Fracture Characteristics of Vinylester Resin under Impact Fatigue

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ABSTRACT: The impact fatigue behavior of a vinylester resin was studied with a pendulum-type repeated-impact tester especially designed and fabricated for the determination of single-impact and repeated-impact strengths. A well-defined energy–endurance impact fatigue curve was obtained with a progressive endurance at values of the impact energy below the critical value, with the endurance limit set at an energy level of 31 N mm, 17.4% of the single-impact energy. The nature of the crack propagation was investigated for a single impact as well as high, medium, and low impact energy levels with progressively longer endurance. The fracture characteristics varied with the impact energy imparted and the number of cycles endured. The rate of lip growth was high at the higher impact energy levels with a lower number of endurance cycles and low at the lower impact energy levels with longer endurance; the repeated impacts created large and small compressive zones through the bending of specimens with the development of long and short lips, respectively. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1995–2001, 2002

Key words: resins; fatigue analysis; fracture

INTRODUCTION

Fiber-reinforced composites using thermosetting resins as matrix materials are very common in many applications. For their effective use, the resin matrix plays a dominant role in the cohesive binding of the reinforcing fibers and load transfer characteristics. As such, the fracture behavior of the resin component under load, with either single or repetitive fatigue conditions, particularly impact fatigue, has remained open for further investigation. Hertzberg et al.[1] performed a series of tensile fatigue tests on some thermoplastic polymers such as nylon-66, low-density polyethylene, acrylonitrile–butadiene–styrene resin, polycarbonate, and poly(methyl methacrylate) and also on a thermosetting epoxy resin. They observed a strong correlation between the fatigue crack propagation (FCP) rate and the stress intensity factor range prevailing at the advancing crack tip. They concluded that the improved resistance to crack propagation required a substantial internal energy dissipation mechanism, which could have arisen from secondary transitions or flow due to the mobility of the chain segments in the thermoplastic polymers. However, the thermosetting epoxy resin was found to be extremely brittle, with catastrophic failure being predominant. The fatigue crack growth characteristics under tension were studied for polystyrene[2] and polyacetal,[3] and crystalline polymers were found to be more fatigue-resistant than amorphous polymers.

There have been a few reported studies on the impact fatigue response of polymers. Bhateja et al.[4] studied the response of an ultrahigh molecular weight linear polyethylene under a low cycle (<20), repeated the impacting of notched samples under three-point bending. Ohishi et al.[5] studied unnotched polycarbonate under a repeated drop weight with a three-point bending apparatus and produced a curve of the applied stress versus the number of cycles to failure. Sacher et al.[6] examined the effect of repeated impacts on polymer surfaces in terms of heat generation and mechanochemical reactions. Studman and Field[7] investigated surface damage due to low-velocity, angled impacts on poly(methyl methacrylate). Takemori[8] studied the biaxial impact fatigue response of polycarbonate. He designed an instrument in which a thin, platelike sample was rigidly held by a plunger, and cracks were found to initiate at the bottom surface, where high biaxial stresses were present. The cracks propagated along the radial lines and also normal to the surface. He observed that the load-bearing capacity and the residual impact strength decreased as the cracks propagated. Two distinct regions of crack development were identified, one central region surrounded by another annular region. He showed that in the annular region the tangential stress exceeded

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the radial stress, so the radial cracks were preferred to tangential cracks. In uniaxial tensile fatigue tests[9] and four-point bending fatigue tests of polycarbonate,[10] the fatigue cracks initiated from the surface crazes, which were oriented normal to the tensile loading direction. The crazes grew in length along the free surface and in depth into the sample in a semielliptical shape. The surface growth was terminated by the formation of a pair of shear bands at each end of the craze opening. At the higher applied loads, the free surface craze length was shorter than at the low applied loads. However, the examination of fractured surfaces for the determination of failure modes under fatigue conditions has been somewhat neglected.

