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FORWARD TO BETTER UNDERSTANDING OF OPTICAL CHARACTERIZATION AND DEVELOPMENT OF COLORED POLYAMIDES FOR THE INFRA-RED/LASER WELDING: *PART II – FAMILY OF COLORED POLYAMIDES*

Abstract

Recent developments were oriented towards optical characterization (laser transmission, absorption, etc.) at a wide range of the infrared wavelengths and optimized mechanical performance of polyamides (PA) for the infrared/laser through-transmission welding technology (TTLW).

The influence of coloring technology and type of pigments being used was also analyzed. During this study recommendations were developed for optimizing the non carbon black pigment loading in various non-reinforced and fiberglass reinforced PA 6 grades. Additionally we will discuss the efficiency of an advanced method of J-color technology (structural methods of coloring effects) for TTLW of the colored PA based plastic.

Introduction

It is well known how to color thermoplastics using dyes and pigments [1-4]. Also it is possible to use the recently developed *"J- (Physical) Colorant Technology"* to color amorphous and semi-crystalline plastics [5]. Pigments and dyes are different types of colorants. Pigments are incorporated by a dispersion process (do not dissolve) into the polymer(s), while it is in a liquid phase. A dye dissolves into the polymeric application medium. From a manufacturing point of a view, pigments are generally preferred to dyes for the coloration of thermoplastics due of their superior fastness properties, heat stability and migration resistance [1-3].

The main reason for incorporating pigments into plastic is to introduce color, either for aesthetic reasons or because of functional needs. Sometimes, the incorporation of pigments may produce problems in plastics, such the changes of mechanical performance and optical properties. Pigments are conveniently classified as *organic* or *inorganic.* The particle size and shape, the nature of the particle surface and dispersion of pigments are very important parameters that influence the optical properties of thermoplastics. Organic pigments generally show in increase in energy transmittance (due to decreased light scattering), as the particle size is reduced but these colorants are very difficult to disperse. It is recommended [6-7] when selecting colorants for transparent optical polymers, to use either dyes, which dissolve in the polymer, or organic pigments. Organic pigments generally have lower refractive indices and finer particle sizes, much smaller then wavelength of visible light (Attachment 1). Inorganic pigments (such as titanium dioxide TiO_2 and carbon black) are usually high refractive index materials and highly light scattering.

In selecting a colorant for laser welded (LW) parts the following issues related to near-infrared (IR) wavelength processing, should be taken into account:

- Type of proposed LW technology (non-contact NCLW or through-transmission - TTLW)
- Requirements of joined thermoplastic(s) to transmit or absorb laser energy.
- Optical properties of selected colorant at near-infrared wavelength.

Experimental

Optical Performance of Various Colored Unfilled PA 6 Plastics

We used PA 6 based plastics (commercially available and experimental), having typical mechanical properties (unfilled state) presented in Table 1 (left column). We evaluated the transmittance of the following color versions at two wavelengths (830 nm and 1,064 nm, Figures 1-4):

- Natural state
- Red (organic)
- Yellow (organic)
- Green (organic)
- White (inorganic)
- Black (carbon black, colorant content is from 0.2 wt.% to 2.0 wt.%)
- Black (non carbon black, laser admissible, colorant from 0.25 wt.% to 1.0 wt.%)

All four versions of carbon black pigmented plastics do not transmit laser energy at near infrared (IR) wavelengths [6-10]. Very low transmittance was found for green and white color versions (less than 10%). These plastics may be used for manufacturing of the part **B** (thermoplastics that absorb the laser energy (see Figure 1, Paper 302, Antec 2001). In general a high carbon black content (or any other pigment which has a high absorption constant) in the absorbing part may be used as the part **B**. A similar temperature distribution and symmetric melt-layers formation can be expected in both thermoplastic parts being welded together.

Reference [6] details the influence of carbon black on the ratio of the melt-weld (weld inter-phase) thickness for non-reinforced/filled PA 6 as a function of the TTLW parameters (laser power intensity and scanning rate). With the laser scanning rate increase from 4.6 mm/s to 7.7 mm/s the carbon black content of the absorbing plastic part increased from 0.2 wt. % to 1 wt. %. This increase changed the melt thickness ratio ($\mathbf{m_{A,\ natural}/m_{B,\ black}}$) from 0.1 to 1.0. If the carbon black content of the absorbing part is high (more than 1 wt. %), the thickness of the melt layers will be similar in the non-colored/transparent ($\mathbf{m_{A,\ natural}}$) and absorbing/colored ($\mathbf{m_{B,\ black}}$) plastic parts.

