Is Polymethly Methacrylate Stain Friendly when used in Extra-Oral Maxillofacial Prosthesis…?

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Abstract

Background & Objectives: The present study was conducted to find out a stain material that can retain its color in acrylic for a long period, by assessing its chemical interaction with the parent material and to evaluate the color stability of commonly used acrylic resin-stain combinations after exposure to weathering.

Method: This experiment was carried out on PMMA-stain combination specimens. The acrylic blocks were divided into two categories. Scrapings from first category were subjected to spectroscopy to determine the interaction of the four PMMA-stain combinations at molecular level. And scrapings from second category were tested with spectrophotometer after being subjected to weathering. The comparison between the graphs obtained was made using absorbance variance.

Results: Glass paint, acrylic emulsion, and organic dye produce changes which are evident in the spectrograph. Fabric paint does not produce much change in the spectrograph. Before and after subjecting the acrylic resin-fabric paint combination to natural weathering, suggest that the colorant is most stable. On the contrary organic dye and glass paint are least stable of all the four stains.

Conclusion: The addition of colors to PMMA for staining definitely produces changes in the structure of the PMMA at the molecular level. The addition of inorganic group stains produce change but which are insignificant, whereas the addition of organic group stains produce changes at the molecular level which are significant. Inorganic coloring agent (fabric paint) was the most color stable over time whereas the organic colorants (glass paint, acrylic emulsion, organic dye) were the least color stable.

Keywords: Chemical interaction, color stability, PMMA-stain combination, weathering.

Access this article online	
Quick Response Code:	Website: www.innovativepublication.com
	DOI: 10.5958/2395-499X.2016.00001.0

Introduction

Prosthetic reconstruction is indicated in patients with facial defects that are the result of congenital anomalies, trauma, resection after cancer, or some combination of these occurrences. The Primary Purpose of a maxillofacial prosthesis is therefore to restore the patient's appearance and protect the resection site, allowing improvement in self-esteem to help the patient lead as normal a life as possible[1].

Though silicon prosthesis has an good reproduction detail[2,3], acrylic resin has been employed for all types of maxillofacial defects, owing to its easy method of fabrication, ease to stain and economic advantage[4]. The wearing time for maxillofacial prosthesis averages from 3 months to 1 year. The limited service of facial prosthesis is a result of short term durability and its color instability. Deterioration is mainly caused by environmental exposure to ultraviolet (UV) light, air pollution, changes in humidity and temperature[3].

Acrylic resin is stained using two type of pigments - Organic and Inorganic. Both when added to acrylic resin, may or may not react with the polymer and alter the structure of polymer[5]. Hence the need for this study was –

1. To evaluate the effect of stains on polymethyl methacrylate at the molecular level, by using Ultraviolet/visible spectroscopy.
2. To determine the color stability of stains using colorimeter in polymethyl methacrylate when exposed to weathering.
3. To find out a stain material that can retain its color in acrylic for a long period, by assessing its chemical interaction with the parent material.
4. To evaluate the color stability of commonly used acrylic resin - stain combinations after exposure to weathering.

Materials and methods

Stainless steel dies measuring 2 cm x 2 cm in length and breadth, 3 mm in thickness were fabricated. These dies were then invested in dental plaster (type II). Once the plaster was set the dies were removed creating a mold space. Clear heat cure acrylic resin (DPI) was selected for the study. Stains used were Fabric paint, Glass paint, Acrylic emulsion, and Organic dye[6]. The stains were added to the monomer. Acrylic powder and stained monomer was mixed in a ratio of 3:1 by volume, packed into the mold space in dough stage and subjected to heat curing. The acrylic blocks made were divided into 5 groups: Group I - No Stain (Control), Group II - Fabric Paint, Group III - Glass Paint, Group IV -Acrylic Emulsion, Group V - Organic Dye.

1. **For assessing the chemical interaction of the stain material with PPMA:** Scrapings from each group of acrylic blocks was mixed with potassium bromide, made into pellets using Potassium Bromide Press (Model MP-15) and then subjected to infrared spectroscopy [Spectrometer (Infrared; Perkin Elmer Spectrum Gx FT_IR system, USA)][7]. The Principle behind infrared spectroscopy is that infrared rays, when passed through PMMA molecule, absorb and emit certain wavelength, which is characteristic of certain functional groups. The results were obtained in spectrographs with percentage of transmittance in Y- axis and wave number in x-axis[8,9].
2. **For evaluating weathering effect on color stability of commonly used PPMA-stain combinations:** Each category was subjected to natural Weathering, for which specimens were suspended from wooden racks by stainless steel suture material and the assembly was placed on the roof-top for 3 months, for a period of eight hours (9 am to 5 pm) each day. At the end of the treatment period, specimens were removed and cleaned in an ultrasonic cleaner with tap water, wiped dry and then tested[2,10,11,12,13].

A spectrophotometer [Spectrophotometer (Analytik Jena Specord 600, Germany)] was used to calculate color change from spectral reflectance measurements in the visual range of 400 to 700 nm, before and after subjecting the specimens to the test condition. All data collection was performed at ambient room temperature and humidity.

Result

The present study investigates the effect of addition of commonly used stain materials to polymethyl methacrylate at molecular level. In addition evaluates the effect of weathering on the color change of polymethyl methacrylate used for Maxillofacial Prosthesis[7,10,11,12,13]. The grouping of the samples and the stains used are given in table I.

Table 1: Grouping of the Samples and the stains

Group number	Type of stain material
Group I	No Stain (Control)
Group II	Fabric Paint
Group III	Glass Paint
Group IV	Acrylic Emulsion
Group V	Organic Dye

