Interfaces in Repair, Recycling, Joining and Manufacturing of Polymers and Polymer Composites

J. RAGHAVAN,¹ R. P. WOOL²

¹ Department of Mechanical and Industrial Engineering, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2

² Center for Composite Materials and Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716-3144, USA

Received 14 November 1997; accepted 13 July 1998

ABSTRACT: A basic set of 10 thermoset polymer-polymer interfaces has been identified to play a vital role in the technical and economic aspects of composite manufacturing (RIM/RTM, compression molding, autoclave lamination), recycling, repair, welding, and joining of polymer composites. Knowledge of the chemical interactions and molecular connectivity at these interfaces and their influence on processability and mechanical properties of the polymers and polymer composite is essential, and has been the focus of this research. Presented in this report are the results of an exploratory study performed to understand the interactions at the polymer-polymer interface and their influence on the interfacial fracture toughness of a thermoset vinyl ester, which is widely used in liquid molding applications. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 775–785, 1999

Key words: interfaces; polymer composite; manufacturing; joining; welding; repair; recycling

INTRODUCTION

Polymer Matrix Composites (PMC) are utilized to meet the structural and nonstructural functional requirements in high-volume applications such as automotive, trucking, agricultural equipment, rail cars, high-speed civil transportation (HSCT), off-shore and in-shore marine, sporting goods, civil infrastructure, and bridge rehabilitation. While one important interface in polymer composites is the fiber-matrix interface, the polymerpolymer interface plays a crucial role in the economic competitiveness of composite manufacturing and in the ability of polymer composites, especially thermoset polymers and polymer composites, to be repaired, recycled, and bonded. Hence, the focus of this article is primarily on thermoset polymer–polymer interfaces. Depending on the physical and chemical nature of the polymer surface associated with a manufacturing process, the interfaces can be numerous.

Ten polymer–polymer interfaces of prime importance have been identified and tabulated in Table I. These interfaces can be studied using a simple experiment (Fig. 1) involving compact tension (CT) specimens with A- and B-halves. By assembling together two halves of a CT specimen, an interface can be formed at the A-B contact plane. The A-half can be a liquid (L), a virgin solid with as-cast surface (S_V), a solid with fractured surface (S_F) or a solid with fractured and chemically treated surface (S_{FC}). Similarly, the B- half can be either of the four. Thus, there are 10 in-

Correspondence to: R. P. Wool.

Contract grant sponsors: University and State of Delaware; Army Materials Research Lab, Maryland; and the National Science Foundation (contract grant number DMR 9696267).

Journal of Applied Polymer Science, Vol. 71, 775-785 (1999)

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/050775-11

	Liquid B (L)	Solid with As-Cast Surface (S _V)	Solid with Fractured Surface (S_F)	Solid with Fractured and Treated Surface (S_{FC})
Liquid A (L)	L–L Virgin (Control)	L–S _V Repair/recycling	L–S _F Repair/recycling	L–S _{FC} Repair/recycling
Solid with as-cast surface (S_V)		$S_V - S_V$ Welding	S _V –S _F Welding/repair	S _V –S _{FC} Welding/repair
Solid with fractured surface $({\rm S_F})$			S _F –S _F Crack healing	S _F –S _{FC} Wear/repair
Solid with fractured and treated surface (S_{FC})				S _{FC} –S _{FC} Wear/repair

 Table I
 Table of Interfaces Encountered during Repair, Recycling, Joining, and Manufacturing of Polymer Composites

terfaces consisting of three liquid-solid interfaces, six solid-solid interfaces, and a control (virgin) liquid-liquid interface, encompassing joining, repair, recycling, welding, crack healing, and wear. These interfaces are further discussed below.

During the service life of a structural composite member damage may occur, and repair of this damage may be practical and more economical than complete replacement. The repair may involve different procedures as follows: (a) fresh liquid polymer mixture may be poured on the fractured solid surface and cured *in situ*. This procedure would involve L–S_F interfaces. (b) The damaged parts may be held together and annealed at a temperature above T_g , so that the



Figure 1 Schematic of the compact tension specimen and typical load displacement curve.

crack can heal. This procedure would involve S_F-S_F interfaces. (c) An adhesive can be used to bond the damaged parts together. This would involve $\mathbf{S}_{FC}\text{--}\mathbf{S}_{FC}$ and $\mathbf{S}_{F}\text{--}\mathbf{S}_{FC}$ interfaces. Whichever repair technique is used, it is expected to restore the virgin strength of the repaired material. Complete repair is essential to the structural integrity and long-time durability in applications such as HSCT, CAV, infrastructure, bridges, and automobiles. In addition, a fundamental knowledge of these repair techniques is essential in designing smart materials that can repair itself while in service.¹ A critical question addressed herein is whether the original strength is restored in thermoset polymers and polymer composites after repair.