Although thermosetting resins are most commonly used as matrix materials in polymer composites, the study of their fatigue behavior has been very limited. An attempt has, therefore, been made to investigate the impact fatigue behavior of vinylester resin. The fatigue data are presented in the form of the impact energy versus the number of cycles to failure. The nature of failure under single and repeated impacts was investigated. The initiation and propagation of cracks at different impact stress levels were observed macroscopically, and the crack zones were examined under a scanning electron microscope. A comparative study was also made between the flexurally fractured and impact-fractured surfaces.

EXPERIMENTAL

Materials

Vinylester resin (grade HPR 8711, Bakelite Hylam) was used. Methyl ethyl ketone peroxide, conapthenate, and *N,N*-dimethyl aniline were used as the catalyst, accelerator, and promoter, respectively.

Sample fabrication

The resins were mixed with the accelerator, promoter, and catalyst (1% each) and poured into hollow cylindrical glass tubes with internal diameters of 6 mm. They were allowed to cure at room temperature for 24 h and were postcured in an oven at 80°C for 4 h. The glass tubes were broken and cleaned to release the resin rods. Each rod was cut to a 120-mm length for flexural testing and to a 60-mm length for repeated-impact studies.

Test methods

Flexural testing

Three-point bending tests were performed in an Instron 4303 machine (U.K.) in agreement with ASTM Standard D 790M-81 to measure the flexural strength of the vinylester resin rods. A span of 100 mm was employed with a crosshead speed of 2 mm/min.

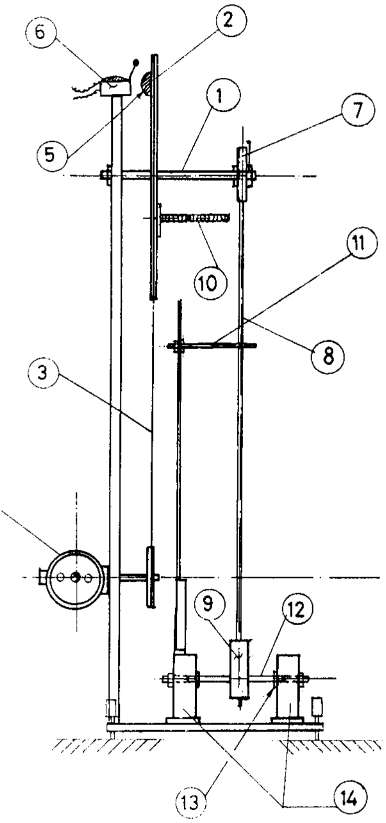

Figure 1 Side view of the repeated-impact tester: (1) horizontal shaft, (2) circular disc, (3) geared pulley, (4) motor, (5) trigger, (6) limit switch, (7) bearing support, (8) pendulum arm, (9) hammer, (10) spring-loaded pickup arm, (11) release trigger, (12) specimen, (13) conical grip, and (14) specimen support platform.

The flexural strength and flexural modulus were measured with the following equations:

$$\text{Flexural strength} = 8 \,.\, F \,.\, L \,/\, \pi.d^3$$

$$\text{Flexural modulus} = 4 \,.\, m \,.\, L^3/3 \,.\pi.\, d^4$$

where F is the load, L is the span, d is the diameter of the specimen, and m is the slope of the initial straight-line portion of the load–displacement curve.

Impact fatigue testing

A swinging pendulum-type repeated-impact tester described earlier[11,12] was designed and fabricated essentially on the principles of the Charpy impact tester (Fig. 1). It consisted of a rotating circular disc attached to a horizontal shaft at one end. The circular disc was rotated by a geared pulley system attached to a motor. A pendulum-type hammer arm was mounted on the ball bearings at the other end of the horizontal shaft, to

TABLE I
Mechanical Properties of Vinylester Resin

Modulus (GPa)		Flexural strength (MPa)		Breaking energy (J)		Toughness (kJ/m^2)	
Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
2.915	0.10	120.7	11.18	0.8227	0.33	34.0	13.63

the lower end of which a cylindrical hammer was attached. A trigger-type mechanism was fixed to one side of the circular disc, which touched the limit switch once during each revolution, thereby registering the number of impacts. A spring-loaded pickup arm attached to the circular disc carried back the pendulum arm to a predetermined angle during the rotation. Upon contact with the release trigger set at a predetermined angle, it retracted, allowing the pendulum hammer arm to fall, making an impact on the specimen held horizontally between two tapered conical cups that were screw-mounted to the two adjacent platforms. After each impact, the freely hanging hammer was picked up and released again until the specimen fractured.

