



Novel Transparent PMMA Composites for Optical Tagging

by Jian H. Yu, Alex J. Hsieh, and Gregory C. Rutledge

ARL-TR-5354

September 2010

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ARL-TR-5354

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Jian H. Yu and Alex J. Hsieh
Weapons and Materials Research Directorate, ARL

Gregory C. Rutledge
Massachusetts Institute of Technology, Dept. of Chemical Engineering,
Institute for Soldier Nanotechnologies, MIT, Cambridge, MA 02139

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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1. REPORT DATE (DD-MM-YYYY) September 2010		2. REPORT TYPE		3. DATES COVERED (From - To) 2008	
4. TITLE AND SUBTITLE Novel Transparent PMMA Composites for Optical Tagging				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Jian H. Yu, Alex J. Hsieh, and Gregory C. Rutledge				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory ATTN: RDRL-WMM-B Aberdeen Proving Ground, MD 21005-5069				8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-5354	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Institute for Soldier Nanotechnologies Massachusetts Institute of Technology NE47, 4 th floor Cambridge, MA 02139				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This report describes the success of a feasibility demonstration in making novel transparent poly(methyl methacrylate) PMMA composites with ultraviolet (UV)-dye-embedded electrospun fibers that have the ability to change color and transparency reversibly upon exposure to UV irradiation. A light scattering model for transparent fiber-modified polymer composites is used to guide the materials selection and fiber processing. The key to achieving optical clarity with reduced haze is to match closely the refractive indexes between the fiber and the matrix material, as well as to reduce the fiber diameter to well below the wavelength of visible light. In addition, the exploitation of dye-embedded electrospun fibers facilitates the design of desired fiber patterns, thus affording transparent PMMA composites with optical tagging capability.					
15. SUBJECT TERMS transparent PMMA composites; electrospun; electrospinning fibers; refractive index; UV-dye; optical tagging					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 18	19a. NAME OF RESPONSIBLE PERSON Jian H. Yu
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (401) 306-0968

Contents

List of Figures	iv
List of Tables	iv
Acknowledgments	v
1. Introduction	1
2. Material and Method	3
2.1 Electrospinning of PVB Fibers	3
2.2 In-situ Polymerization/Cast Processing	3
3. Results and Discussion	4
3.1 Design Approach for Transparent Fiber Composites	4
3.2 Optical Properties of PMMA PVB-fiber Composites	6
3.3 Transparent PMMA PVB-fiber Composites with Chromatic Functionality	7
4. Summary	8
5. References	9
Distribution List	10

List of Figures

Figure 1. Two composites with similar transmittance; the PMMA+PVB composite on the left has 3.5% haze, whereas the PMMA+PAN composite on the right has 20% haze.	2
Figure 2. An electrospun PVB mat, 4 in. ² (Insert: SEM micrograph displaying the uniform size distribution of electrospun fibers).	3
Figure 3. (a) PVB mat soaking in PMMA-MMA-AIBN solution; (b) PVB after 5 h of soaking and vacuum egression.	4
Figure 4. Transparent PMMA electrospun PVB-fiber composite.....	7
Figure 5. A transparent PMMA composite with patterned, dye-embedded PVB-fibers: (a) before UV excitation; (b) after UV excitation.....	7

List of Tables

Table 1. Calculated values of transmittance and haze for three composites with different embedded fiber radius and different refractive indexes.	6
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Acknowledgments

This research was supported by the U.S. Army through the Institute for Soldier Nanotechnologies, under Contract DAAD-19-02-D0002 with the U.S. Army Research Office. The content of this report does not necessary reflect the position of the Government, and no official endorsement should be inferred. We thank Dr. John J. LaScala of the U.S. Army Research Laboratory (ARL) for technical discussions.

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1. Introduction

The emerging threats caused by improvised explosive devices (IEDs) currently encountered in Iraqi and Afghanistan have drastically increased concerns about Soldier survivability. Additionally, Soldiers serving guard duty at check-points often become the frontlines of defense against impending attacks. Therefore, the ability to identify “Friend vs. Foe” of any approaching vehicles clearly, quickly, and from a distance, is invaluable to ensure a Soldier’s safety, as well as critical to providing protection of facilities at strategic locations. The current state-of-the-art uses externally applied coatings or markings onto vehicles that are not seen in the visible light spectrum, yet are detectable with the use of an ultraviolet (UV) or infrared (IR) interrogation device. The drawbacks of this coatings approach are such that coatings can wear off or wash off, and are susceptible to being counterfeited or tempered. This approach is also not very practical for use by special operation forces to mark any identified locations of insurgents’ or terrorists’ cells, or by Soldiers to identify the safeguard house to prevent “friendly fire” during combat.