The red colored PA 6 (Figure 1) has a high transmittance, very close to natural state. The specimens colored in yellow have significantly reduced transmittance relative to natural and red. This reduction is wavelength independent in the near infrared and most likely is due to diffuse light scattering. The reduced transmittance at 830 nm relative to 1064 nm for the green specimen most likely represents intrinsic absorption of the colorant. The overall low absorption in the near IR region suggests that diffuse scattering is also a component. The white colored PA 6 has very low transmittance at both wavelengths (830 nm and 1,064 nm). Titanium dioxide (TiO_2) is the most important white pigment used for hiding power in thermoplastics. TiO_2 provides a high degree of opacity and *whiteness* (maximum light scattering with minimum light absorption). We were not able to weld colored in white PA 6 based plastic due to the inability to deliver needed laser energy at joint area (due to high scattering performance, etc.). Type of colorant and content of white pigments should be optimized for the best results in LW.

"J - (Physical) colorant technology" is a new, very attractive method, which allows thermoplastic coloration using particle scattering. Details of this coloring method and compositions are presented in [5]. This has the potential to capture almost every color needed for industrial applications. Pigment and dye coloration suffer fading effects due to exposure to ultraviolet (UV) light, ozone or bleach, etc. In contrast, *"J colorant technology"* is free from these problems due to the physical nature of the coloring processes. One of the advantages of this technology is the ability to switch from one color state to another. Such color changing compositions can be used to design welded parts for color-changing applications (military, aerospace, etc.). In this study we evaluated (Figure 4) the efficiency of *"J - (Physical) colorant technology"* for injection molded PA 6 applications. For three out of four evaluated color versions (gold, pink and dark red) the transmittance is more than adequate (ranging from 61 to 38%) for welding applications. For gray version the transmission is low, and close to 11%.

Optical Performance of Transmissible FiberGlass Reinforced PA 6 Plastics Colored in Black

Coloring/pigmenting in black is very important for many industrial applications. In general carbon black is the most important black pigment and is the second most used pigment, by volume, in the thermoplastic industry. Black color is typical for many welded under-the-hood and powertrain components, such as air intake manifolds, resonators, covers, etc. As a rule, carbon black pigments exhibit optimized mechanical performance, and color fastness at relatively low cost. Properly selected carbon black grades may improve either the electrical conductivity or insulation properties of plastics as well as UV resistance. Optimized content of carbon black can maintain temperature profile and thickness of weld-melt from the side of the laser energy (LE) absorbing part (**B**).

For NCLW both welded parts may be selected from carbon black colored plastics. These parts are non-transmittable, are able to absorb LE, providing material heating and melting at localized areas (inter-phase).

For TTLW it is possible to use the carbon black colored plastic for one part only (LE absorbing part **B**). The thermoplastic for the part **A** should not absorb LE and be transmittable. The selected thermoplastic for the part **A** can not be colored using carbon black pigments; alternative, near IR transmitting, black colorants must be employed. We evaluated the efficiency of LE transmission for two black colorants, received from different colorant manufacturers (Figures 2-4). The data represent the *maximum* achieved for part **A** (ability to transmit LE to the parts in intimate contact area through the thickness of part **A**). The content of the black colorants (0.2 to 2.0 wt.%) reduces the transmittance compared to unfilled PA 6. *Maximum transmittance* was achieved for the lower level of colorant loading (0.2 wt.%). With increase of the thickness of specimens (B1 specimens), the transmittance is decreased by four times (in range of thickness from 0.8 mm to 6.25 mm). The same effects for transmittance were found at evaluated wavelengths (830 nm and 1,064 nm). Overall, the transmission is lowered at 830 nm relative to 1064 nm, especially for B2 specimens. This suggests that B2 samples absorb more strongly at 830 nm than B1 specimens.

Transmittance data for two grades of fiber-glass-reinforced (0, 14 and 33 wt.%) black (0.25 and 0.5 wt %) PA 6 plastics is presented in Figure 6. The most obvious effect is that of fiberglass content. Colorant concentration has a lesser effect. Increasing the near-infrared wavelength from 830 nm to 1,064 nm increases transmittance for both levels of black colorants. The transmittance of these black PA 6 based plastics is slightly higher than similar data developed for natural (non-colored) fiber-glass filled nylon 6 specimens (see Figure 5, paper 302 Antec 2001). The reasons for this are unclear at present.