The L-S_F interfaces are also encountered during recycling of thermoset polymer composites. During recycling, the composite is first shredded, and the reinforcing fibers are separated. The separated polymer is mechanically ground into flakes and particles known as "regrind." The regrind particles with their fractured surfaces are normally compounded (10-15 wt %) with fresh liquid resin and molded either by compression molding (such as SMC involving $S_V - S_V$ or $S_F - S_F$ interfaces) or, liquid injection molding processes, such as resin transfer molding (RTM), reaction injection molding (RIM), vacuum-assisted resin transfer molding (VARTM), all involving L-S_V or L-S_F interfaces. Once again, the strength of these interfaces is a key factor that influences the decision to recycle or repair a composite. This problem will be magnified while recycling a thermoset material into structural applications.

Joining/bonding is another important fabrication process that has considerable potential in advanced applications such as composite armored vehicle (CAV), agricultural equipment, wherein composites of various types are bonded to each other and to metals using thermoset adhesives. Other applications involve adhesive bonding of crosslinked dental teeth to denture base resin,² electronic material fabrication, net shaping using thermosets, etc. The joining/bonding procedure would involve L–S_V interfaces and the strength of the bonded material is dependent on the strength of the L–S_V interface.

In addition to their influence on the repair, recycling, and joining of thermoset polymer and its composites, such polymer-polymer interfaces can also influence the economic competitiveness of a manufacturing process. For example, polymer-polymer interfaces dominate the property development during on-line consolidation manufacturing process characterized by lower cycle times, higher quality, reduced complexity, and low capital and operational costs compared to traditional processes such as autoclave lamination. This process involves robotically controlled placement and bonding of pre-preg tows, and subsequent consolidation under heat and pressure using hot nitrogen torches, lasers, and rollers. Because the entire process can be automated, it is very attractive for large component applications such as the HSCT wings and fuselage. The quality of the consolidated composite part depends on process variables such as deposition rate, temperature, and compaction force. The process variables also influence the cycle time and economic competitiveness of the process. To optimize the process variables to obtain optimum quality at a reasonable cost, knowledge of interactions at the polymer-polymer $(S_V - S_V)$ interface (formed by two layers of pre-pregs) is needed. The structure of the interface and subsequent strength development is determined by such factors as surface contact, wetting, surface rearrangement, interdiffusion, and chemical reactions.¹ Similar considerations apply to the strength development in conventional processes such as autoclave lamination and compression molding.

To summarize, the chemical interactions and the molecular connectivity achieved across the 10 interfaces (Table I) determine the ability of polymers and polymer composites to be repaired, recycled, and joined, as well as impact the economic competitiveness of the manufacturing processes. Hence, a systematic exploratory study was initiated by the authors to understand the variables that influence the formation of molecular connectivity across interfaces in a thermoset composite. The study included the three liquid-solid interfaces tabulated in Table I, as well as three solidsolid interfaces that are important in compression molding, repair, recycling, crack healing, and adhesive bonding. Details of the study and the results are presented and discussed in the following sections.

EXPERIMENTAL

Thermoset Material

Vinyl ester thermosetting resin (Derakene 411-C50 manufactured by The Dow Chemical Company) was chosen for this study due to current interest in this resin for high-volume applications in infrastructure, bridge rehabilitation, and renewal. The resin was cured at room temperature using an organic peroxide (USP-245) initiator and cobalt napthenate catalyst. The initiator to catalyst ratio used was 10 : 1. Reference specimens were cured with 1.5 wt % initiator and 0.15 wt % catalyst.