A completely different way of addressing this technology gap is to design and exploit novel transparent polymer composites that contain internally embedded taggant materials, which preserve transparency while being capable of patterning for optical tagging. The idea for making a transparent fiber-modified polymer composite is not new (1, 2, 3). However, in case of making nanofiber composites, the technical challenge is in the difficulty of fabricating and dispersing the nanofibers in the matrix. Transparency of a material is influenced by both the extent of light transmittance and the percentage of haze. Transmittance is a measure of the percentage of the incident light transmitted, regardless of the scattered beam angle. Haze, on the other hand, is a measure of the percentage of the forward scattered light to total transmitted light. A material may have an excellent transmittance, but may or may not be low in haze percentage. Thus, a translucent material may look transparent if it is directly held against an image; yet its visibility is greatly changed if it is held slightly above the image. Figure 1 illustrates this effect. Furthermore, the scattering of light in polymer fiber composites is greatly influenced by the compounding effects from the diameter of fibers, and the difference in refractive index between matrix and fiber. For example, poly(methyl methacrylate) (PMMA) and polyacrylonitrile (PAN) have a small difference between their refractive indexes (1.49 and 1.52, respectively) that would produce significant haze.

In this work, the approach for making optically-clear, fiber-modified polymer composites is based on the match of refractive index of selected fiber and matrix polymers. PMMA has been used widely in many transparent materials applications and is the matrix polymer of choice in this feasibility study. Poly(vinyl butyral) (PVB) has an attractive combination of chemical, mechanical, and optical properties, and it has been used in a wide array of commercial

applications, such as structural adhesives for glass laminates, coatings, and matrix polymer for fiber-reinforced thermoset composites. In particular, PVB has the same refractive index as PMMA, and is, therefore, selected for the production of electrospun fibers. PVB, however, has extremely high melt viscosity and is generally not melt spun into fibers. In most applications, PVB is either mixed into a resin or coated onto a laminate.



Figure 1. Two composites with similar transmittance; the PMMA+PVB composite on the left has 3.5% haze, whereas the PMMA+PAN composite on the right has 20% haze.

NOTE: Top picture shows the composites held directly against the background image; bottom picture shows the composites held at one centimeter above the image.

Electrospinning offers a simple and robust method to produce submicron PVB fibers. In addition, electrospinning has the following advantages: (1) electrospinning can produce very fine fibers (average diameter ranging from 100 nm to 500 nm) that can minimize the scattering of light if there is a slight mismatch in the refractive indices; (2) it can produce a fibrous mat that has a large surface area to mass ratio for better bonding to the matrix material; (3) it allows the dye to disperse in the spin solution; and (4) it does not compromise the chemical stability of the dye during spinning and composite fabrication. Electrospun fibers have also found increased uses in many other applications, including biodegradable electrospun nonwoven fabrics for tissue engineering and drug delivery, highly efficient filtration membrane materials, and high surface area fabrics for protective clothing and sensors.

The scope of this work is to demonstrate the feasibility of making transparent composites that possess chromatic functionalities capable of changing color and/or optical clarity, reversibly, upon exposure to an external irradiation. In-situ polymerization/cast process is used for fabrication of PMMA PVB-fiber composites. This study examines the stability of an embedded

fluorescent dye within the electrospun fibers and their capability of patterning for optical tagging.

2. Material and Method

2.1 Electrospinning of PVB Fibers

We first dissolved PVB ($M_w = 300,000$, Scientific Polymer Product Inc.) of 12 wt.% in a mixture of N,N-Dimethyl formamide and tetrahydrofuran (DMF/THF: 10 to 1 by volume). A UV dye (Fluorescent 28, Sigma-Aldrich) was added to the solution at a concentration of 1 mg/cc for the UV-active fibers. The PVB solution was then electrospun into a fiber mat. The flow rate was set at 0.03 ml/min, the voltage was 35 kV, and the collector distance was at 45 cm. The electrospinning process was very steady; the process could persist for more than 24 h without interruption. Figure 2 is a photograph of an electrospun PVB mat. The fiber diameter is about 500 nm to 600 nm.

