Properties of Rubber-Modified Cellulose-Fiber–Epoxy Laminates

Cellulose fibers are a potential source of cheap reinforcement for brittle materials. Already they are used commercially to improve the strength and fracture toughness of cements.[1,2] These materials also displayed a slow crack growth resistance curve. Cellulose fibers are also widely used in the strengthening and toughening of polymers. Cellulose-fiber-reinforced polymer composites (CPC) can replace metals in many applications. They offer superior corrosion resistance, lower costs, lighter weight, good fracture resistance, and better flexibility in part design. Two most widely used methods for fabricating CPC materials are: (a) impregnation of wood with liquid monomers,[3,4] and (b) compounding of polymer with cellulose fibers.[5,6] Improved physical mechanical properties have been achieved for these materials.

Recently, we successfully synthesized cellulose-fiber–epoxy laminates with improved mechanical and fracture properties.[7] In this note, we report the synthesis and properties of cellulose-fiber–epoxy laminates modified with carboxyl-terminated butadiene–nitrile (CTBN) rubber. Probable toughening mechanisms for these materials are discussed.

Hardwood aspen (*Pinus radiata*) in the form of bleached chemithermomechanical pulp (CTMP) was used as reinforcing fibers. Sheets of CTMP were made and cut into rectangular specimens of 2 mm (thick) × 50 mm (breadth) × 200 mm (length). A mixture of commercial epoxy resin and hardener (Kit 36) was used for impregnating the fiber boards. The mixture was obtained by mixing 1 part of the hardener in two parts of the resin. A liquid rubber based on CTBN (CTBN × 1300) was used as a toughening agent for the epoxy mixture.

Table I shows the compositions of the cellulose-fiber–epoxy laminates with or without the addition of CTBN rubber. The layers of fiber boards ranged from 1 to 5 while the amount of rubber varied from 5 to 20 parts per hundred by weight of resin (phr). Laminate sample of a particular composition was fabricated by an initial soaking of the fiber boards in a tray of resin mixture (with or without CTBN rubber), followed by casting of uniformly wetted boards into a greased mold made of natural rubber. All the samples were cured at the room temperature (27°C) for at least 24 h.

Rectangular bars of 60 × 10 mm were cut from the fully cured laminate samples for three-point bend tests[5] to evaluate the flexural strength (S), flexural modulus (E), and fracture toughness (K_{1c}). Notching of specimens for fracture toughness measurements was performed in the following manner. Machined slots were initially cut to approximately the required notch length and the last few millimeters were completed by tapping a liquid-nitrogen-cooled razor blade into the notch to give a sharp crack.

Three-point bend tests were performed with an Instron machine (Model 1196). A displacement rate of 0.5 mm/min was used for measuring E while a higher rate (1.0 mm/min) was used for measuring S and K_{1c}. At least three specimens of the same composition were used for each measurement. Fracture surfaces of tested samples were sputtered-coated with gold and examined using a Joel 35C scanning electron microscope.

The flexural and fracture properties of unmodified and rubber-modified cellulose-fiber–epoxy laminates are shown respectively in Table II and Figure 1. Several features are noteworthy. First, when compared to pure epoxy sample (ECF0), the addition of four layers of fiber board imparted a 45% increase in flexural strength and 100% increase in flexural modulus. However, the presence of rubber reduced the flexural properties by virtue of its much lower strength and modulus. Up to 40% in strength and 65% in modulus were reduced when the rubber was added. Second, up to threefold improvement in the fracture toughness of epoxy resin was achieved when four layers of fiber board was added.[7] A further 20% increase was obtained when a small amount of rubber (i.e., 5 phr) was added (Fig. 1). Addition of more rubber (> 5 phr) resulted in lowering of fracture resistance. These results are unexpected because CTBN had been successfully used to improve the fracture toughness of epoxy resins by at least twofold with the optimum rubber content of approximately 15 phr.[5,8–12] It is believed that the addition of rubber raised the viscosity of Kit 36 epoxy mixture and prevented the complete impregnation of cellulose-fiber laminars [Fig. 2(b)]. This can significantly reduce the extent of adhesion between the fibers

Table I Formulations of Cellulose-Fiber–Epoxy Laminates

Sample	Matrix	CTBN Rubber (phr)	Fiber Board Layers
ECF0	Epoxy	0	0
ECF4	Epoxy	0	4
ERCF5	Epoxy	5	4
ERCF10	Epoxy	10	4
ERCF15	Epoxy	15	4
ERCF20	Epoxy	20	4

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Table II Flexural Properties of Unmodified and Rubber-Modified Cellulose-Fiber–Epoxy Laminates

Sample	Flexural Strength (MPa)	Flexural Modulus (GPa)
ECF0	60.0	0.85
ECF4	87.0	1.58
ERCF5	69.0	1.34
ERCF10	62.8	1.05
ERCF15	57.5	0.93
ERCF20	51.5	0.56

and epoxy, resulting in a weak laminate with poor fracture toughness. Finally, a pronounced rising crack-growth resistance (R) curve was observed for these laminates during compact-tension test[7] where the fracture initiated at 4.13 MPa $m^{1/2}$ and reached a plateau of approximately 8 MPa $m^{1/2}$. The origin of this phenomenon is believed to arise from the increasing development of a microcracked zone that provided desirable crack bridging in the wake of advancing crack tip.[12]

In summary, we have successfully utilized sheets of cellulose fibers in improving the mechanical and fracture properties of rubber-modified epoxy resin. The presence of fiber laminars has imparted considerable strength, stiffness, toughness, and crack-growth resistance. The failure micromechanisms near the crack tip are currently being studied using scanning electron microscopy and will be reported in the near future.

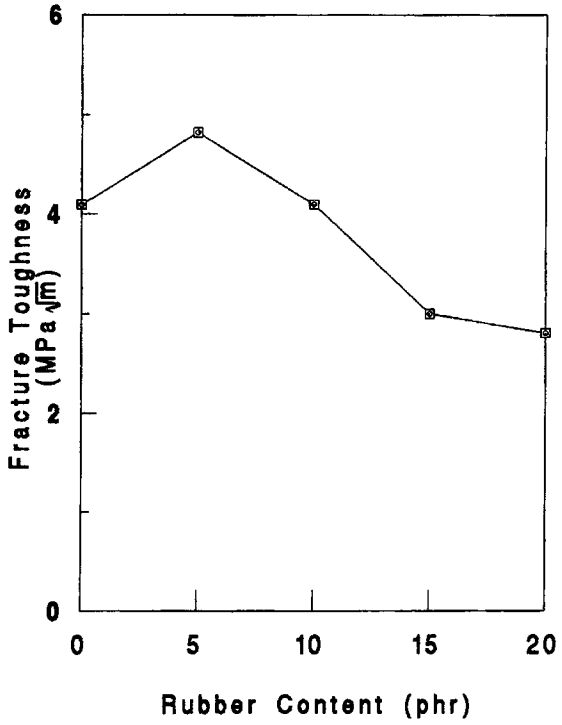

Figure 1 Variation of fracture toughness vs. rubber content for the rubber-modified cellulose-fiber–epoxy laminate system.

(a)

(b)

Figure 2 Scanning electron micrograph of the fracture surface of (a) sample ECF4 and (b) sample ERCF15. Note the evidence of poor wetting between epoxy and fiber board in the latter.

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