Test Specimens

The CT test specimen configuration is shown in Figure 1(a). The specimens were molded using a silicone mold. Carnuba wax was used as a release coating in the mold. The CT specimens had a cured-in or glued Kapton film placed along the interface plane, and because of poor bonding with the resin, it helped to initiate the starter crack at the interface. During the final machining operation of the molded specimens, 2–3 mm of Kapton film was left in the interface plane of the specimens to ensure that the fracture initiated at the tip of the Kapton film, and thus, at the interface. Initial experiments were carried out by machining a V-notch in the CT specimen with the notch tip sharpened by a razor blade. However, this method did not ensure the initiation of crack growth at the interface. While casting virgin (L-L) specimens, both halves were molded simultaneously with the Kapton film, equal in length to the starter crack, in place. The initiator concentration in the L-L samples varied from 1.5 to 5.0

wt %, and these specimens served as reference specimens. The specimens with various interfaces were prepared in the following manner.

Solid Virgin Surface (S_V)

Initially, one-half of the CT specimen was molded in a silicone mold with a partition plate at the center of the mold. The aluminum partition plate was wrapped with a Kapton film with a silicone release coating. This ensured the easy removal of the solid with an even as-cast surface. This step resulted in the solid–virgin surface, S_v .

Liquid–Solid Virgin Interfaces (L–S_{Vi})

Preparation B-1: the S_V was glued, using crazy glue, with another Kapton film with release coating and of length equal to the starter crack length (a). It was placed in the mold, and the liquid resin was poured over it to mold the second half over the first half. The cured specimen was machined to dimensions given in Figure 1(a) to obtain L-S_{V1} specimens. During manufacturing by RTM/RIM, a gradient in the initiator concentration may be introduced due to poor mixing, and this would lead to nonuniform gel time and curing. This, along with the nonuniform flow through the mold, may introduce gradients in crosslink density in the cured solid. To study the influence of crosslink density of the solid on repair, recycling, and joining, the initiator content in the solid was varied in the range 1.5 to 5 wt %, while maintaining that in the liquid constant at 1.5 wt %. Similarly, to study the influence of gel time, the initiator concentration in the solid was maintained constant at 1.5 wt % while varying that in the liquid in the range 1.5 to 5 wt %. This step resulted in specimens containing L-S_{V1} interfaces, which were used to investigate the bondability of vinyl ester.

Preparation B-2: the above steps were repeated by casting the first half against a steel partition plate instead of the Kapton film wrapped aluminum to study the influence of the mold surface. This resulted in specimens with $L-S_{V2}$ interfaces. The initiator concentration was 1.5 wt %.

Liquid–Solid Fractured Interfaces (L–S_{Fi})

Preparation C-1: after step (a), the as-cast surface was ground to a depth of 300-400 microns, using a diamond wheel without any coolant. This produced the $S_{\rm F1}$ surface. The Kapton film of length equal to the starter crack was glued and the second half was molded over it by pouring the liquid

resin over the first half. This resulted in specimens with $L{-}S_{\rm F1}$ interfaces, which were used to study the reparability and recyclability of vinyl ester.

 $\label{eq:preparation C-2: liquid-liquid samples were first fractured under tensile loading to produce the S_{F2} surfaces. Fresh liquid was poured over the fractured half to obtain specimens with L-S_{F2} interfaces.$

Liquid–Chemically Treated Fractured Solid Interfaces (L–S_{FiC})

After step (a), the as-cast surface was ground to a depth of 300-400 microns, using a diamond wheel without any coolant to produce the S_F surface. The Kapton film of a length equal to the starter crack length was glued, and the exposed S_F surface was subjected to two chemical treatments, (1) *in situ* polymerization of styrene monomer, and (2) solution casting of polystyrene films.

Preparation D-1: A styrene monomer with a 5.0 wt % initiator and a 0.5 wt % catalyst was applied to the exposed S_F surface as a thin film and was cured *in situ* at 100°C for 1 h, to leave behind a polystyrene film. This created the S_{F1C} surface. The liquid resin was molded over the PS film to obtain specimens with L- S_{F1C} interfaces.

Preparation D-2: polystyrene of three different molecular weights (220, 596, and 4340 K) were dissolved in toluene to give 2.0 wt % solutions. These solutions were then applied as a thin film on the exposed S_F surface and dried at room temperature for 48 h, to leave behind a polystyrene film, and this yielded the S_{F2C} surface. The liquid resin was poured over the first half and was cured to obtain specimens with L– S_{F2C} interfaces that were used to study the influence of surface treatments on the toughness of the repaired and recycled vinyl ester.