Electrical continuity across the sample was maintained by a fine metal wire connected to the screw mounts of the tapered grips. On specimen fracture, the circuit was deactivated; this stopped the machine. A magnetic damping device prevented the hammer from making multiple contacts after each impact during each revolution, but it could be deactivated during single-impact studies.

The frequency of impacts during fatigue testing was set at six impacts per minute.

For repeated-impact tests, a pendulum length of 28.3 cm and a hammer weight of 227.75 gm were used. The impact energy was calculated with the following formula:

$$E = mgh\,(1 - \cos\theta),$$

where m is the mass of the hammer, g is the gravitational constant, h is the length of the pendulum, and θ is the angle of the hammer release.

Energy losses due to windage, friction, and toss were determined with a broken specimen placed between the grips. The hammer was released from various angles between 70 and 10°, and the final swing angle was noted. From the difference between the two angles (the initial angle of release and the final angle of swing), the energy loss was calculated. The impact energy imparted to the specimen was obtained after subtraction of the energy losses.

The single-blow impact energy was determined by the impacting of the specimen from a high angle, with the angle decreasing at intervals of 5° to an angle at which the sample endured a single impact without failure. The angle just above this was taken as the single-impact value. The angle of swing was then progressively reduced at intervals of 5°, and the number of impacts was recorded until the material failed. The fatigue testing was carried out for at least five specimens at each stress level. Tests were terminated beyond 10^4 impacts.

RESULTS AND DISCUSSION

The flexural strength properties of the vinylester resin are shown in Table I. A typical load–displacement curve is shown in Figure 2. A 19% strain was observed at fracture. A true linear relationship between the load and displacement was not found. However, after a load of about 0.065 kN, a large displacement occurred for a small increase in the load, which is indicative of sufficient flexibility of the material.

The samples broke at a single-impact energy of 177 N mm. With the progressive reduction of the impact energy, the samples sustained a larger number of impacts, with an endurance limit at 31 N mm. The fa-

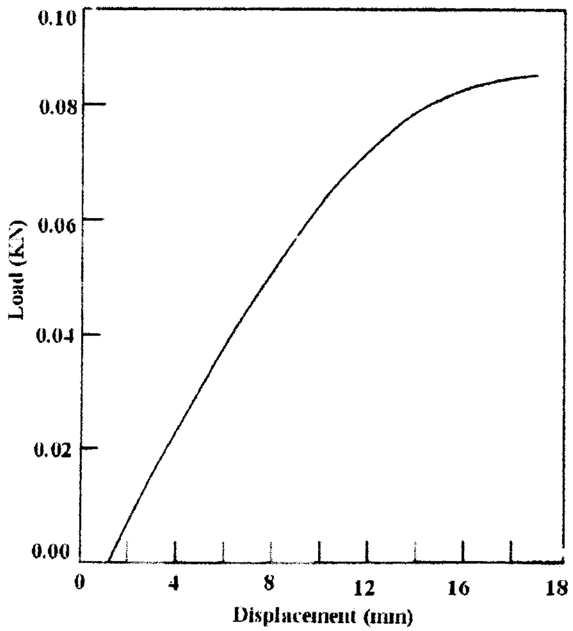

Figure 2 Load–displacement curve of the vinylester resin under the three-point bending test.