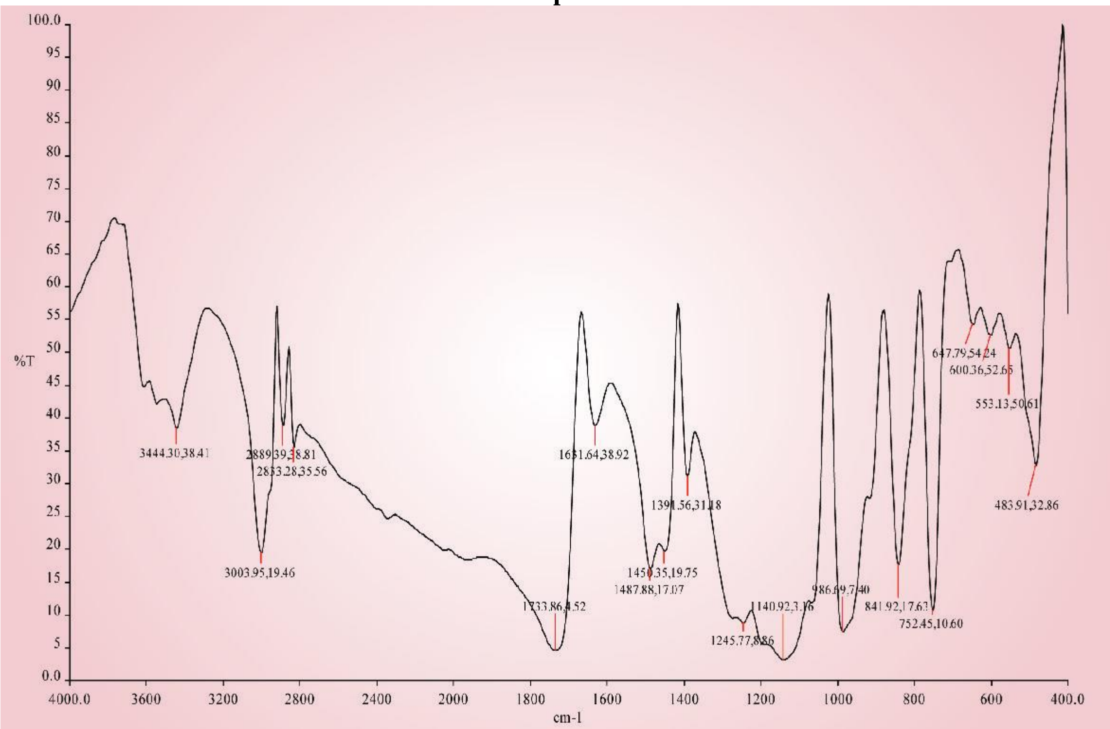
PMMA has C-C main chain and a pendant methyl hydrogen and carboxymethyl group and a terminal double bond with a functional group of C=O and $CH=CH_2$. Infrared absorption of functional group related to PMMA is given in table II[7].

Table 2: IR frequency absorption of functional group related to PMMA

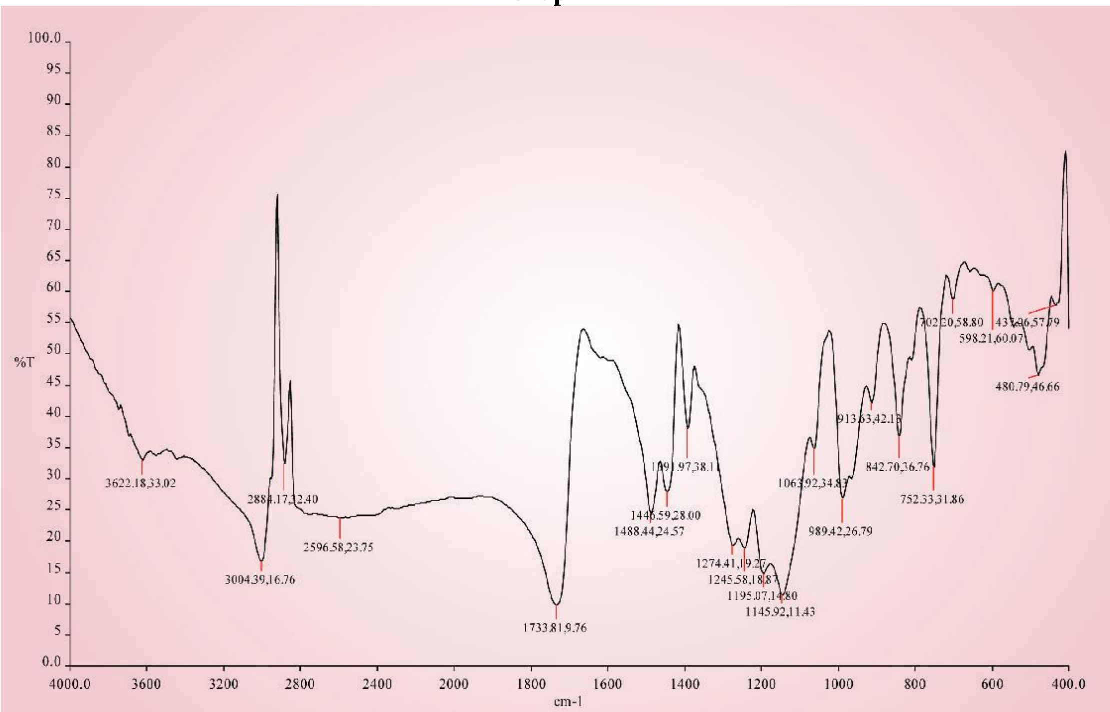
Group	Frequency Cm^{-1}
-C=O (Carbonyl group) $-CH=CH_2$ (Vinyl group)	1740 3040-3040 840-790 1675-1655
(CH_2) n	785-770(w-m) n=1 745-735(w-m) n=2 735-725(w-m) n=3 725-720(w-m) n=4

Graph 1 is the spectrograph with % transmittance of the control group. Graph 2 is the spectrograph with % transmittance of acrylic resin stained with fabric color used for paintings. Graph 3 is the spectrograph with % transmittance of acrylic resin stained with glass paint. Graph 4 is the spectrograph with % transmittance of acrylic resin stained with acrylic emulsion. Graph 5 is the spectrograph with % transmittance of acrylic stained with organic dye.