Solid Virgin–Solid Virgin Interfaces (S_V–S_V)

The specimens with S_V-S_V interfaces were prepared to investigate the welding of thermoset vinyl ester. Step (a) was repeated to obtain two solid halves with as-cast S_V surfaces. Kapton film was then glued on to one solid half to fit a recess with dimensions equal to that of the Kapton film. This recess was introduced by filing, to ensure that the two solid halves were not prevented from making intimate contact due to the thickness of the Kapton film. Both halves were gently pressed together, held in place using a C-clamp, and annealed for 24 h at temperatures 30° above the glass transition temperature (T_g) of 119°C for 1.5 wt % specimens. The annealing temperatures for 4.0 wt specimens were 10°, 30°, and 50° above the T_g of 100°C.

Fractured Solid–Fractured Solid Interfaces $(S_{F2}-S_{F2})$

The specimens with S_{F2} - S_{F2} interfaces were prepared to investigate crack healing in the thermoset vinyl ester. Virgin (L–L) specimens with cured-in Kapton film were initially molded and tested to fracture. The fractured pieces were pressed against each other gently and held in position using a C-clamp. They were then annealed for 24 h at temperatures used for the welding experiment. This experiment was performed on specimens with 1.5 wt % and 4.0 wt % initiator concentrations.

Fractured Solid–Chemically Treated Solid Interfaces $(S_{F2}-S_{F2C})$

The specimens with $S_{F2}-S_{F2C}$ interfaces were prepared to investigate repair in thermoset vinyl ester. Virgin (L–L) specimens, with cured-in Kapton film for crack initiation, were initially molded and tested to fracture. The fracture surface of one-half of the fractured solid was coated with Super glue gel, and the two halves were gently held together using a C-clamp, until the gel cured. Specimens with initiator concentrations 1.5 wt and 4.0 wt were used.

Fracture Test Method

The critical strain energy release rate, $G_{\rm IC}$, for the interfaces shown in Table I, was measured as per ASTM 5045. All the specimens were tested under tensile mode I at a crosshead rate of 0.21 mm s⁻¹. A schematic of a typical load vs. displacement data is shown in Figure 1(b). At the critical maximum load, fracture initiated at the starter crack tip, and the crack propagated. The area (*U*) under this curve corresponding to the maximum load was evaluated and used in the eq. (1) to calculate G_{IC}.

$$G_{IC} = U/(TW_p) \tag{1}$$

where T and W are shown in Figure 1(b) and p is the energy calibration factor, which was calculated using the equation provided in ASTM 5045.

Dynamic mechanical analysis (DMA) tests were performed using TA instruments 983 Dynamic Mechanical Analyzer to measure the glass



Figure 2 G_{IC} as a function of initiator concentration.

transition temperature and the rubbery modulus. The typical sample size was $20 \times 9 \times 2.5$ mm. The rate of heating was 5°C/min, and the frequency was 1 Hz. The glass transition temperature (T_g) was defined by the peak in the loss modulus (E''). The rubbery modulus was defined as the plateau modulus above T_g .

RESULTS AND DISCUSSION

Liquid–Liquid Virgin Interface (L–L)

The G_{IC} values for virgin specimens, with cured-in Kapton film (to act as a starter crack), and consisting of the same liquid on both sides of the interface, are plotted in Figure 2 as a function of initiator concentration. The G_{IC} value for 1.5 wt % specimen is 488 (+110; -80) Jm⁻². Comparing this with the values of 1503 (+886; -875) Jm⁻² for specimens with machined and sawed-in starter cracks, it can be surmised that the cured-in Kapton film resulted in a sharper starter crack. In addition, as discussed in the previous section, the Kapton film also ensured the crack initiation at the interface. Hence, the cured-in Kapton film was used as starter crack for all interfaces in the entire study.