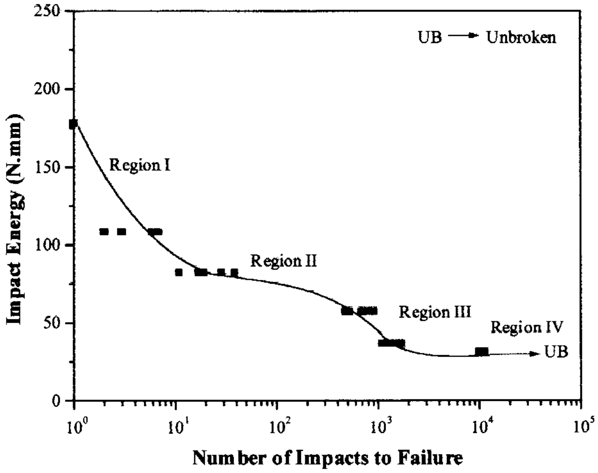

Figure 3 Impact fatigue (energy–endurance) curve of the vinylester resin.

tigue behavior is depicted as the impact energy versus the endurance in Figure 3. Four regions were demonstrated. Region I had a steep slope, and the samples endured about 7 cycles only for a large drop in the impact energy from 177 to 108 N mm. Region II had a much shallower slope, and there was a progressive increase in endurance from 7 to 904 cycles for a drop in the applied impact energy from 108 to 57 N mm. In region III, there was a small increase in endurance from 904 to 1709 cycles with a decrease in the impact energy from 57 to 36 N mm. An endurance limit, shown by region IV, was reached at 31 N mm. The endurance limit was 17.4% of the single-impact energy.

Fracture characteristics

The samples were not devoid of microcracks and macrocracks, but few of these ran vertically. The stress mode produced in the sample during impact loading is shown in Figure 4. As for a flexural test, the outer surface, because of bending, had to sustain a tensile force, whereas the inner surface region had a compressive force acting inward. Therefore, the rod sample experienced two opposite forces distributed within the body of the sample.

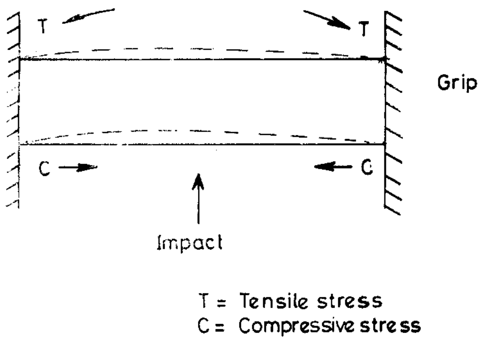

Figure 4 Stress mode developed in the sample with impact loading.

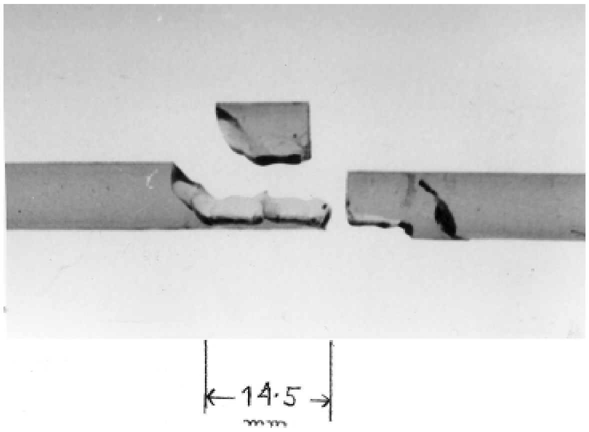

Figure 5 Single-impact fracture of the vinylester resin (impact energy = 177.35 N·mm, endurance = 1 cycle).

With a single impact, the majority of the samples broke into three pieces, with double-lip formation on the compressive side, as shown in Figure 5. The crack appeared to have started from a flaw on the tensile side and propagated vertically down through the tensile zone to the boundary of the compressive stress zone. The crack path changed its course at the boundary of the compressive zone and ran tangentially upward, forming a lip and generating a chip and a large new surface. The lip length was nearly 14–15 mm. From the lip thickness, a compressive zone in the sample of nearly 2 mm, that is, one-third of the sample diameter, was measured. A small ridge was also observed where a crack existed, blunting the crack propagation momentarily.