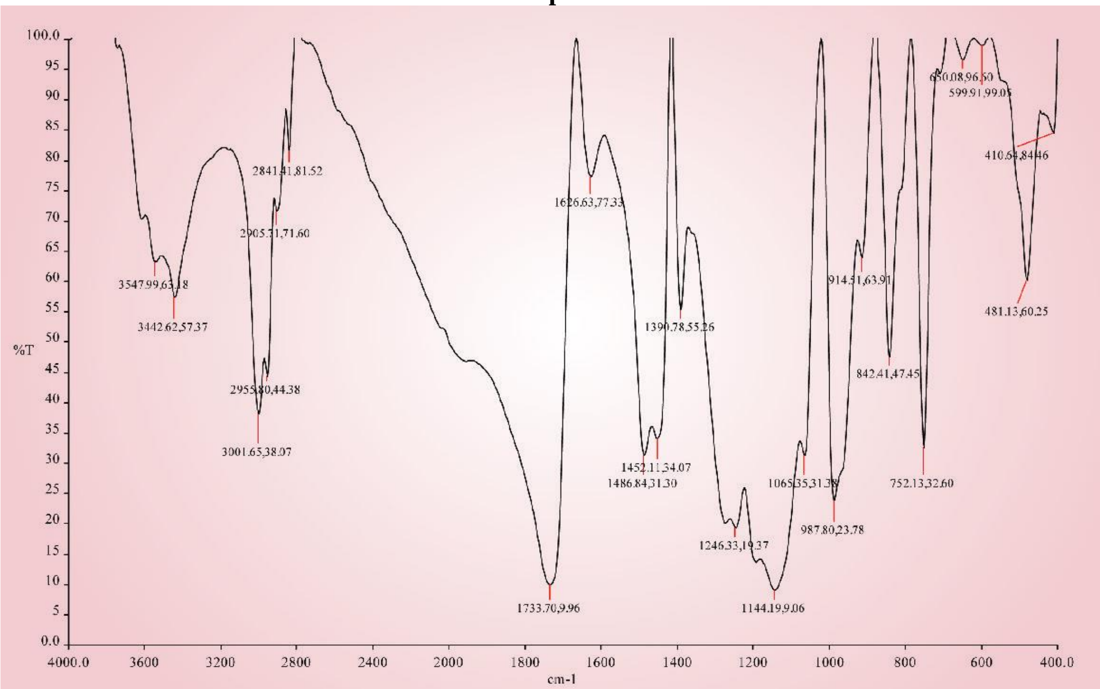
Graph 1



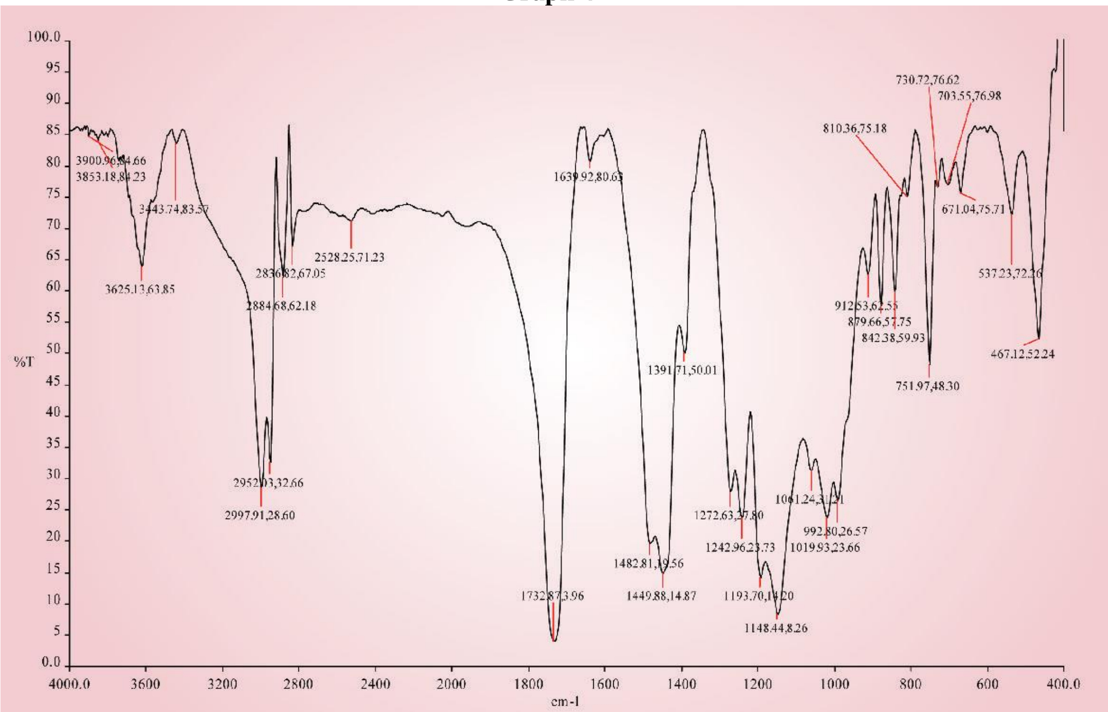
Graph 2



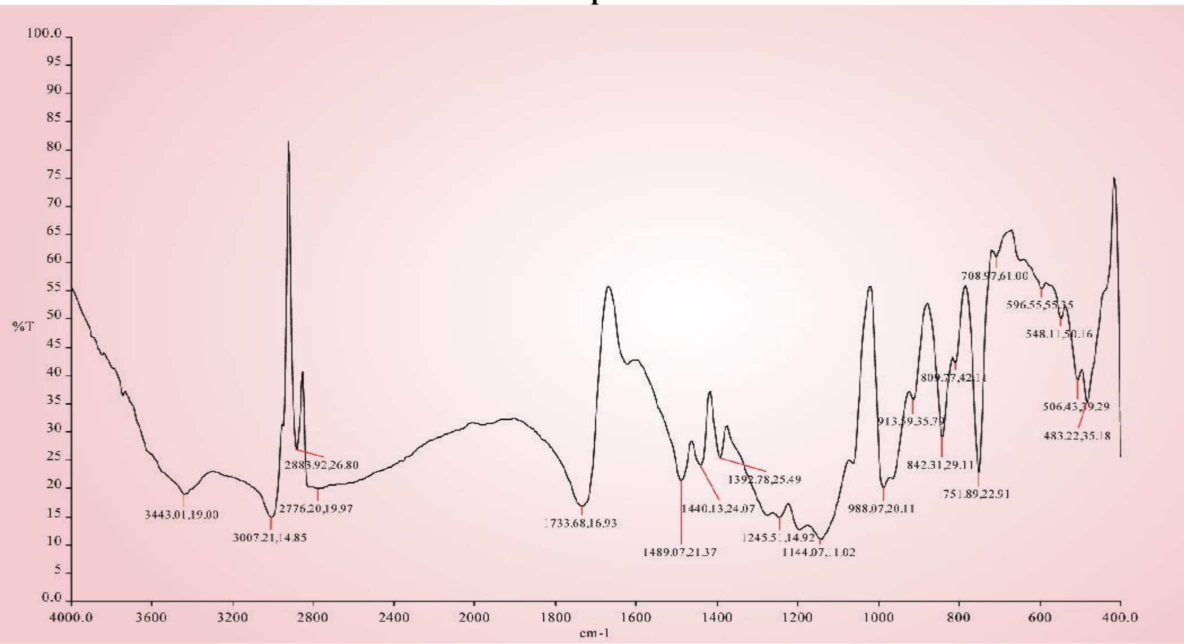
Graph 3



Graph 4 -



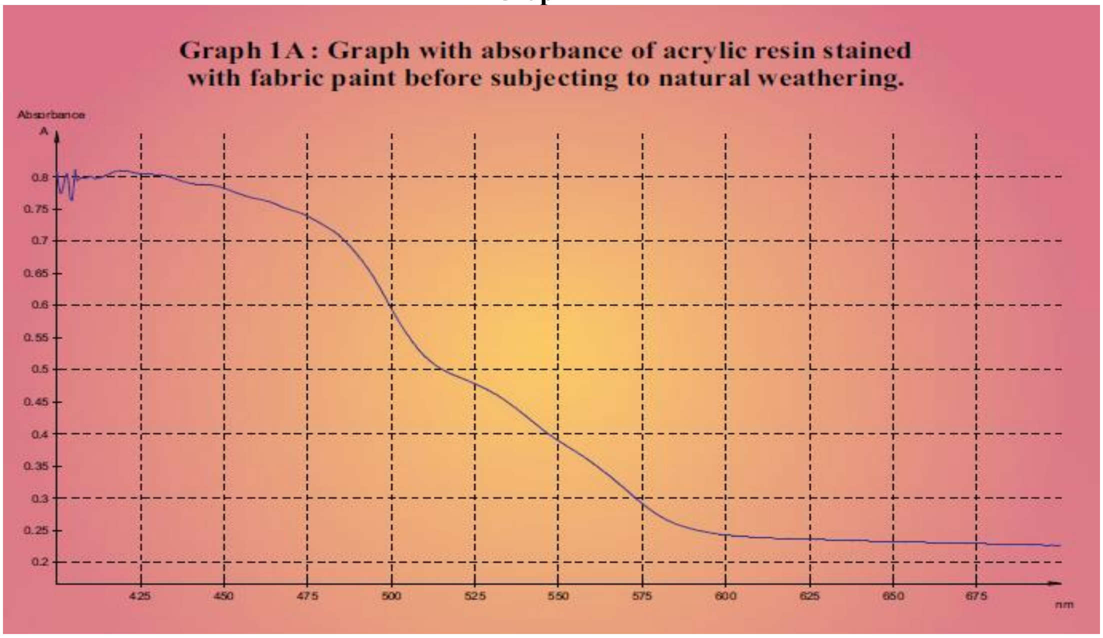
Graph 5



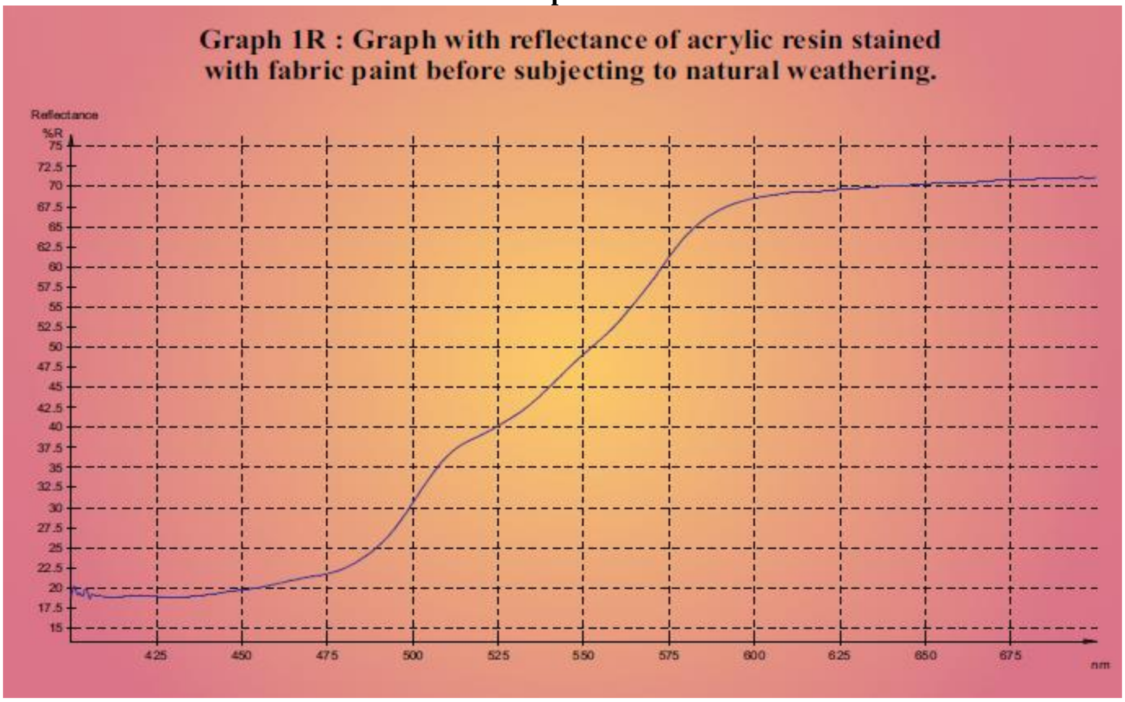
Color change from spectral reflectance measurements in the visual range of 400 to 700 nm was calculated. A spectrophotometer was used to measure light reflectance and absorbance through each specimen before and after subjecting the specimens to natural weathering. The results of the evaluations appear in the following graphs.

Graph 1A is the graph with absorbance and 1R is the graph with % reflectance of acrylic resin stained with fabric paint before subjecting to natural weathering and graph 1A' is the graph with absorbance and 1R' is the graph with % reflectance of acrylic resin stained with fabric paint after subjecting to natural weathering .