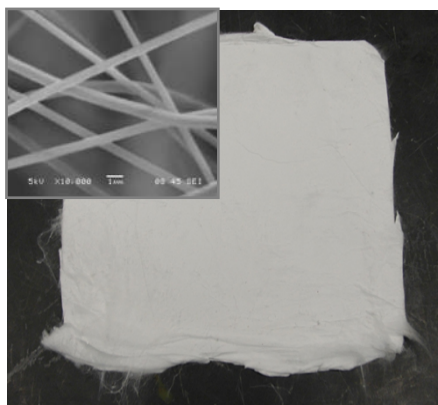


Figure 2. An electrospun PVB mat, 4 in.²
(Insert: SEM micrograph displaying the uniform size distribution of electrospun fibers).

2.2 In-situ Polymerization/Cast Processing

The PMMA matrix resin was prepared by mixing PMMA polymer ($M_w = 540,000$, Scientific Polymer Product Inc) in methyl methacrylate. The resulting solution was 10% PMMA by weight. A polymerization initiator, 2,2'-Azobisisobutyronitrile (AIBN), was added to the solution at a concentration of 2.5 mg/cc. While MMA can also be used without the addition of PMMA, adding it helped to lower the volatility of the MMA.

In-situ polymerization/cast was used for preparation of PMMA PVB-fiber composites. The electrospun PVB mat was cut into 4 in $\times$ 4 in pieces. Then several layers of PVB pieces were compacted in a hydraulic press. The stack of PVB mats was soaked in the PMMA-MMA-AIBN solution for 5 h.

Figure 3 shows the optical clarity of a presoaked fiber mat after degassing. The degassed resin-impregnated fiber mat was then transferred to an aluminum mold. The interior dimensions of the mold are 4 in $\times$ 4 in $\times$ 0.02 in. The inner surfaces of the aluminum mold have a mirror-polished finish. The mold surfaces were sprayed with a release agent (LPS, Dry Film Silicon Lubricant). First, the PVB mat was laid flat into the mold; then an excess amount of PMMA-MMA-AIBN solution was added to the mold. The mold was placed in a hot press for curing. The pressure was set at 1000 kPa and the temperature was set to 55 °C. The curing process lasted for 12 h, and then cooled down slowly to room temperature.

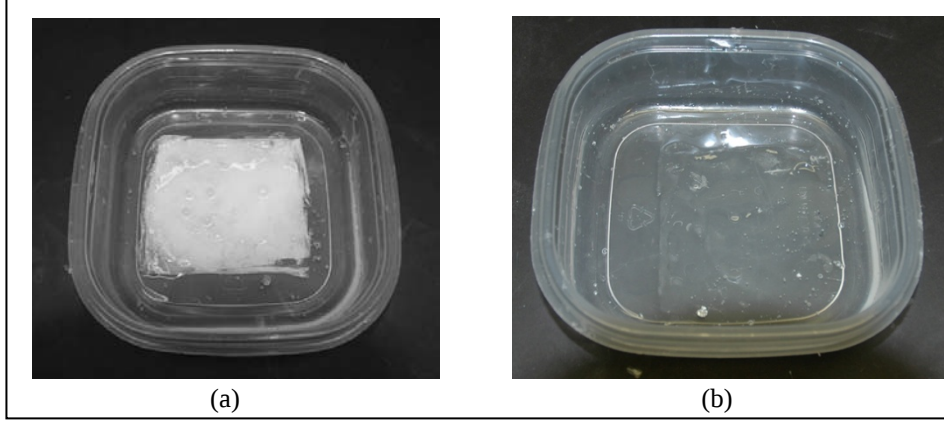


Figure 3. (a) PVB mat soaking in PMMA-MMA-AIBN solution; (b) PVB after 5 h of soaking and vacuum egression.