The nature of the failure under repeated impacts at a high stress level (82 N mm) with 11 impact cycles is shown in Figure 6. The fracture mode was similar here

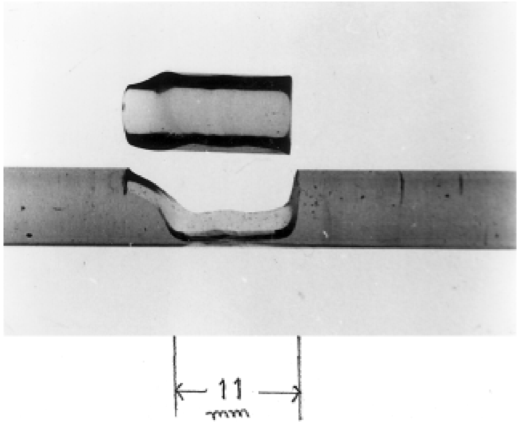

Figure 6 Repeated-impact fracture of the vinylester resin at a high impact energy level (impact energy = 81.95 N·mm, endurance = 11 cycles).

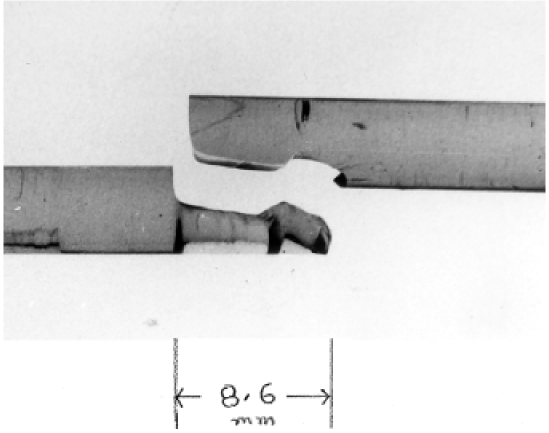

Figure 7 Repeated-impact fracture of the vinylester resin at a medium impact energy level (impact energy = 56.91 N·mm, endurance = 703 cycles).

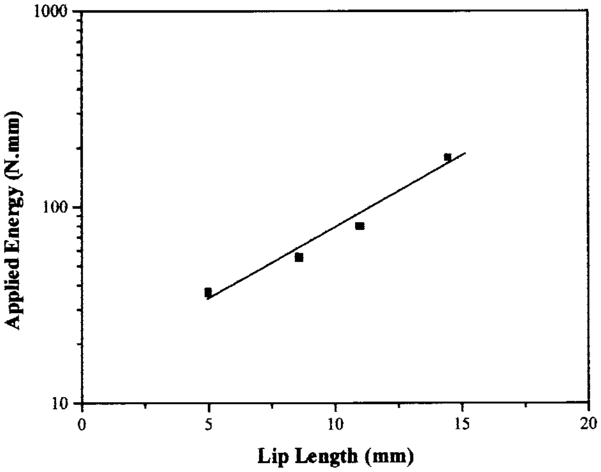

Figure 9 Variation of the lip length with the applied impact energy.

as well when the compressive zone opposed the crack penetration and the crack returned back through the tensile zone separating the chip out. The specimen did not part into two halves. Fatigue striations were observed in this zone. At a medium stress level (57 N mm), with 703 cycles, the crack propagated vertically into the compressive zone, finally breaking the sample into two halves (Fig. 7). Vertical surface cracks were also visible. The lip length, however, was reduced to 8–9.2 mm. At a low stress level (36 N mm), with 1523 impacts, the crack propagated through the compressive zone (Fig. 8). Here the crack progressed vertically down and had a much shorter lip of 4.8–5.2 mm.