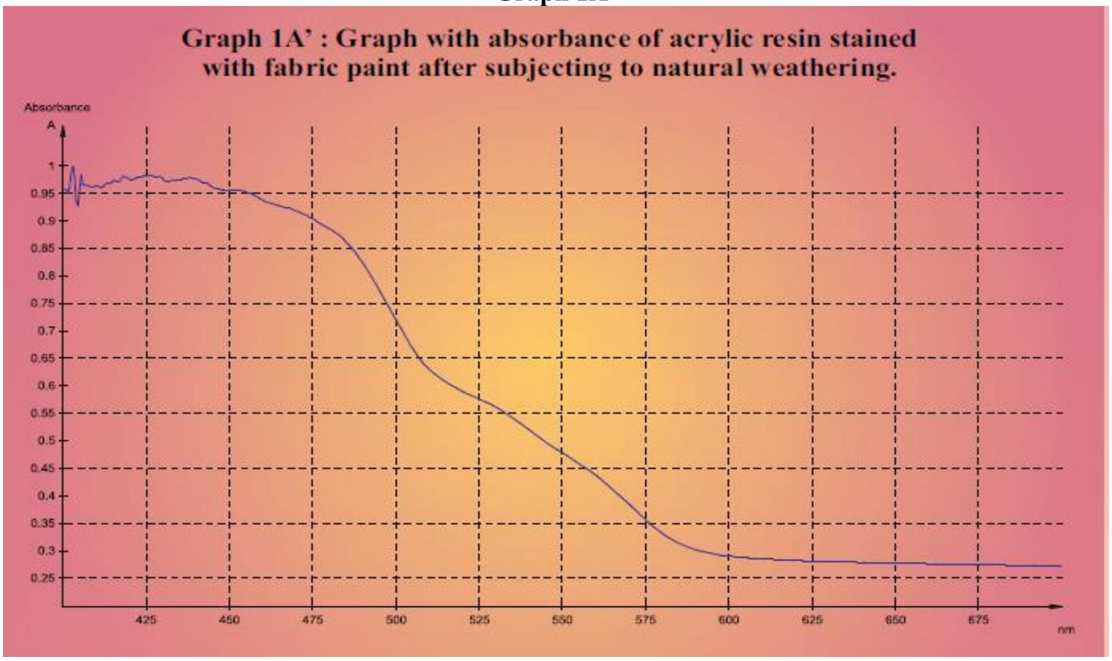
Graph 1A



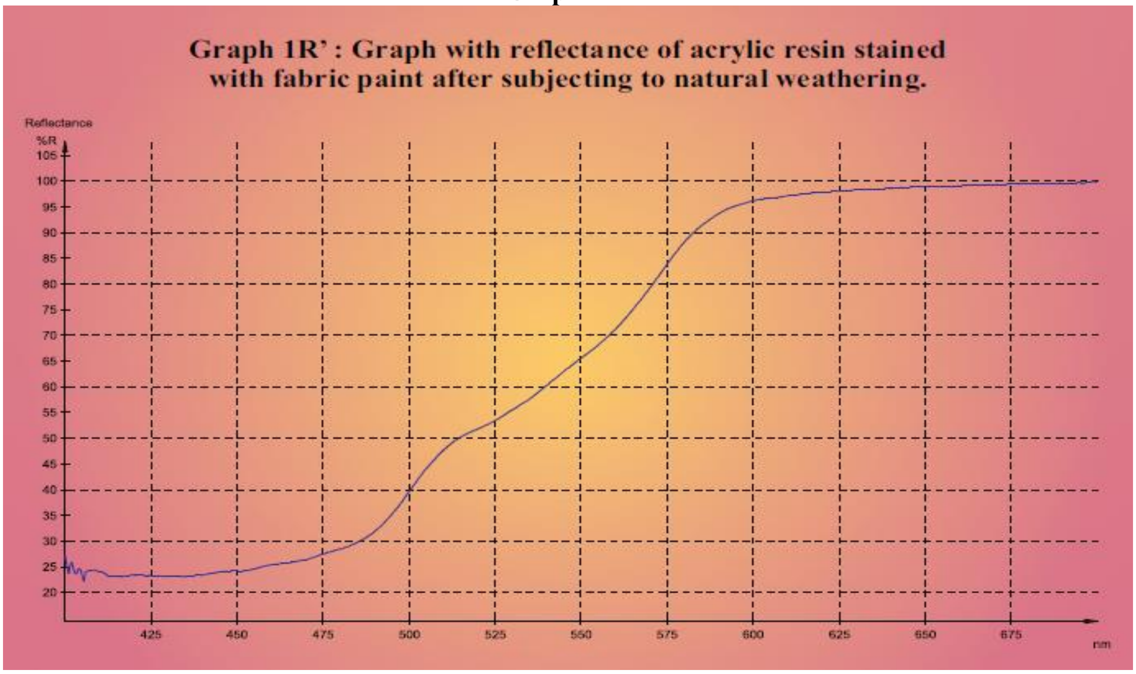
Graph 1R



Graph 1A'

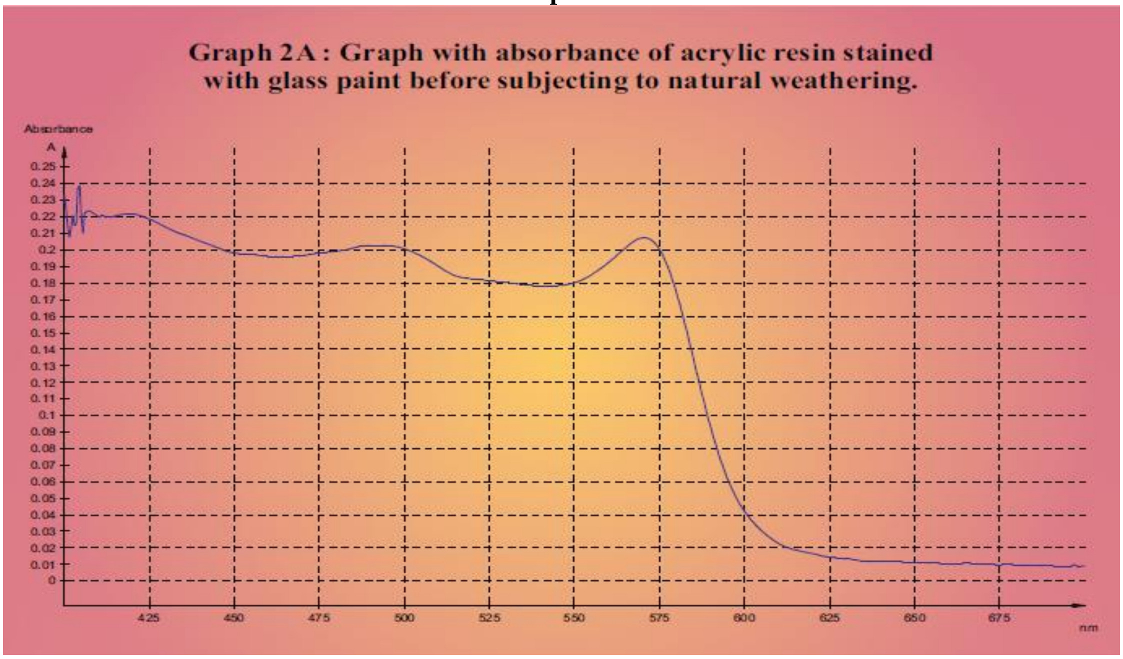


Graph 1R'