The G_{IC} values (Fig. 2) appear to be constant within the error band up to 4.0 wt % initiator concentration, beyond which it decreases. Because the molecular weight between crosslinks M_c , would decrease with increasing initiator concentration, a decrease in G_{IC} values with increasing concentration is to be expected. The critical stress in the deformation zone at the crack tip behaves according to percolation theory¹ as, $\sigma \sim M_c^{-1/2}$, and the critical crack opening displacement δ , behaves as $\delta = \lambda R_c$, where λ is the draw ratio between crosslinks and R_c



Figure 3 Rubbery flexural modulus as a function of initiator concentration.

is the radius of gyration of the chain segments between crosslinks. Because $R_c \sim M_c^{1/2}$ and $\lambda \sim M_c^{1/2}$, it follows that $\delta \sim M_c$, and therefore, when $G_{IC} \sim \sigma \delta$, we expect $G_{IC} \sim M_c^{1/2}$. Thus, when M_c decreases for a single phase material, G_{IC} decreases. However, the characterization by DMA points to a dual phase structure. The rubbery flexural modulus is plotted in Figure 3 as a function of initiator concentration for both as-cured and postcured specimens. The measured rubbery modulus decreased with increase in initiator concentration for both as-cured and postcured specimens. This is contrary to what one would expect because the modulus would increase with increase in crosslink density, and the latter would increase with increase in initiator concentration. Knowledge on the cure kinetics and the structure of the cured vinyl ester is needed to understand the observed trend.

Ganem et al.,³ by studying the kinetics of curing of vinyl ester using FTIR, observed that beyond the gelation point, which is around 20-30%conversion, the styrene monomer homopolymerized into polystyrene instead of copolymerizing with vinyl ester prepolymer to yield crosslinked vinyl ester. A consequence of this would be the formation of a two-phase structure consisting of crosslinked vinyl ester and linear polystyrene. Initial exploratory studies using Atomic Force Microscope (AFM) indeed point to such a dual phase structure. The specimen cured with 1.5 wt % initiator exhibited crosslinked vinyl ester microgel regions of diameter 50–150 nm surrounded by apparently linear polystyrene.

It is suggested that with an increase in the initiator concentration, due to the increased homopolymerization of styrene, the volume fraction of linear polystyrene in the two-phase structure increases. Because the crosslinked vinyl ester has a much



Figure 4 T_g as a function of initiator concentration.

higher modulus than the linear polystyrene, the decrease in rubbery modulus with an increase in the initiator concentration tends to corroborate the above suggestion. This is also borne out by the behavior of T_g , which decreases with increase in initiator concentration and approaches that of linear polystyrene, as shown in Figure 4. In view of this finding, the trend observed in Figure 2 is thought to be due to the influence of both crosslinked vinylester and linear polystyrene. The influence of such a microstructure on the strength of various interfaces is further explored, and the results are presented and discussed below. The increase in modulus and T_g beyond 4.0 wt % initiator is a true effect because such a trend has been observed in other results presented in subsequent figures. The reason for such a trend is unknown at this time, but is most likely due to the composition of the dualphase structure.

Liquid–Solid Virgin Interface (L–S_V)

 $G_{\rm IC}$ for the virgin specimen (L–L) and for specimens with L–S $_{\rm V1}$ and L–S $_{\rm F1}$ interfaces, represent-



Figure 5 G_{IC} for various interfaces.

ing joining, and repair and recycling, respectively, are plotted in Figure 5. All specimens were cured with 1.5 wt % initiator. Surprisingly, the virgin material toughness of 488 Jm^{-2} was reduced to 31 and 43% of its value after joining and repair and recycling, respectively. This degradation in toughness suggests that good molecular connectivity across the liquid-solid interfaces have not been achieved. It would be expected that the liquid monomers, when reacted with a crosslinked network of the same monomers, would regain the original structure and strength. However, this is not the case, and it is believed that the tight crosslinked structure ($M_C~\sim~700)$ prevents sufficient chain extension during free radical polymerization to give the desired connectivity across the interface. By analogy with linear polymers, for example, polystyrene, each chain at a welded interface needs to cross the interface back and forth from side-A to side-B, on average, about 16 times to maximize the fracture energy.

To realize good molecular connectivity and thus good interfacial bonding, the different constituents of the liquid vinyl ester mixture, poured on the solid, should diffuse into the solid, and cure *in situ* by forming chemical bonds with sites in the solid surface. The factors that can influence this are as follows: (1) interphase formed at the solid surface due to the interactions with the mold surface, (2) wettability of the solid surface, (3) crosslink density of the solid surface, and (4) gel time.

Results of the exploratory study performed to understand the influence of the above four factors are presented and discussed in the following paragraphs.

