP data in this table were calculated using the half-time method on desorption data.
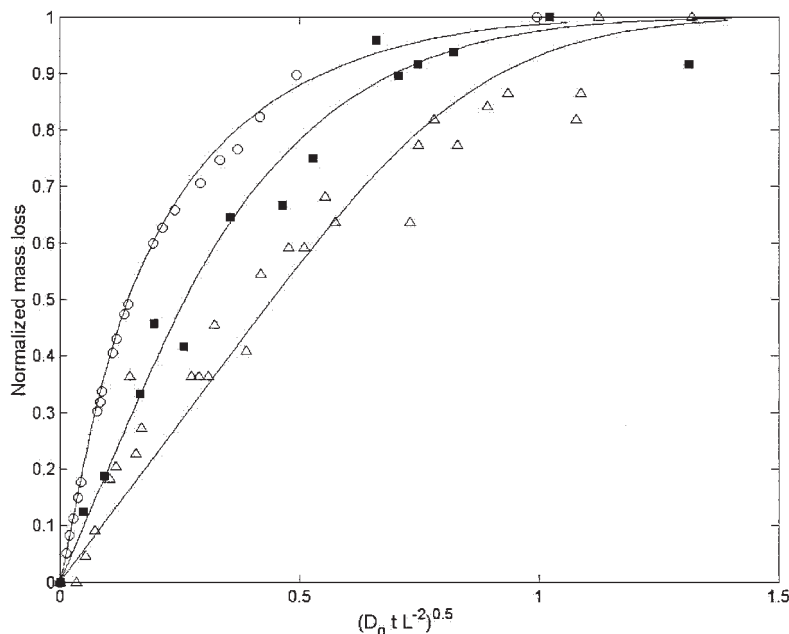[c] Transport properties calculated using the half-time method based on sorption data.

Figure 2 Desorption of methanol in the uniaxially oriented LCP film, in FEP and in the vinyl ester at 35°C. Data were fitted using eqs. (3)–(6) ($\bigcirc$, vinyl ester; $\blacksquare$, FEP; $\triangle$, LCP).

pared with our results. Ramathal et al.[18] reported permeabilities of methanol and toluene vapor in an LCP of type LN001 (Eastman Chemical, Kingsport, TN) at 50–60°C. It was found that the permeability of methanol is higher than that of toluene in LCP. Miranda et al.[7] reported diffusion coefficients of methylene chloride and acetone vapors at 35°C in an LCP, similar to Vectra A950, on the order of 10^{-11} to 10^{-12} cm^2/s, respectively.

Polyphenylene sulfide (PPS) is another high-performance polymer that can be used as a lining material for FRP. PPS is known to have good chemical resistance to nonoxidizing acids, alkali, and organic solvents. However, it turns brittle in nitric acid and sodium chloride environments.[19] Wolf[20] reported transport properties of toluene in annealed and as-received PPS at 50°C obtained from sorption data. The equilibrium sorption coefficient in the as-received material was found to be 12.1% and the diffusion coefficient 2.05×10^{-9} cm^2/s. In comparison to the LCP grade studied at 60°C, the diffusivity and the permeability of toluene in PPS are already several orders of magnitude higher at 50°C. Ma et al.[21] studied the sorption of water in carbon-fiber–reinforced PPS (fiber content 65 wt %). The water diffusion coefficient at 80°C and 75% relative humidity was 37.9×10^{-9} cm^2/s, which is approximately 10 times higher than the diffusion coefficient of liquid water in the LCP studied. The scatter in the data did not permit any definite conclusion to be drawn regarding the influence of the orientation of the LCP film on the transport properties. For water and methanol, however, it seemed that the equilibrium concentrations in the uniaxially oriented film were lower than those in the biaxially oriented film.

The transport properties in the vinyl ester could be obtained only for water, methanol, and hydrochloric acid and the diffusivities and the transmission rates ranged, respectively, from 10^{-7} to 10^{-9} cm^2/s and from 10^{-9} to 10^{-11} g cm/cm^2 s. Because of extensive swelling, the vinyl ester crazed in toluene and in TCE. This occurred when the concentrations approached 33 and 43 g liquid/100 g polymer, respectively. The diffusion of methanol in the vinyl ester was highly concentration dependent ($\alpha_D = 35.5$, $D_{C0} = 1.17 \times 10^{-10}$ cm^2/s, $\bar{D} = 3.47 \times 10^{-8}$ cm^2/s). The diffusion of water in the vinyl ester was also concentration dependent (Table III). The diffusion coefficient for hydrochloric acid, shown in Table III, is an average diffusion coefficient representing both the diffusion of water and that of hydrochloric acid molecules.[22]