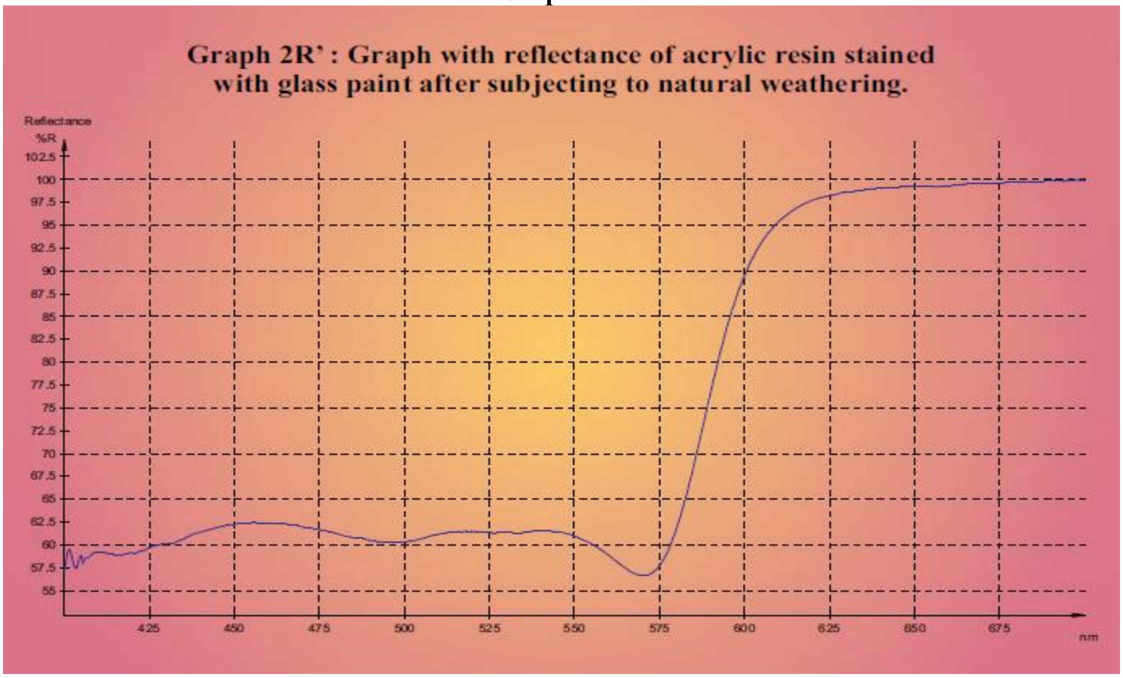


Graph 2A is the graph with absorbance of acrylic resin stained with glass paint before subjecting to natural weathering and 2R' is the graph with % reflectance of acrylic resin stained with glass paint after subjecting to natural weathering.

Graph 2A

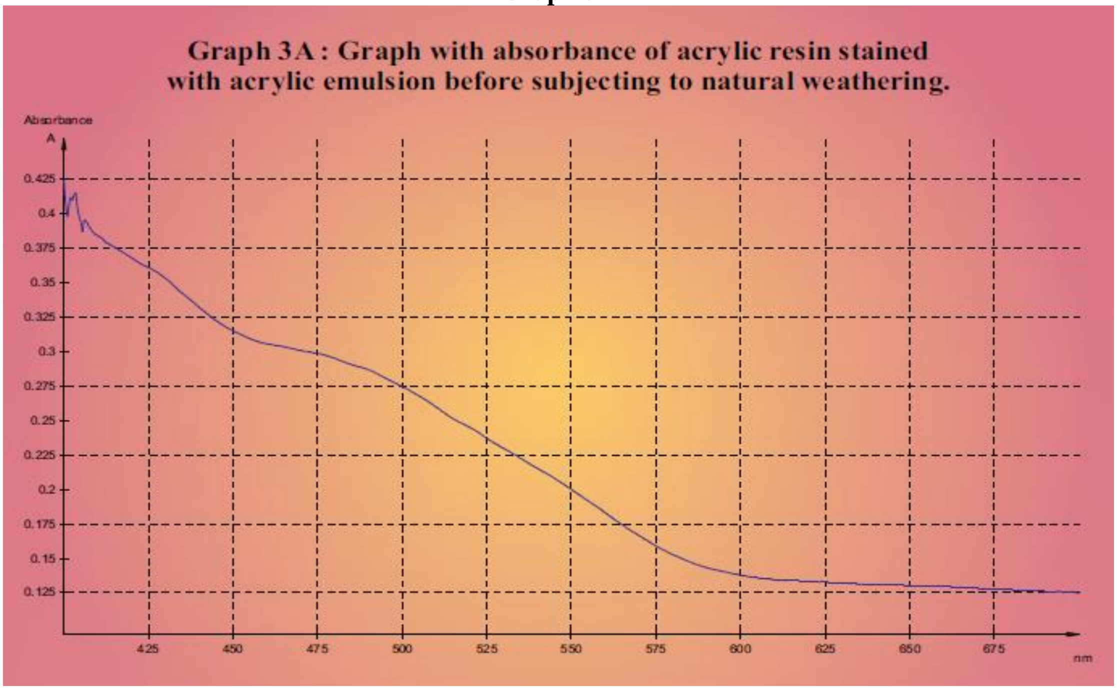


Graph 2R'