Influence of Interphase

When a solid is molded, it is possible that preferential adsorption and segregation of some chemical groups of the constituents of the liquid mixture occur near the mold surface. This, in turn, can influence the cure reaction, causing a gradient in the chemical composition of the cured solid near the surface. Such an interphase (a) can affect the wettability of the solid, and (b) if weak, can provide an easy path for crack propagation resulting in poor toughness. The existence of such an interphase was reported in vinyl ester by Dirand et al.⁴ They observed a gradient in the cure percentage, which increased from about 68% at the surface to a bulk composition of 84% over a depth of 300 μ m. This interphase was noticed

Table II Influence of Wettability

% Initiator in Solid	G _{IC} (Jm ⁻²) (Kapton with Release Coating)	$\begin{array}{c} G_{\rm IC}~(Jm^{-2}) \\ (Kapton \ without \\ Release \ Coating) \end{array}$
3	130	209
4	100	122
5	162	237

irrespective of the mold material. The same magnitude of G_{IC} , given in Figure 5, for L-S_{V1} specimens (where the solid surface was formed by molding against a Kapton film with silicone release coating) and for $L-S_{V2}$ specimens (where the solid surface was formed by molding against a steel surface) corroborates the above observation that the nature of the interphase is independent of the mold surface material. In specimens with liquid-solid fractured $(L-S_F)$ interfaces, this interphase layer was removed by grinding. However, the G_{IC} values for these specimens were still 43% of the virgin strength, and this suggests that the interphase is not a major factor influencing the ability of thermoset vinyl ester and its composites to be bonded, repaired, and recycled.

Influence of Wettability

Because the interphase can influence the wettability of the solid surface, which is a prerequisite for subsequent diffusion and bond formation, the wettability of the solid surface was varied by molding the solid against a Kapton film, with and without silicone release coating. The former had a contact angle of about 80° with water, confirming poor wettability, while the latter had a much smaller contact angle, suggesting a better wettability. The G_{IC} values for specimens with $L-S_{V1}$ interfaces formed by these two solid surfaces are tabulated in Table II. Higher G_{IC} values for specimens with the surface molded against a Kapton film without the release coating suggests that wettability does influence the G_{IC}. However, these values are still lower than the virgin strength, suggesting that wettability is not a major factor influencing the ability of thermoset vinyl ester and its composites to be bonded, repaired, and recycled. This also corroborates the results discussed in the previous paragraph.

Influence of Crosslink Density/Network Structure

Processing conditions such as poor mixing, nonuniform flow, and curing can cause a gradient in



Figure 6 Influence of crosslink density/network structure.

the crosslink density in the cured polymer composite. Hence, the influence of crosslink density/ network structure on interfacial bonding was studied by varying the initiator concentration [I] in the solid while maintaining that in the liquid constant. The results of the test are plotted in Figure 6. We see that within experimental error that G_{IC} is essentially independent of [I]. A moderate decrease with increasing [I] could be expected because the resulting increase in crosslink density would reduce the diffusion of reacting constituents of the liquid mixture into the solid and impede bond formation. However, the important point in Figure 6 is that the fracture energy of the L-S_V interfaces remains a smaller fraction of the virgin strength, which is unexpected from a manufacturing perspective.

Influence of Gel Time

Because the gel time defines the process/fabrication time, the influence of gel time was investigated by varying the initiator concentration in the liquid while maintaining that in the solid constant at 1.5 wt %. The gel time varied from 9 h at 0.5 wt % initiator to 1.5 h at 5.0 wt % initiator. The results of this test are plotted in Figure 7. G_{IC} remains fairly constant with an increase in the initiator concentration up to 4.0 wt %. A decrease in gel time would mean less diffusion into the solid, leading to poor bonding. However, because the gel time can also influence homopolymerization, the results are thought to emphasize more the importance of network structure rather than gel time.

Liquid–Fractured Solid Interface (L–S_F)

During grinding (e.g., encountered in recycling) of thermosets, the bonds would be broken and the



network structure would be damaged. To investigate the influence of this factor on interfacial bonding, the initiator concentration in the solid with the fractured surface was varied while maintaining that in the liquid constant. The results are plotted in Figure 8. Though the scatter in the data is appreciable, it is observed that the average G_{IC} values (and the error band) for 0.5 and 5 wt % specimens are farther apart, suggesting that the average G_{IC} increases marginally with increasing [I]. If we compare the G_{IC} values in Figure 8 with those for the as-cast surface, plotted in Figure 6, it can be observed that the relative increase in G_{IC} due to the network damage increases from 19% at 0.5 wt % initiator to a maximum of 96% at 4.0 wt % initiator, and then decreases to 66.7% at 5 wt % initiator. These data support the above observation that the average G_{IC} increases with increase in initiator concentration. The availability of broken bond sites as well as enhanced diffusion of liquid constituents due to a damaged network structure may be causing an increase in G_{IC}.