Mechanical Performance

For the base investigation we used T-shape butt joints [10]. All tensile test results were conducted at room temperature (23°C) and used to optimize performance of the TTLW. Tables 2-3 summarize the results of the tensile strength of short fiberglass reinforced nylon 6 based plastics and welded joints from frictional (linear vibration welding) and the TTLW technologies. Colored plastics had very good mechanical performance for linear vibration welding technology and the similar results are expected for the TTLW also. It was found, that the mechanical performance (tensile strength at 23 °C) of laser welded PA 6 plastics is equal or close to the tensile strength of frictionally (linear vibration and orbital vibration) or hot plate welded joints. For thermoplastic components welded from PA 6 based plastics, all these technologies (including laser transmission) are three times more efficient than ultrasonic welding.

Concluding Remarks

Colored nylons (polyamides - PA) are high performance semi-crystalline thermoplastics with a number of very attractive mechanical and technological properties for various welded parts. Colored welded PA components are most widely used in the automotive, lawn and garden, power tools, etc. industries. The developed family of colored nylon 6 based plastics has enriched mechanical and technological properties and may be successfully used for both LW technologies (NCLW and TTLW). Results from this report will help designers, technologists and material developers, in selection of nylon based plastic for infrared/laser technology, welded parts design and infrared/laser welding technology optimization with and without the presents of colorants.

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References

1. Pritchard, G., *"Plastics Additives: An A-Z Reference"*, Charman & Hall, London-New York, 663 pages (1998).
2. Kohan, M., *"Nylon Plastic Handbook"*, Hanser/Gardner Publications, Inc., New York, 598 pages (1997).
3. *"Plastics Handbook" Vol. 4, Polyamide*, Hanser Publishing, Munich, 905 pages (1998).
4. *"Engineering Plastics"*, Engineered Materials Handbook, Vol. 2, ASM International, Metals Park OH, 882 pages, 1988.
5. Smith, T., et. al., US Patent # 5,932,309 *"Colored Articles and Compositions and Methods for their Fabrication"*, August (1999).
6. Potente, H., Becker, F., *SPE/Antec'99* Conference Proceedings, Vol. 1 pp. 1402-1405 (1999).
7. Grimm, Robert. A. and Yeh, Hong Jun, *SPE/Antec'98* Conference Proceedings, Vol. 1, pp.1026-1029 (1998).
8. Grewell, David, *SPE/Antec'99* Conference Proceedings, Vol. 1, pp. 1411-1415 (1999).
9. Kagan, V., Bray, R. G., Kuhn, W, *ATEC'2000*, Proceedings of the 58th Annual Conference and Exhibits, pp. 1171-1781 (2000).
10. Kagan, V., and Pinho, G. P., *ANTEC'2000*, Proceedings of the 58th Annual Conference and Exhibits, pp. 1782-1789 (2000).

Key Words

Laser welding, polyamide, optical characterization.

Table 1. Properties of Capron® Nylon 6 Based Plastics (all HS – Heat Resistance Package. At 23°C, Dry-as Molded, DAM. Color Version: Natural State).

Mechanical Properties and Capron Version (all HS)	**8202**	**8231G**	**8233G**
Fiber-glass content, wt.%	0	15	33
Density, gm/ cm^3	1.13	1.26	1.40
Tensile Strength, MPa	85	134	192
Young Mod. ($x10^3$), MPa	3.43	5.96	9.88
Ultimate Elongation, %	70	3.5	3.0
Flexural Strength, MPa	112	180	270
Notched Izod Impact, J/m	55	60	115

Table 2. Influence Of fiberglass Reinforcement On The Tensile Strength Of Linear Vibration And Infra-Red/Laser Welded Butt Joints (Optimized Processing Conditions). Color Version: Natural State.

Wt. %, GF	Tensile Strength of Fiber Glass Reinforced Plastic (MPa)	***Vibration Welding Technology*** Tensile Strength of Weld (MPa)	***Laser Welding Technology*** Tensile Strength of Weld (MPa)
0	82	81	≥ 82
14	125	90.7	78.3
33	185	83.6	75.4

Table 3. Influence of Color Versions On Mechanical Performance (Tensile Strength at 23°C, DAM) Of Butt Welded Joint (At Optimized Welding Conditions)

Color Version	**Tensile Strength of Weld, MPa**
Natural State	81.6
Carbon Black	85.2
Gray	83.8
Red	88.4
Blue	86.0

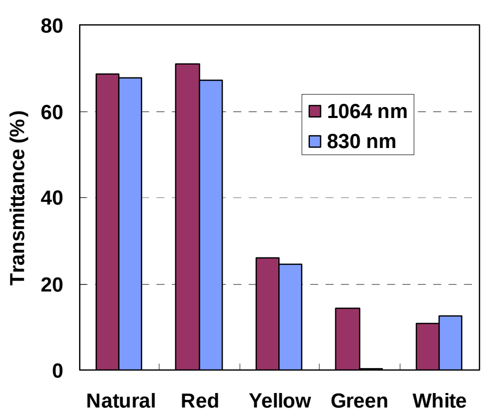


Figure 1. Influence of wavelength (at 830 and 1,064 nm) on transmittance for colored (red, yellow, green, white, natural) PA 6 plastics. Specimen thickness is 3.2 mm.