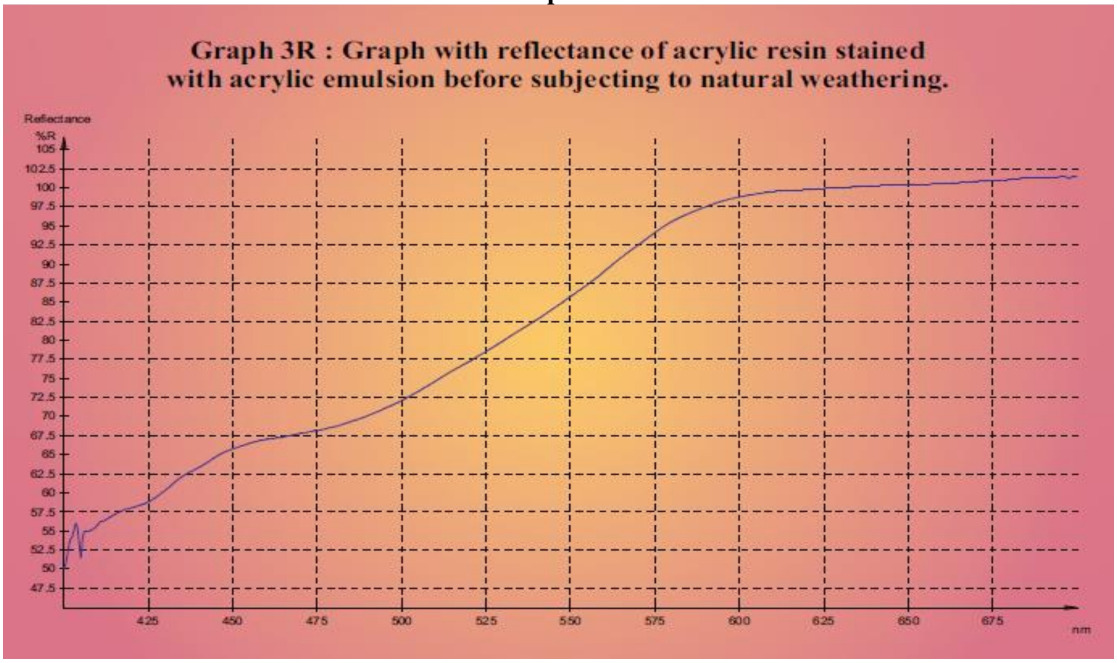


Group 3A is the graph with absorbance and 3R with % reflectance of acrylic resin stained with acrylic emulsion before subjecting to natural weathering and graph 3A' is the graph with absorbance and 3R' is the graph with % reflectance of acrylic resin stained with acrylic emulsion after subjecting to natural weathering.