The variation of the lip length (L) with the different impact energy levels (E) is shown in Figure 9. A linear relationship was indicated, with the lip length becoming shorter with the progressive lowering of the applied impact energy with longer endurance. The ratio L/E remained almost constant with the increase in endurance, as shown in Figure 10, indicating that the number of endurance cycles had no effect on the L/E ratio. The lip formation and its length were more dependent on the impact energy applied. It became apparent that the depth of the compressive zone that formed affected the lip length. The greater the applied impact energy was, the greater the compressive zone formation was and, therefore, the larger the lip formation was. The condition was the opposite at a lower impact with a longer endurance.

Deriving information from studies of general fatigue crack growth against the stress intensity factor, we attempted to ascertain a relationship from the lip growth against the stress intensity factor Δk The rate of FCP in the form of a lip was plotted against Δk, as shown in Figure 11, Δk being calculated by the standard formula.[13] A two-way fatigue crack growth process appeared to be operative. At low impact energies, the rate of lip formation was much less with a low stress concentration, having long endurance, whereas

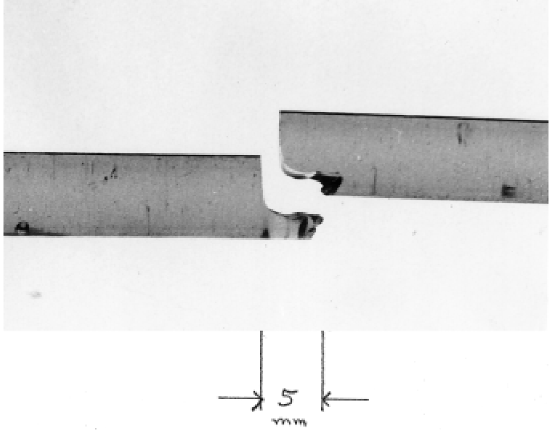

Figure 8 Repeated-impact fracture of the vinylester resin at a low impact energy level (impact energy = 36.23 N·mm, endurance = 1523 cycles).

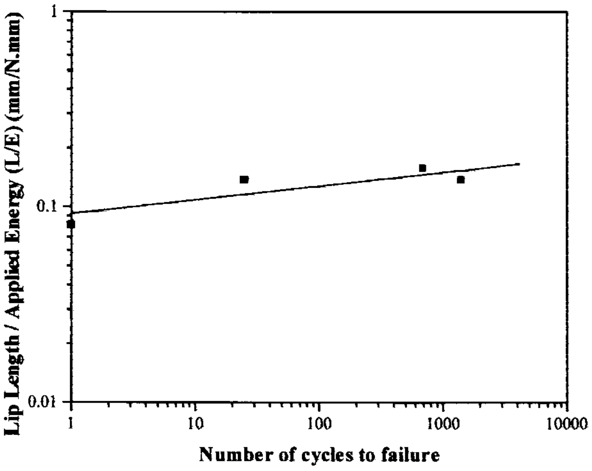

Figure 10 Variation of the L/E ratio with the number of endurance cycles.

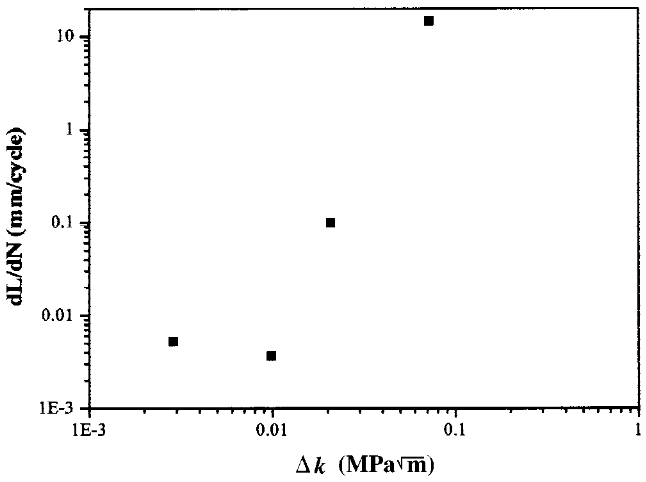

Figure 11 Effect of Δk on the lip growth rate (dL/dN) of the vinylester resin.