Interestingly, the coefficients of diffusion of water and methanol in FEP and in the vinyl ester were of the same order of magnitude. The transmission rates of water and methanol in FEP, however, were about three orders of magnitude lower than those in the vinyl ester because of the extremely low equilibrium concentrations in FEP. The concentration dependency of the diffusivity in FEP was highest for methanol and toluene (α_D, Table III). Compared to the vinyl ester, however, the concentration dependency was smaller, as observed by comparing the ratios of the average diffusion coefficient to the zero-concentration diffusion coefficient, $\bar{D}/D_{C0}$. This ratio was 36.6 and 6.3, respectively, for the vinyl ester and FEP in methanol.

The evaluation was generally based on the initial thickness of the specimens. As already indicated, sorption could lead to extensive swelling of the specimens; for example, the vinyl ester and FEP swelled 12.9 and
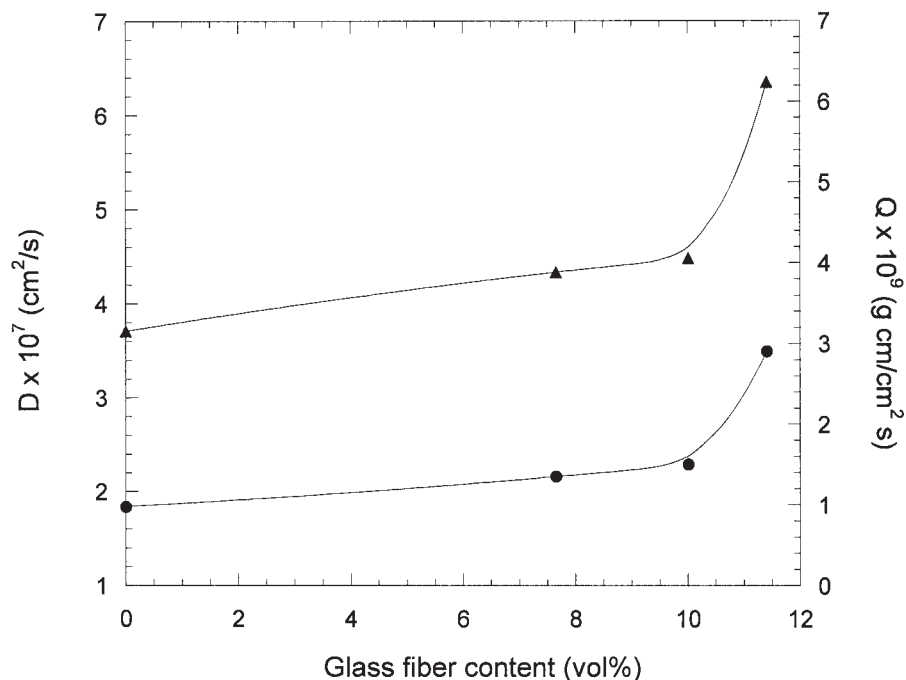
Figure 3 Diffusivity and transmission rate of water in vinyl ester at 80°C as a function of the glass fiber content (●, diffusivity; ▲, transmission rate).

7.1% in methanol, respectively, along the specimen thickness. Swelling of the LCP films, on the other hand, was negligibly small. Calculations of the transport properties, based on the swollen thickness, resulted in higher diffusivities and higher transmission rates. For example, the average diffusivity of methanol in the vinyl ester was 7.39×10^{-8} cm^2/s based on the swollen thickness and 3.64×10^{-8} cm^2/s based on the initial thickness. The choice of thickness thus affects D_{C0} and, consequently, the average diffusivity and permeability. However, provided diffusivity data are available for a given thickness, it can easily be recalculated to a new thickness on the basis of simple time/thickness scaling.