3. Results and Discussion

3.1 Design Approach for Transparent Fiber Composites

The best strategy to achieve transparency, and keep the fiber transparent regardless of temperature variation, is to closely match the refractive index of the materials and to reduce the fiber diameter to about 100 nm. The following is an example that illustrates the influence of refractive index mismatch between the fiber and matrix, as well as the effect of fiber size on the overall transmittance and haze of the composites (4). The optical transmittance of an object can be described by the Lambert–Beer law:

$$T = \frac{\Phi_t}{\Phi_i} = \exp(-\sigma_{ext} z_m) \quad (1)$$

where Φ_t and Φ_i are the fluxes of the transmitted light and the incident light, respectively; σ_{ext} is the extinction efficiency; and z_m is the total light path length. The transmitted flux is equal to sum of un-scattered and forward-scattered flux (Φ_u and Φ_s respectively) (5):

$$\Phi_t = \Phi_u + \Phi_s \quad (2)$$

The haze is calculated as follows:

$$H = \frac{\Phi_s}{\Phi_t} = \frac{\Phi_s}{\Phi_i \exp(-\sigma_{ext} z_m)} \quad (3)$$

where Φ_s is the flux of the forward scattered light at angles greater than 2.5° . The extinction efficiency for randomly oriented non-interacting cylinders is (2):

$$\sigma_{ext} = \frac{2V_f Q_{sca}}{\pi r} \quad (4)$$

where V_f is the total volume fraction of cylinders; Q_{sca} is the scattering efficiency of one cylinder; and r is the radius of the cylinder. The scattering efficiency for an infinite cylinder is (5):

$$Q_{sca} = \frac{1}{x} [|a_0|^2 + 2 \sum_{n=1}^{\infty} (|a_n|^2 + |b_n|^2)] + \frac{1}{x} [(|b_0|^2 + 2 \sum_{n=1}^{\infty} (|b_n|^2 + |a_n|^2))] \quad (5)$$

where

$$x = \frac{2\pi N_1 r}{\lambda} \quad (6)$$

$$a_n = \frac{[D_n(mx)/m + n/x] J_n(x) - J_{n-1}(x)}{[D_n(mx)/m + n/x] H_n^{(1)}(x) - H_{n-1}^{(1)}(x)} \quad (7)$$

$$b_n = \frac{[mD_n(mx)/m + n/x] J_n(x) - J_{n-1}(x)}{[mD_n(mx)/m + n/x] H_n^{(1)}(x) - H_{n-1}^{(1)}(x)} \quad (8)$$

$$D_n(mx) = \frac{J_{n-1}(mx) - \frac{n}{mx} J_n(mx)}{J_n(mx)} \quad (9)$$

$$m = \frac{N_2}{N_1} \quad (10)$$

N_1 and N_2 are the refractive indexes of the matrix (medium) and the fiber (cylinders), respectively; λ is the wavelength; $J_n(x)$ is a Bessel function of the first kind; and $H_n^{(1)}$ is a Hankel function of the first kind.

According to Wind and Szymanski (6), the scattered flux can be expressed as:

$$\Phi_s = \sigma_{ext} \frac{\Phi_i}{2} \int_{z=0}^{z=z_m} 2 \int_{\theta=2.5^\circ}^{\theta \rightarrow 90^\circ} p(\theta) \sin(\theta) \exp(-\sigma_{ext} \frac{z_m}{\cos(\theta)}) \exp(-\sigma_{ext} z(1 - \frac{1}{\cos(\theta)})) d\theta dz \quad (11)$$

(note: the factor 2 in front of the second integral accounts for the integration from $\theta = -2.5^\circ$ to $\theta \rightarrow -90^\circ$)

where $p(\theta)$ is the phase function. For randomly oriented particles that are small compared to the wavelength, the phase function is (7):

$$p(\theta) = \frac{y + \cos^2 \theta}{y + 1/3} \quad (12)$$

where $y \in [1, 13]$. For spherical scatters, y is unity ($y=1$). For cylinders, y is assumed to be 13, which leads to the most isotropic phase function.

For a refractive index mismatch ($N_1 - N_2$) of 0.03, the calculated haze percentage of the polymer-fiber composite is about 7% (table 1), and the composite appeared to be hazy (6). One way to improve the transparency is to reduce the fiber radius to about 50 nm or less. The second way is to select a polymer or a matrix material that can minimize the refractive index mismatch. In this study, we selected PVB with an identical refractive index as PMMA for electrospinning of submicron-sized fibers to make PMMA PVB-fiber composites for optical evaluation.

Table 1. Calculated values of transmittance and haze for three composites with different embedded fiber radius and different refractive indexes.