the rate of lip growth increased sharply at a high stress intensity zone with a lower number of endurance cycles, for which the repeated impacts could have created small and large compressive zones, respectively, under bending affecting the lip formation vis à vis the crack propagation. FCP in the form of a lip occurred within a Δk range of 0.0029–0.0715 MPa$\sqrt{}$m. This is in contrast to thermoplastic polymers such as poly(methyl methacrylate), polysulfone (PSF), polyphenylene oxide (PPO), and nylon, for which FCP was observed within a Δk range of 0.5–10 MPa$\sqrt{}$m.[1]

The flexurally fractured specimen revealed a typical brittle fracture, with its source (S) shown in Figure 12. It had two zones, one a smooth-surface (A), mode I type and the other a hackle-zone (C), mode II type with radial ridges, with a mixed zone between them.

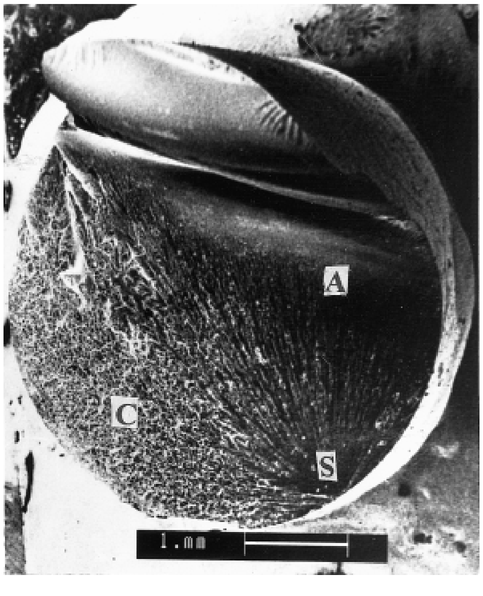

Figure 12 Flexurally fractured surface of the vinylester resin showing different crack zones.

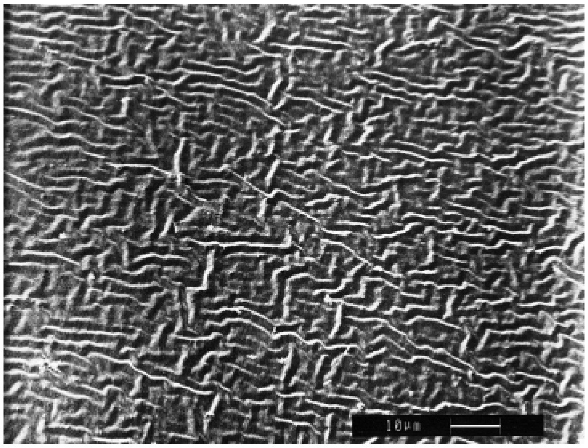

Figure 13 Matlike carpet structure of the mirror zone of the vinylester resin under the three-point bending test.

The transition from A to C was apparent. This was indicative of the tensile force being responsible in the beginning, until it reached the compressive zone into which the crack path deviated, for a small lip occurring.

In a close examination of a mirror fractured surface (A), a matlike carpet structure was revealed (Fig. 13), whereas a turbulent river pattern in a zone (C) occurred, as shown in Figure 14. The tangential fractured surfaces were examined and found to have ridgelike patterns with a wavy fractured zone at the junction of the compressive and tensile regions (Fig. 15). A region higher up showed a mixed pattern of smooth ridges with a heckled river pattern (Fig. 16) of a sandy sea beach indicative of the wavy manner in which the crack had propagated.

