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Polymer matrix, polymer ribbon-reinforced transparent composite materials

D.J. O'Brien *, W.K. Chin, L.R. Long, E.D. Wetzel

U.S. Army Research Laboratory, Weapons and Materials Research Directorate Aberdeen Proving Ground, MD 21005, United States

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ABSTRACT

Composites of a polymer–matrix reinforced by polymer ribbon monofilaments are investigated as mechanically robust, transparent composite materials. Transparent nylon monofilaments are mechanically worked to form flattened nylon ribbons, which are then combined with index-matched epoxy resin to create transparent composites. A range of optical and mechanical experiments are performed on composites and surrogate systems in order to quantify properties and guide system design. The results show that these polymer–polymer composites provide good transparency over a wide temperature range, and superior ballistic penetration resistance compared to monolithic transparent polymers.

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1. Introduction

Continuous fiber-reinforced, polymer–matrix composite materials have emerged as mass-efficient protection materials for a range of ballistic and blast applications [1,2]. Compared to monolithic materials, composites provide a unique combination of high fracture toughness and low density [3]. This enhancement in properties is due in part to the use of high performance fibers, such as S-glass, carbon, and aramid [4,5]. Composites also offer energy-absorbing damage modes, such as delamination and fiber pullout, that are not available in monolithic materials. In addition, the mechanical properties of composites can be tailored to a given application through selection and control of reinforcement type, orientation, and volume fraction.

Transparent protection materials are required for specialized applications such as visors, windshields, and optical sensors. Conventional transparent armors are constructed of monolithic or layered plates containing transparent polymers, glasses, and ceramics [6]. A fiber-reinforced transparent composite could provide enhancements in mechanical properties and design flexibility relative to these conventional monolithic or laminated materials. Unfortunately, traditional composite materials are rarely transparent. Most conventional composite constituents, such as carbon fibers and aramid fibers, are highly absorptive or scattering over the visible spectrum and cannot be directly used to create transparent composites. Other materials, such as amorphous polymers and glass fibers, can be visually transparent but may have limited practical transparency due to the presence of voids or other impurities that can scatter or absorb light. Finally, even when two perfectly transparent materials are combined into a composite, if their spectral refractive indices are not identical then refraction, reflection, or scattering effects lead to a loss in visual clarity.

To create transparent composites, two general approaches have been taken. One technique is to reduce the reinforcement size below the critical scattering length, typically less than ca. 200 nm for visual transparency [7]. For example several authors have manufactured transparent composite materials by infiltrating monomers into nanoporous silica foams and polymerizing *in situ* [8–11]. Other researchers have shown that electrospun polymer fiber mats can be infiltrated with a polymer to obtain transparent materials [12–14] while Liu et al. [15] filled PMMA with cellulose nanocrystals and maintained transparency. While these approaches typically yield materials with high transparency, most do not have mechanical properties similar to high performance composites because the reinforcement is either discontinuous, of low volume fraction, and/or randomly oriented.

A second approach is to engineer the matrix and reinforcement phases to have matched refractive indices. This approach is attractive since common materials such as glass fibers and epoxy resins have similar refractive indices. Weaver et al. [16] pursued transparent continuous glass-PMMA composites while Iba et al. [17] developed transparent continuous glass–epoxy composites. A serious limitation of the index-matching approach arises from the temperature dependence of the refractive index, described by a material's thermo-optic coefficient, dn/dT, where n and T are refractive index and temperature, respectively. Since thermo-optic behavior is driven mostly by density, materials with higher

* Corresponding author. Tel.: +1 410 306 0843.
E-mail address: daniel.j.obrien58.civ@mail.mil (D.J. O'Brien).

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coefficients of thermal expansion tend to have greater thermo-optic coefficients. As a result, polymers typically have thermo-optic coefficients of approximately -1×10^{-4}/°C while glasses are near zero [18]. Since transparency requires constituent indices to be matched to approximately 1×10^{-3} [19], the polymer's dn/dT leads to a significant refractive index mismatch after a relatively minor (e.g. 10 °C) temperature change. As a result, composite transmissivity tends to be highly temperature-dependent, with high transparency only possible within a narrow window of temperature. Furthermore, this sensitivity tends to increase as volume fraction increases [20].

In order to reduce the requirements on index matching and increase the useful temperature window of index matched composites, researchers have used ribbon reinforcements [21–23], in which the reinforcement cross-sectional shape is prismatic (i.e. square or rectangular). Due to its flat surfaces, such reinforcement does not refract light like circular fibers, preserving optical properties as the light propagates through the medium. Nevertheless, ribbon reinforcement reduces, but does not eliminate, the temperature dependent transmission [22].