Fiber radius, r	250 nm	50 nm	250 nm
Refractive Index of the fiber N_2	1.52	1.52	1.49
Refractive Index of the matrix N_1	1.49	1.49	1.49
Wavelength, λ	633 nm	633 nm	633 nm
Q_{sca}	0.02420	0.00051	0.0
Volume fraction of the fiber, V_f	0.01	0.01	0.01
Composite thickness or the light path, z_m	0.508 mm	0.508 mm	0.508 mm
σ_{ext}	619 m^{-1}	64.6 m^{-1}	0.0 m^{-1}
Φ_s/Φ_i	0.171	0.029	0.0
Transmittance	73.0%	96.8%	100%
Haze	23.4%	3.0%	0.0%

3.2 Optical Properties of PMMA PVB-fiber Composites

Figure 4 reveals the optical clarity of a typical PMMA PVB-fiber composite containing 20 wt.% of electrospun PVB fibers. The refractive indexes of PMMA and PVB are matched perfectly. These PMMA PVB-fiber composites are completely transparent in the visible light spectrum, similar to the PMMA control.



Figure 4. Transparent PMMA electrospun PVB-fiber composite.

3.3 Transparent PMMA PVB-fiber Composites with Chromatic Functionality

In addition to optical clarity, we attempted to develop PMMA PVB-fiber composites with chromatic functionality. Our approach was to first prepare dye-impregnated PVB fibers for use in the subsequent composite fabrication. A UV dye, Fluorescent 28, was selected for use in this feasibility study. The dye was first dissolved in the PVB solution at a concentration of 1 mg/cc. The PVB-dye solution was then electrospun into a mat with a pre-selected pattern. The in-situ casting process allows us the ability to keep the electrospun fiber patterns in place, and is, thus, a viable approach for fabrication of PMMA composites with desired fiber pattern designs. The resultant PMMA PVB-fiber composites, when exposed to a UV excitation, fluoresce at locations where PVB fibers are present. Figure 5 demonstrates the success of fiber patterning in conjunction with chromatic functionality. Evidently, the UV dyes were not leached out from the electrospun fibers during the composite fabrication. This further indicates the stability of impregnated dye within the PVB fibers, presumably due to interaction of hydrogen bonding between PVB with the selected dye.

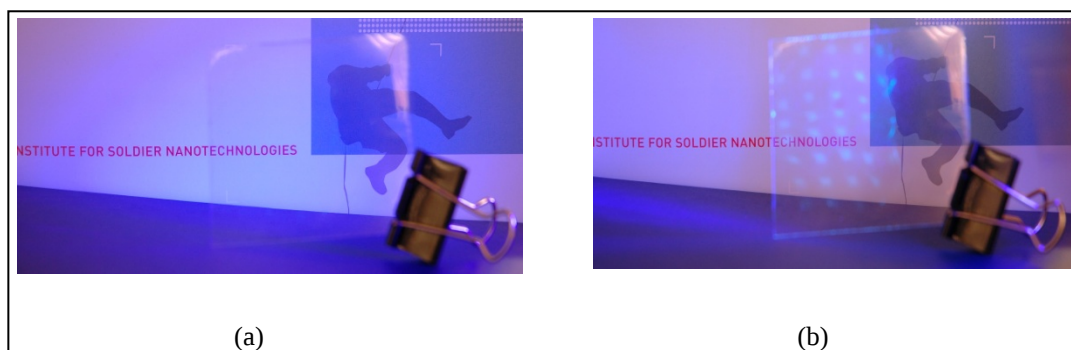


Figure 5. A transparent PMMA composite with patterned, dye-embedded PVB-fibers: (a) before UV excitation; (b) after UV excitation.

4. Summary

A robust approach to achieving novel transparent PMMA PVB-fiber composites, particularly those possessing optical tagging capability, was demonstrated successfully. PVB fibers with embedded UV-dye were first electrospun and then subsequently incorporated into a PMMA matrix in a select pattern for composite fabrication. PVB has same refractive index as PMMA, and as a result, the PMMA PVB-fiber composites were completely optical clear. The stability of the selected UV-dye within the electrospun fibers appeared to be excellent, even long after fabrication. This feasibility demonstration clearly identifies an alternative for the design and production of new transparent taggant systems as a replacement for the current DoD decals required for vehicle identification. Furthermore, transparent fiber-modified polymer composites with the incorporation of different types of dyes have many other potential applications, including the use of near-IR dyes in compliance with night-vision technology for tagging.

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