Sorption experiments in laminates with different glass-fiber contents

In practice, the transport properties of liquids in the pure resin matrix of FRP are of less practical importance because a reinforcement is always incorporated into the matrix. The influence of the glass-fiber content on the transport properties was examined for specimens exposed to water at 80°C and methanol at 35°C. Figures 3 and 4 show the diffusion coefficients and the transmission rates of water and methanol in vinyl ester laminates as a function of the glass-fiber content. Surprisingly, the diffusivity and the transmission rate of methanol increased significantly with increasing glass content. In water, the diffusion and the transmission rate coefficients were approximately constant at low glass-fiber contents, but they increased at higher

contents. It would have been expected that the diffusivity would decrease with increasing content of the impermeable glass fibers. Good agreement was observed between the measured and the calculated composite densities; thus the increase in the diffusivity could not be explained by the existence of voids created during the fabrication of the laminate. However, the swelling of the laminates in water and methanol and the interaction of the penetrant with the glass-fiber sizing may have led to debonding between the resin matrix and the glass fiber and this may explain the observations. To reveal whether a transport of water and methanol occurred through capillary diffusion, in addition to "normal" bulk diffusion, capillary diffusion calculations were made. The capillary diffusion of water and methanol inside an annulus between the resin matrix and a glass fiber was estimated according to the following treatment. The driving force for capillary flow, Δp, is calculated as[23,24]

$$\Delta p = \frac{N}{A} - \frac{G}{A} - p_a - p_e \qquad (8)$$

where A and N are the cross-sectional area and the surface tension force, respectively; G is the gravitational force; and p_e and p_a are externally applied pressures. If the gravitational force is neglected, Δp can be estimated from the surface tension acting along the circular contact line between the liquid and the annulus:
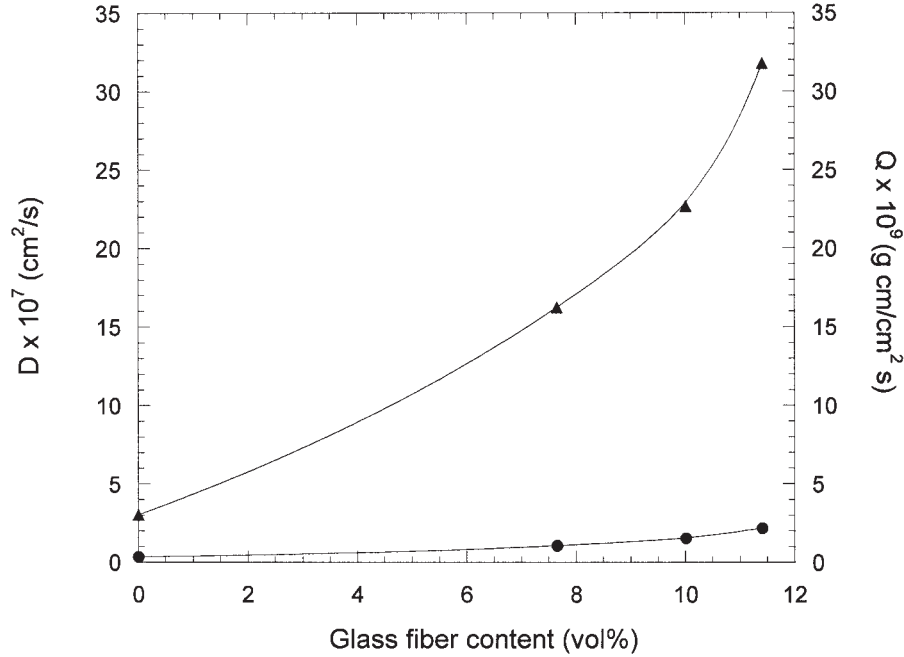
Figure 4 Diffusivity and transmission rate of methanol in vinyl ester at 35°C as a function of the glass fiber content (●, diffusivity; ▲, transmission rate).

$$\Delta p = \frac{N}{A} = \frac{2\gamma \cos\Theta}{r_o - r_i} \tag{9}$$

where γ is the surface tension; Θ is the average contact angle between the liquid surface and the annulus wall; and r_o and r_i are, respectively, the outer and inner radii of the annulus. Applying the Hagen–Poiseuille equation, the capillary flow in an annulus between the resin matrix and the glass fiber can be described as[25]

$$\frac{h^2}{t} = \frac{\Delta p r^2}{4\eta} = \frac{\gamma \cos\Theta}{2\eta(r_o - r_i)}\left[r_o^2 + r_i^2 - \frac{(r_o^2 - r_i^2)}{\ln(r_o/r_i)}\right] \tag{10}$$

where h is the distance traveled by the solute during time t, and η is the viscosity. Providing the capillary swells only in the direction perpendicular to the fiber axis, its volume change can be expressed as

$$\frac{\Delta V}{V_i} = x = \frac{r_a^2 - r_i^2}{r_i^2} \tag{11}$$

and the flow can be expressed as

$$\frac{h^2}{t} = \frac{\gamma \cos\Theta}{2\eta} r_i \left[\frac{2 + x - \frac{x}{\ln(1 + x)^{0.5}}}{(1 + x)^{0.5} - 1}\right] \tag{12}$$