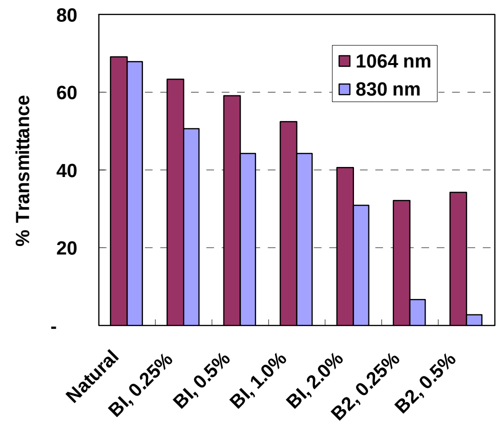


Figure 2. Influence of wavelength (830 and 1,064 *nm*), type of colorant and colorant concentration on the transmittance of unfilled PA 6. Specimen thickness is 3.2mm. Color version: non-carbon black.

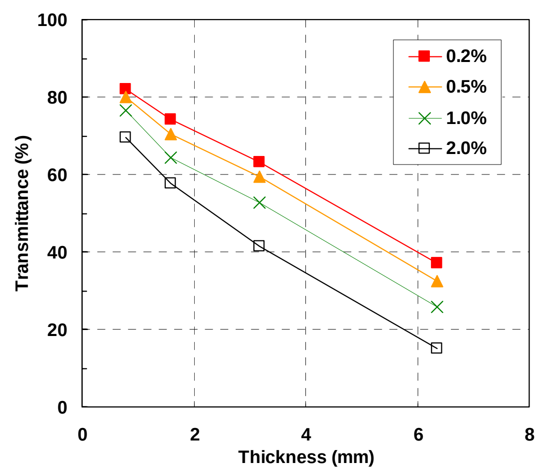


Figure 3: Influence of thickness on transmission (1064 nm) of unfilled, black colored (0.25 to 2 wt %) PA 6.

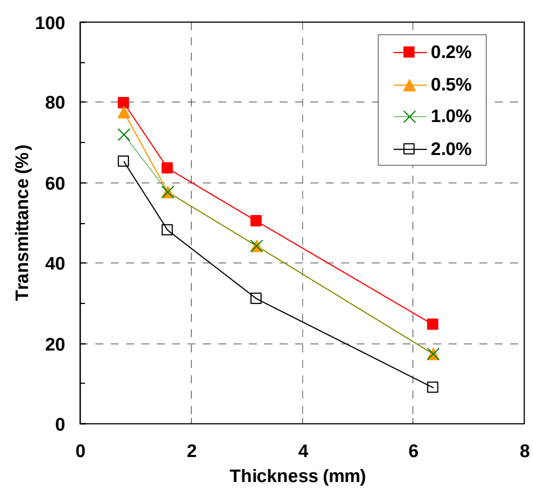


Figure 4: Influence of thickness on transmission (830 nm)

of unfilled, black colored (0.25 to 2 wt %) PA 6 plastics.

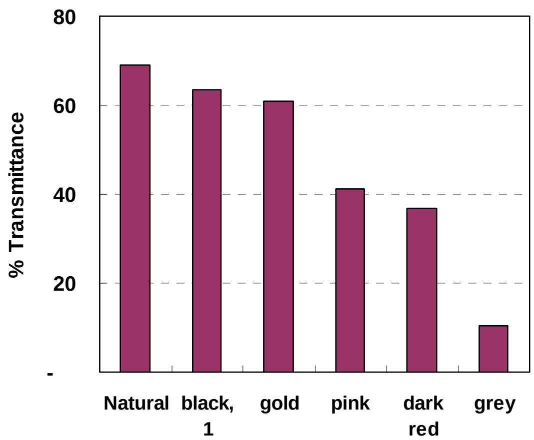


Figure 5. Efficiency of *"J – Technology"* on the transmittance of the various colored PA 6 plastics (at the wavelength 1.06 µm). Sample thickness is 3.2 mm. Color versions: natural state, gold, pink, dark red and gray.