In addition to improved optical behavior, ribbon composites also have the potential to improve mechanical properties, via superior in-plane stiffness and potential for higher reinforcement volume fractions [24–27]. Interest in these materials appears to have diminished since the 1970s, possibly due to relatively low strength of glass ribbons. More recently, Larcombe et al. studied the ballistic properties of transparent, glass-ribbon epoxy composites and found mass-normalized ballistic efficiency similar to PC, while thickness-normalized behavior was measurably superior to PC [28]. Interestingly, the ribbon composite showed less ductility than a conventional fiber-reinforced epoxy of the same fiber volume fraction. Velez et al. [23] manufactured transparent glass-ribbon composites with strengths as high as 772 MPa. They also studied the impact behavior of the material via simulation and experiment, emphasizing bird impact for aircraft applications.

"Polymer–polymer" composites (also sometimes called "self-reinforced" composites), consisting of polymer fibers in a polymer matrix, have generated significant interest recently [29]. These materials offer many of the same advantages in terms of strength and toughness as conventional composites while also providing their own unique advantages including lower density [30], better matrix–fiber compatibility, and recyclability [31–33]. Polymer fibers also allow for a range of ductilities and stiffnesses, from compliant, lightly drawn fibers with very high elongation-to-failure to highly drawn, very stiff fibers that are relatively brittle. This tailorability could prove useful in design of protective materials.

A polymer–polymer composite offers a number of advantages for creating transparent protection. The use of polymers for both matrix and reinforcement increases the likelihood of matching both the nominal refractive indices and the thermo-optic coefficients of the constituents, enabling optical transparency over a much wider temperature scale compared to glass-reinforced polymer systems. In addition, while glass fibers require fine diameters to mitigate mechanical flaw sensitivity, tough polymer fibers can be made mechanically robust at large diameters. This size scaling provides advantages for optical transparency, since larger fibers result in fewer fiber–matrix interfaces, decreasing the likelihood of undesirable scattering or reflection effects.

Self-reinforced composites have been employed for making transparent materials by Rojanapitayakorn et al. [34]. In that work, composites were manufactured by consolidating polyethylene terephthalate fiber bundles to demonstrate the effect of processing on optical and mechanical properties. While the final material showed improved optical properties compared to the starting fiber bundles (which appeared white) the composite suffered from high crystallinity and could only be considered translucent. In other studies, transparent polymer–polymer composites have been proposed and demonstrated as scattering-type polarizing filters [35–37]. Conventional polarizers are manufactured by doping a polymer film with a dichroic dye, a technique that results in a significant absorbtion and a decrease in the intensity of the filtered light. A collection of aligned, birefringent fibers embedded in a matrix index matched to either the fiber's axial or transverse refractive index results in a material that preferentially scatters one of two orthogonal polarization modes. Totani et al. manufactured such filters with nylon and poly(ethylene) terephtalate fibers embedded in a polymer matrix [35,37]. While the composites appeared to display excellent transparency, they were relatively thin (~100 μm) and mechanical properties were not investigated.

In the present work we investigate the feasibility of transparent polymer–polymer ribbon composites for protective applications. Polymeric ribbon fibers are produced by mechanically deforming commercial, round nylon monofilament. These flattened fibers are embedded in an epoxy matrix to create an optically transparent composite that captures many of the unique advantages of both ribbon composites and polymer–polymer composites. In the sections that follow, the rationale for choosing the constitiuent materials is described first, followed by a description of the process for manufacturing the transparent ribbon composites. The characterization techniques and results are then presented, including refractive index matching of constituent phases; composite optical transmission measurements as a function of temperature; mechanical testing of as-received and flattened monofilament; and composite ballistic impact performance compared to monolithic PC and epoxy plates.

2. Experimental

2.1. Materials

In order to minimize optical scattering, both fibers and matrix should be optically isotropic and homogeneous. That is, they should either be amorphous or have crystallites smaller than visual interaction lengths, approximately 200 nm [7]. These properties are difficult to maintain in polymer fibers where the drawing process tends to promote crystallinity and birefringence. Furthermore, in order to achieve good optical and mechanical properties, the matrix material should easily wet the fibers prior to cure, bond well to the fibers, and develop robust mechanical properties after cure.

In this study transparent polymer–polymer composites were manufactured using commercial nylon monofilament intended for fishing line (Pro Line 4 lb, 200 μm Premium natural clear monofilament; Cabela's, Sidney, NE). This material was chosen since it is readily available; has good mechanical properties such as strength, modulus and strain to failure [38]; and has been engineered for optical transparency [39]. The "4 lb" designation refers to nominal rated loads in tension. In order to compare the difference in temperature-dependent transmission between glass- and polymer-filled composites, particulate composites were manufactured from PMMA (153 μm, BB01N, Bangs Laboratories, Inc., Fishers, IN) or A-glass (200 μm, prod. 1922, Potters Industries Malvern, PA) microspheres embedded in refractive index immersion fluids as described below.

A series of optical immersion fluids (Certified Refractive Index Fluids, Series A, Cargille Laboratories, Cedar Grove, NJ) with $n = 1.460–1.700$ incremented by $\Delta n = 0.004$ were used for estimating the refractive indices of the monofilament. Additionally for temperature-dependent transmission experiments, two immersion liquids (Code 5040, Cargille Laboratories, Cedar Grove, NJ) with refractive indices of $n = 1.4590$ and $n = 1.5700$ were used.