The input data were: $\eta_{H2O\ 80°C} = 0.35$ mPa s^{-1}, $\eta_{Methanol\ 35°C} = 0.49$ mPa s^{-1}, $\gamma_{H2O\ 80°C} = 62.67$ mN/m, $\gamma_{Methanol\ 35°C} = 21.30$ mN/m, $\Theta_{H2O\ 80°C,\ glass}$ $= 60°$, $\Theta_{H2O\ 80°C,\ matrix} = 63°$, $\Theta_{Methanol\ 35°C,\ glass} = 30°$, $\Theta_{Methanol\ 35°C,\ matrix} = 34°$, $\Theta = \frac{1}{2}(\Theta_{Methanol} + \Theta_{water})$. The contact angles were determined in a microscope by dipping a rod of the material into water and methanol, and viscosities were obtained from Lide[26] and Perry.[27] Assuming that the volume change x was closely related to or proportional to the equilibrium concentration, which was approximately 1.5 and 15%, respectively, for water and methanol, the capillary flow was approximately five times larger for methanol than for water. When exposed to water, the diffusivity and the transmission rate of the vinyl ester laminate with a glass-fiber content of 11.7 vol % were increased by a factor of approximately 2 compared to the values for the clear casting. In methanol, however, an increase by a factor of approximately 10 was observed. Thus the ratio of increase of methanol and water diffusivities in the glass-fiber composite was 5, well in accordance with the prediction given by the capillary flow analysis. Consequently, debonding-induced capillary diffusion was most likely the reason for the increase in diffusivity with increasing glass-fiber content.

Cup experiments

The transmission rates for CSM laminates and clear castings with LCP and FEP linings and the equilibrium concentrations in selected laminates were obtained from cup experiments. The results are shown in Table IV and compared to the transmission rate in the vinyl ester obtained in the desorption measurements.

TABLE IV
Transmission Rates (Q) in Laminates With and Without Lining and Equilibrium
Concentrations in Laminates with Lining[a]

Environment	Type of laminate	Q, laminate with lining (g cm/cm^2 s)$\times 10^{-10\ b}$	Q, clear casting/CSM (g cm/cm^2 s)$\times 10^{-10\ b}$	Equilibrium concentration (g solvent/100 g polymer)
H$_2$O, 80°C	U-LCP[c]/CSM laminate[d]	9.92	62.43	0.17
	U-LCP/ clear casting[e]	14.81	31.64	0.16
	B-LCP[f]/CSM laminate	8.33	62.43	
	FEP[g]/CSM laminate	2.74	62.43	
Methanol, 35°C	U-LCP/CSM laminate	4.11	317.89	0.01
	U-LCP/clear casting	0.94	104.54	0.01
	B-LCP/CSM laminate	5.04	317.89	
	FEP/CSM laminate	9.74	317.89	
Toluene, 60°C	U-LCP/CSM laminate	≈0		0.03
TCE, 35°C	U-LCP/CSM laminate	3.04		0.02
HCl 35%, 35°C	U-LCP/CSM laminate	1.28	0.34	0.01
	FEP/CSM laminate	3.91		FEP/CSM laminate

[a] Data obtained from cup experiments.
[b] The values below should be multiplied by this factor.
[c] Thickness of uniaxial LCP film, 36 μm.
[d] Thickness of CSM laminate, 4 mm; glass fiber content, 11%.
[e] Thickness of clear casting, 4 mm.
[f] Thickness of biaxial LCP film, 44 μm.
[g] Thickness of FEP lining, 2.3 mm.

The transmission rates in clear castings and CSM laminates (glass content 11 vol %) with a lining of LCP (thicknesses: 36 and 44 μm) and of FEP (thickness: 2.3 mm) were reduced by factors of 10 and 100, respectively, when exposed to water and methanol. Assuming that the concentration in the LCP lining could be neglected and, consequently, that the equilibrium concentration in the laminate corresponded to the concentration in the vinyl ester laminate, the equilibrium concentration decreased by factors of approximately 10 for water and 1000 for methanol compared to that of the unlined vinyl ester (Tables III and IV). Low transmission rates and equilibrium concentrations were also observed for toluene, TCE, and hydrochloric acid. No sign of any crazing of the resin matrix was observed in the case of toluene and TCE. Approximately the same transmission rates were observed in the LCP- and the FEP-lined laminates (Table IV).