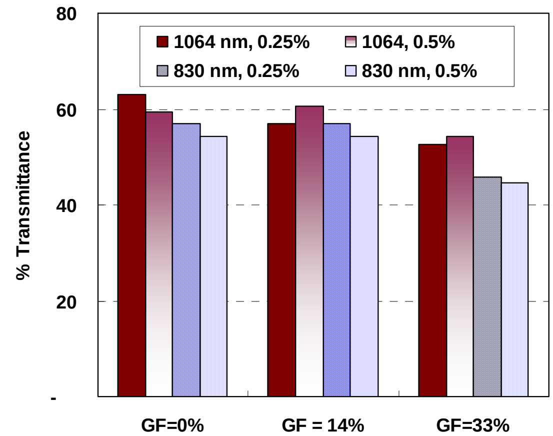
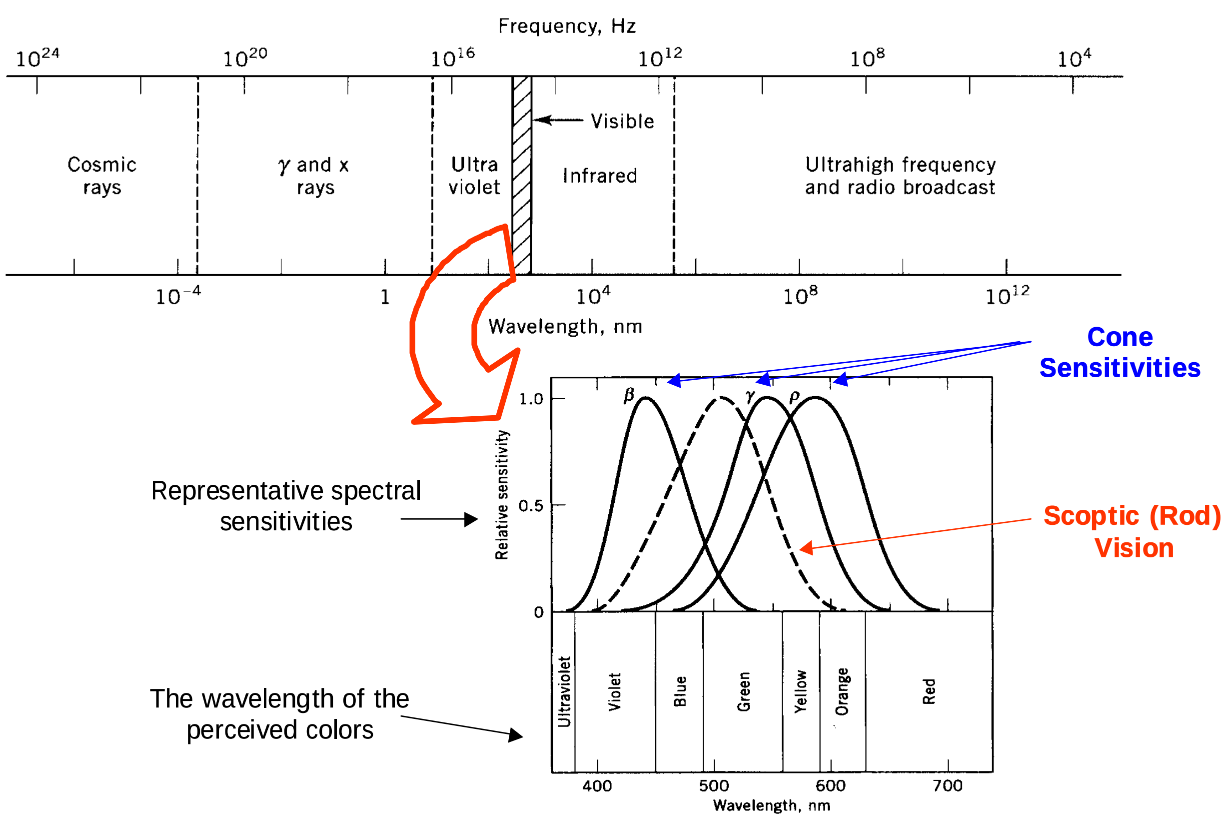


Fig. 6: Influence of wavelength (830 and 1,064 *nm*) and fiber-glass (GF) reinforcement (14 and 33 wt.%) on laser transmission of black PA 6 plastics. Thickness of the specimens is 3.2mm. Color version: black type B (non-carbon black). Legend gives colorant concentration.

Attachment 1. Perceived Colors in Human Vision and Basics of *"J – Technology"*



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