In the impact-fractured specimen, similar fracture zones were seen under scanning electron microscopy (SEM). There, however, the fatigue striations were more evident, being perpendicular to the direction of the crack propagation. Striations were more distinct

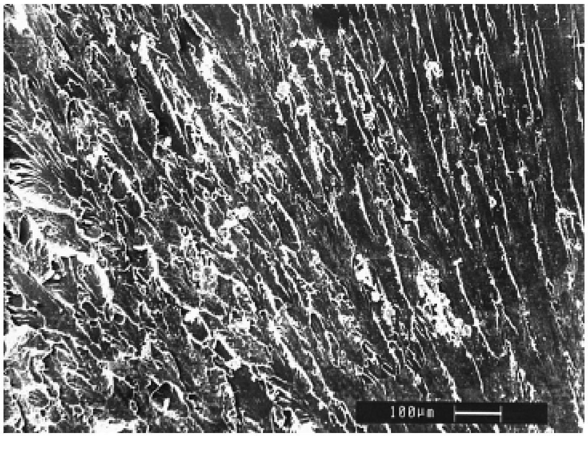

Figure 14 Turbulent river pattern in the hackle zone of the vinylester resin under the three-point bending test.

and prominent for low-stress, high-endurance fractures.

CONCLUSIONS

The susceptibility of vinylester resin to repeated impacts (fatigue) has been demonstrated for the first time. An energy–endurance characteristic curve was established with four regions. Region I had a steep slope with around 7 cycles for a drop in the impact energy from 177 to 108 N mm, whereas region II had a much shallower slope with a drop in the impact energy from 108 to 57 N mm with 904 impacts. In region III, the endurance increased up to 1709 cycles with the lowering of the impact energy from 57 to 36 N mm, and the endurance limit was reached at 31 N mm. The resin showed progressive endurance below the critical fracture energy with decreased applied impact energy, having an endurance limit at 17.4% of the single-impact energy. The fracture characteristics varied with different applied impact energy levels. At the higher impact energy levels with low endurance, the compressive zone created by the bending of the specimen played a dominant role, producing a long lip, whereas at the low impact energy levels with longer endurance, the compressive zone created was much weaker, allowing the crack to run through, easily producing a shorter lip. The flexurally fractured specimen showed a smooth mirror zone followed by a hackle zone containing radial ridges, with a mixed zone between them. The impact-fractured specimen also showed similar crack zones with fatigue striations perpendicular to the direction of the crack propagation. Striations were more prominent for low impact energy, longer endurance fracture.

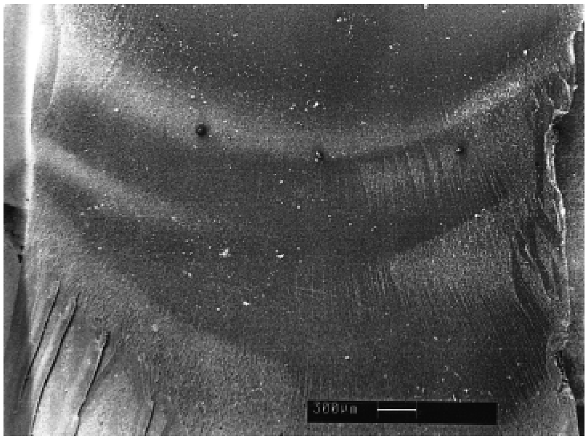

Figure 15 Wavy fractured zone at the junction of the tensile and compressive regions of the flexure-tested vinylester resin.

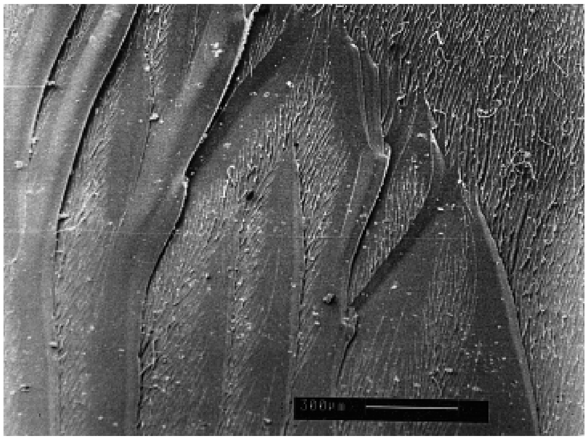

Figure 16 Mixed pattern of smooth ridges with a heckled river pattern of a sandy sea beach of the flexure-tested vinylester resin.

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