It would be interesting to know whether the transmission rate of a laminate with lining obtained in a cup test can be predicted using the transport coefficients obtained in the desorption experiments. The transmission rate of a sheet consisting of two layers of different polymers can be estimated using

$$\frac{l_{\text{total}}}{Q_{\text{total}}} = \frac{l_{\text{lining}}}{Q_{\text{lining}}} + \frac{l_{\text{laminate}}}{Q_{\text{laminate}}} \quad (13)$$

where l_{total} is the thickness of the laminate with lining; l_{lining} and l_{laminate} are the thicknesses of the lining and the laminate, respectively; and Q values are their transmission rates. The predicted and the experimentally determined transmission rates of water and methanol are presented in Table V. For water, the calculated and experimental transmission rates in the

TABLE V
Comparison of the Calculated and Experimentally Determined Transmission Rate

Environment	Type of laminate	Q (g cm/cm^2 s)$\times 10^{-10\ a}$	Calculated Q (g cm/cm^2 s)$\times 10^{-10\ a}$
Deionized water, 80°C	U-LCP/CSM laminate	9.92	1.65
	U-LCP clear casting	14.81	1.59
	B-LCP/CSM laminate	8.33	1.84
	FEP/CSM laminate	2.74	5.53
Methanol, 35°C	U-LCP/CSM laminate	4.11	0.0078
	U-LCP/clear casting	0.94	0.0078
	B-LCP/CSM laminate	5.04	0.0050
	FEP/CSM laminate	9.74	13.20

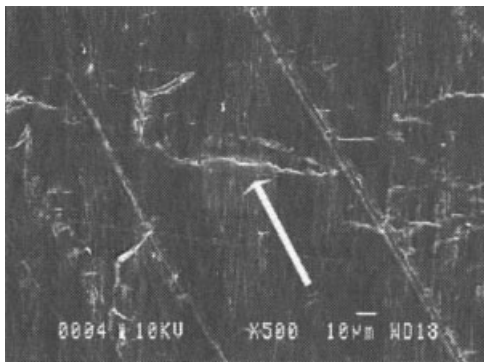[a] The values below should be multiplied by this factor.

Figure 5 Scanning electron micrograph of the outer surface of uniaxial LCP lined onto vinyl ester after exposure to methanol for 6 months. The arrow indicates an irregularity.

LCP- and FEP-lined laminates were found to be of the same order of magnitude. They differed, however, by a factor of 10^3 for laminates with LCP-lining exposed to methanol. Microscope studies were carried out to investigate this issue, and the surface of a uniaxially oriented LCP lining after 6 months of exposure to methanol at 35°C is shown in Figure 5. The surface showed a large number of irregularities with a length of approximately 50 to 150 μm. Interestingly, these irregularities were oriented perpendicular to the orientation direction. They were not observed on the biaxially oriented film used as lining or on the uniaxial film without FRP reinforcement exposed to methanol. The irregularities were probably a consequence of the tensile stresses exerted by the swelling vinyl ester matrix. The uniaxial LCP lining exposed to water and the other chemicals showed only very few of these irregularities. The transmission rate of methanol in laminates made with biaxially oriented film also showed a large deviation, although no microscopically visible irregularities were formed. Further studies should be carried out to investigate those observations more in detail.

Bonding strength

One of the major problems in lined FRP structures is to achieve a sufficient bonding between the lining material and the FRP. As expected, the bonding strength between the surface-cleaned LCP and the vinyl ester was low (0.4 N/mm^2). However, it was improved by surface treatments, as shown in Table VI. A combination of mild abrasion and oxygen plasma treatment increased the bonding strength to 2.3 N/mm^2 as a result of a combination of enhanced surface roughness and surface polarity. Cohesive failure of the LCP material was observed, indicating that the actual bonding strength was higher than the inherent strength of LCP. Gleich et al.[28] showed that both corona treatment and low-pressure oxygen plasma treatment increased the surface energy of a glass-fiber–filled LCP of type Vec-