Figure 8 Influence of network structure damage causing by grinding.



Figure 9 Influence of network structure damage caused by applied load.

The above experiment was repeated with fresh fracture surfaces obtained by fracturing the virgin specimens. The results for the $L-S_{F2}$ interface are plotted in Figure 9, along with the virgin values. Though more specimens need to be tested to obtain a better statistical average, a comparison of this result with that plotted in Figure 8 indicates that a freshly fractured surface yields a stronger interface than a ground surface. It is possible that grinding damages a surface much more than fracture under a load.

The above results can be summarized as follows. The crosslink density/network structure has a major influence on the G_{IC} . Although low crosslink density enhances the ability of crosslinked vinyl ester to be bonded, higher crosslink density favors its ability to be repaired and recycled. Hence, an optimum crosslink density needs to be ascertained. Grinding leads to relatively more damage of the surface than simple fracture under a load.

Liquid–Chemically Treated Fractured Solid Interface (L–S_{FC})

Influence of Surface Treatment

Among the four factors studied, the network structure at the solid surface exhibited the major influence. Hence, attempts were made to modify the network structure. In the *in situ* polymerization treatment, it was expected that one end of styrene monomer would chemically bond to sites in the solid surface while the other end would react with styrene monomer/vinyl ester prepolymer in the liquid mixture. In the second treatment, viz. solution casting of polystyrene film, it was expected that the one end of polystyrene would mechanically interlock with the network structure of the solid surface while the other end would react with styrene monomer/vinyl ester prepolymer in the liquid mixture.

The results for the both the treatments (L– S_{F1C1} and L– S_{F1C2} , respectively) are plotted in Figure 10 along with the values for the virgin sample (L–L) as well as specimen with fractured but untreated surface (L– S_{F1}). Both treatments caused a moderate increase in G_{IC} . The G_{IC} values decreased with increase in molecular weight of polystyrene used in the solution cast treatment. This is to be expected, because higher molecular weight hinders diffusion into the network and subsequent bridging.

For pure polystyrene, G_{IC} attains a maximum value near $M^* \sim 200$ K and decreases rapidly with decreasing molecular weight $M < M^*$. When $M \ge M^*$, as for the 596 K and 4340 K samples, interdiffusion to the crosslinked side becomes increasingly difficult because the diffusion coefficient $D \sim M^{-2}$. Furthermore, the chemical energy U to swell a network with a solvent or diluent of molecular weight M is derived from the Flory relation as,

$$U = kTfM/M_c \tag{2}$$

where f is the dilation and M_c is the molecular weight between entanglements. Thus, when $M > M_c$, the chemical potential for ingress of a high molecular weight material is highly unfavorable. Swelling with monomer is favorable up to small dilations, but reacting polymer chains treading back and forth across the interface will meet with resistance when $M_c \sim 700$ (obtained for vinylester networks).

The *in situ* polymerization treatment resulted in highest G_{IC} value of 320 Jm⁻² that is still less



Figure 10 Influence of surface treatment.

Interface	$G_{IC} \; (Jm^{-2})$	G _{IC} (Jm ⁻²) Virgin Value
S _F –S _F (Crack Healing)	8.4	488
S _{V1} –S _{V1} (Welding)	66	(+110)
S_{V2} - S_{V2}	107	(-80)
(Joining/Bonding)	(+15) (-16)	

Table III Results on Welding, Crack Healing, and Joining of Vinyl Ester

than the virgin G_{IC} value by 34.5%. The molecular weight of polystyrene formed *in situ* is unknown. However, the trend in Figure 10 suggests that it should be less than 200 K. Further work is currently under way to determine the optimum treatment to restore the original toughness after repair and recycling.

Welding Virgin Interfaces (S_{V1}–S_{V1})

Investigation on the welding of solid–solid interfaces was performed using specimens cured with 1.5 and 4.0 wt % initiator concentration. The result is tabulated in Table III. The $G_{\rm IC}$ value of 66 ${\rm Jm}^{-2}$ is 13.5% of the virgin value, and this suggests that complete molecular connectivity has not been established during welding. The 4.0 wt % specimens failed to weld at all the three annealing temperatures, which were 10°, 20°, and 30° above T_g (100°C). Further investigation is currently underway.