tra A410, but that the bonding strength to aluminum was positively affected only with certain adhesives such as a two-component polyurethane system. Cohesive failure in the LCP also occurred when a thin surface veil was melted into the LCP before bonding it to the vinyl ester. The bonding strength in this case was 2.6 N/mm^2. The technique of melting a "backing" of glass or polyester fiber into the lining is frequently used when, for example, fluoropolymer linings are attached to FRP. In the case of LCP, it would be especially interesting to use it for lining pipes. An increase in bonding strength was also observed with other chemical and abrasive surface treatments and when using compatibilizer/tie layers (Table VI). However, compared to the combined abrasive and plasma treatments, their bonding strength was lower and they were therefore of less practical interest. After having evaluated the adhesion test, the question arises: what is the bonding strength required between the LCP lining and the vinyl ester. Different minimum bonding strengths between linings and FRP have been specified in various standards. Those include 3.5 N/mm^2 for PP and PE linings, and 5 and 7 N/mm^2 for PVC and PVDF linings,[29] respectively. Values are not available for LCP and further experiments should be carried out to obtain information about an appropriate minimum bonding strength. This is of course a parameter that depends on several factors, including product design and type of load.

CONCLUSION

LCP was especially suitable for use in contact with organic solvents and nonoxidizing acid environments. Transport coefficients of water, methanol, toluene, and TCE could be established for LCP, FEP, and the vinyl ester and also of hydrochloric acid for the vinyl ester. In general, the diffusivity and transmission rate in LCP were approximately one to several orders of magnitude lower than those in FEP and the vinyl ester. Although the scatter of the gravimetric LCP data was high, the results showed that desorption measurements were suitable to determine the order of magnitude of the transport properties, even in high-barrier materials. The diffusivity of water and methanol in the FEP and in the vinyl ester were of the same order of magnitude. The transmission rates of water and methanol in FEP, on the other hand, were significantly lower because of the very low equilibrium solute concentrations. The glass reinforcement did not improve the barrier properties of the vinyl ester, perhaps because the diffusing solvent reacts with the sizing of the glass fibers and causes debonding. The transport of the solvent in the vinyl ester may then proceed by a combination of capillary diffusion and normal bulk diffusion. It was shown that the effect of capillary diffusion was more pronounced for methanol than for water. Cup experiments confirmed the results of the

TABLE VI
Bonding Strength Between LCP and the Vinyl Ester and Type of Failure After Different Surface Treatments (Lap-Shear Test)

Surface treatment	Bonding strength (N/mm^2)	Type of failure
Solvent cleaning (acetone)	0.4 ± 0.1	100% AF[a]
Abrasive treatment P320	1.3 ± 0.2	60% AF, 40% CF
Abrasive treatment P500	1.1 ± 0.4	60% AF, 40% CF
Chemical treatment with chromosulfuric acid		
20 min	1.1 ± 0.2	90% AF, 10% CF
30 min	1.3 ± 0.2	85% AF, 15% CF
Chlorosulfuric acid treatment	0.3 ± 0.1	100% CF
Sulfuric acid treatment	0.5 ± 0.1	100% AF
Sodium permanganate treatment	1.0 ± 0.2	60% AF, 40% CF
Chemical treatment with chromosulfuric acid and abrasive treatment with P320	1.6 ± 0.2	50% AF, 50% CF
Adhesion polymer EO 5613	0.6 ± 0.2	100% AF
Adhesion polymer Primachor	0.7 ± 0.3	100% AF
Oxygen plasma treatment	1.1 ± 0.3	90% AF, 10% CF
Oxygen plasma treatment and abrasive treatment with P500	2.3 ± 0.3	10% AF, 90% CF
Glass fiber backing	2.6 ± 0.1	100% CF

[a] AF, adhesive failure; CF, cohesive failure.

desorption measurements and that the transmission rates of the laminates were substantially reduced with an LCP or FEP lining. In the LCP-lined materials, the equilibrium solute concentration in the vinyl ester layer was substantially reduced. The transmission rates, obtained from the cup measurements, of laminates with an LCP or FEP lining could be predicted qualitatively for water and, in the case of FEP, also for methanol using transport coefficients obtained from desorption measurements. The bonding strength between the vinyl ester and the untreated LCP was low, but it was improved significantly by a combined abrasive and oxygen plasma treatment. Further experiments should be carried out to determine the minimum bonding strength between the laminate and the LCP for liner applications. To summarize, LCP was suitable as a lining, especially for organic solvents and nonoxidizing acid applications, and the adhesion problems seem solvable.

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