Crack Healing Interfaces (S_{F2}-S_{F2})

Crack healing in vinyl ester was investigated using specimens with 1.5 and 4.0 wt % initiator concentration. The G_{IC} value after crack healing for 1.5 wt % specimen, as tabulated in Table III, is 8.4 Jm⁻². This value is 1.7% of the virgin value and is much less than the value obtained for welding. Similar to the case of welding, the 4.0 wt % specimens did not crack heal. The welding and crack healing experiments suggest that the lower crosslink density favors repair by welding and crack healing.

Adhesively Bonded Interface (S_{V2}–S_{V2})

Investigation of joining/bonding of vinylester composites was investigated using the 1.5 wt % specimens. The CT specimen halves with the ascast surface were coated with Super glue gel, were pressed against each other gently using a C-clamp, and were allowed to cure. The G_{IC} value obtained for this specimen, as tabulated in Table III, is 107 Jm⁻², which is 22% of the virgin value.

S_{F2}–S_{F2C} Interfaces

The ability of the thermoset polymer and its composite to be repaired using adhesives was explored using specimens with 1.5 and 4.0 wt %initiator concentrations. The results of this experiment are tabulated in Table IV, and they indicate that the ability to be repaired using adhesives is poor.

Finally, the scatter in all the results reported here seem to be large. In addition to the inherent statistical variation in the fracture mechanics experiments, the authors believe that specimen preparation and molding operations contributed to a large extent. The silicone mold, used for molding operations, was increasingly distorted with the number of molding operations. Typically, molds were changed after 10–15 molding operations. Moreover, due to the bonding of the vinyl ester polymer to the mold surface, subsequent cleaning steps led to loss of smoothness of the mold as well as molded specimen surfaces. The above factors are thought to have led to loss of parallelism among the edges of the specimen and the interface during machining steps. A consequence of this is that the crack tip might not have been in a plane perpendicular to the loading axis to ensure mode I loading, leading to scatter in the data. This inference is supported by the correlation between the increase in scatter and the molding sequence. For example $L-S_{V2}$ specimens, in Figure 5, were molded after $L-S_{V1}$ specimens (the number of specimens tested in both cases were same). The scatter for the former is much more than for the latter.

Table IV	Results on	Repair of	Vinyl Ester
----------	-------------------	------------------	-------------

%	Sample	$\begin{array}{c} G_{IC} \left(Jm^{-2} \right) \\ Virgin \ Value \end{array}$	G _{IC} (Jm ⁻²)
Initiator	Number		After Repair
1.5 4	$ \begin{array}{c} 1 \\ 2 \\ 3 \\ 1 \\ 2 \\ 3 \end{array} $	504 238 498 271 656 620	$77 \\ 223 \\ 114 \\ 195 \\ 142 \\ 263$

CONCLUSIONS

The strength of thermoset vinyl ester and its composite degrades after repair, recycling, and joining. When compared to various factors such as interphase, wettability, and gel time, crosslink density/network structure has the most influence on the toughness of the repaired vinyl ester and its composite. Chemical treatments such as *in situ* polymerization and solution casting of polystyrene caused a moderate increase in toughness. Thermoset vinyl ester exhibited poor welding, repair, and crack healing capability.

The authors would like to thank the University of Delaware and the State of Delaware for providing financial assistance for this research. R.P.W. acknowledges support from the National Science Foundation, Grant DMR 9696267, and the Composite Materials Research program conducted in collaboration with the Army Materials Research Laboratory in Aberdeen, Maryland.

REFERENCES

- Wool, R. P. Polymer Interfaces; Hanser/Gardner Publications Inc.: New York, 1995.
- Suzuki, S.; Sakoh, M.; Shiba, A. J. Biomed Mater Res 1990, 24, 1091.
- Dirand, X.; Hilaire, B.; Lafontaine, E.; Mortaigne, B.; Nardin, M. Composites 1994, 25, 645.
- Ganem, M.; Mortaigne, B.; Bellinger, V.; Verdu, J. J. Mol Sci Pure Appl Chem 1993, A30, 829.