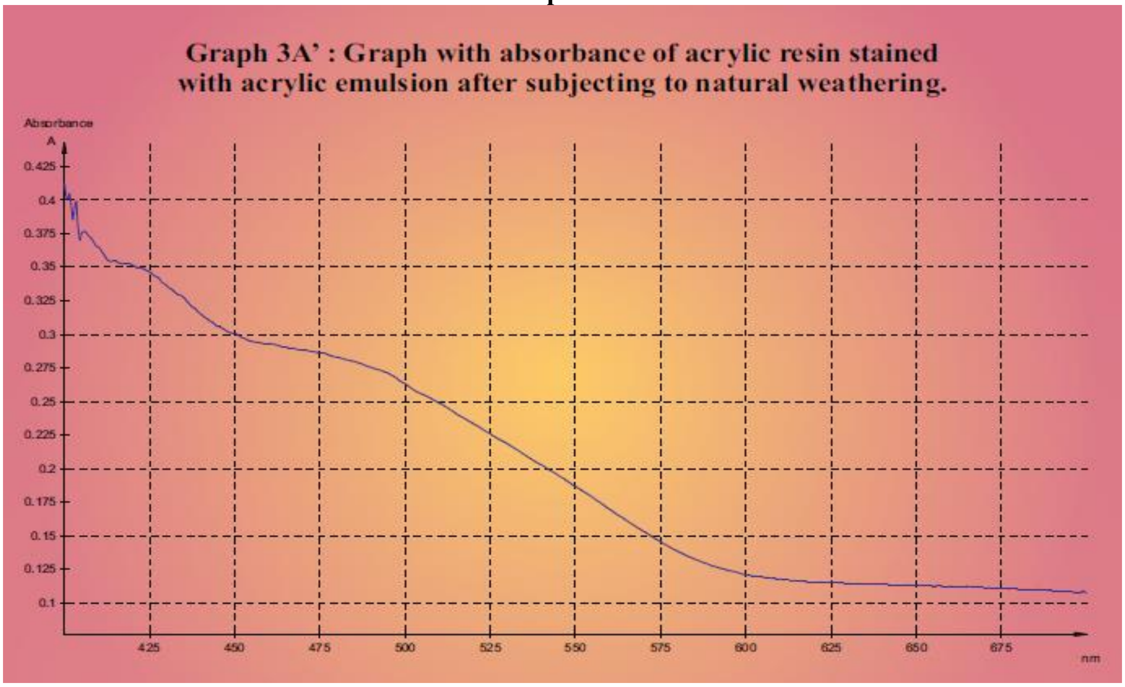
Graph 3A



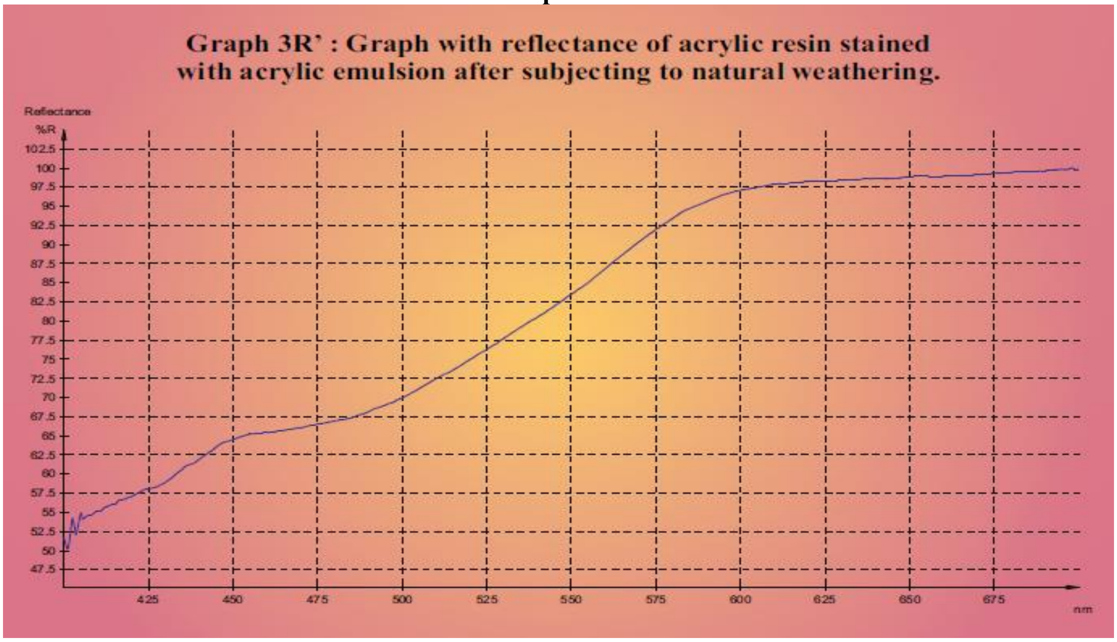
Graph 3R



Graph 3A'

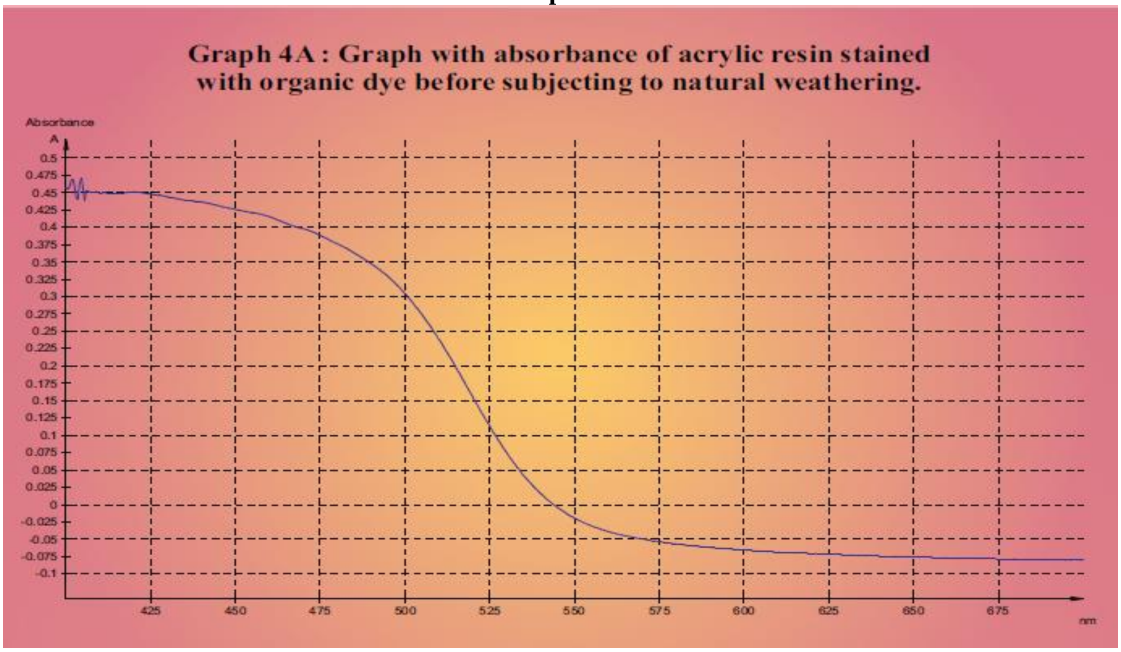


Graph 3R'

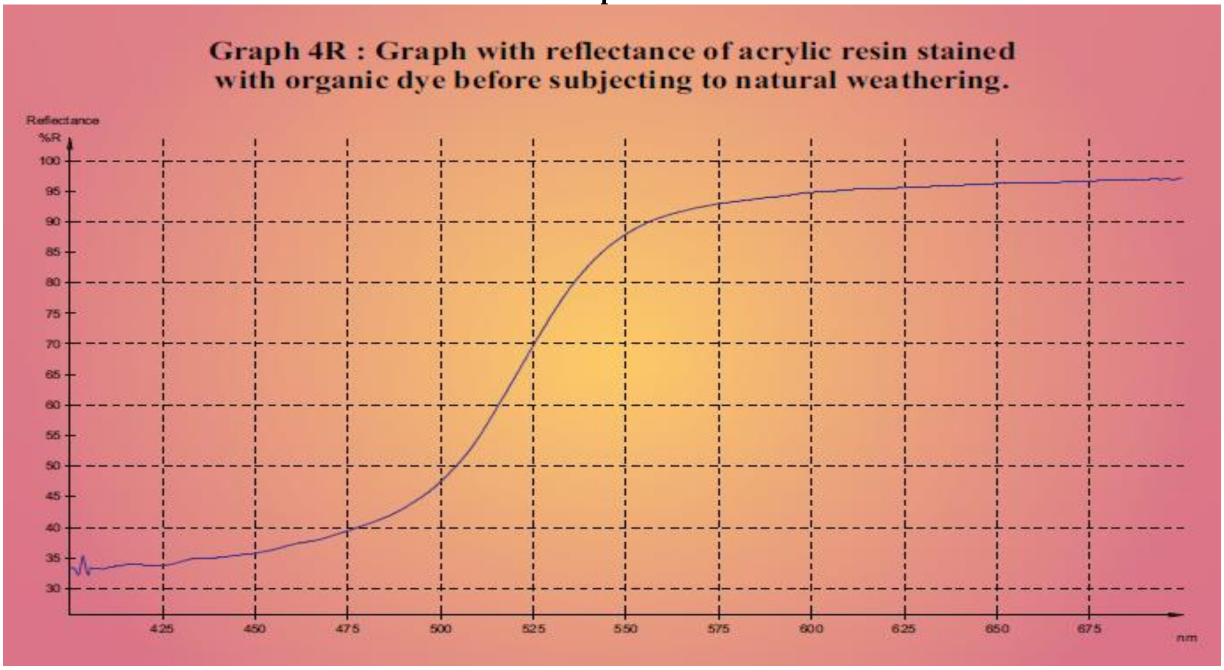


Group 4A is the graph with absorbance and 4R with % reflectance of acrylic resin stained with organic dye before subjecting to natural weathering and 4R' is the graph with % reflectance of acrylic resin stained with organic dye after subjecting to natural weathering .

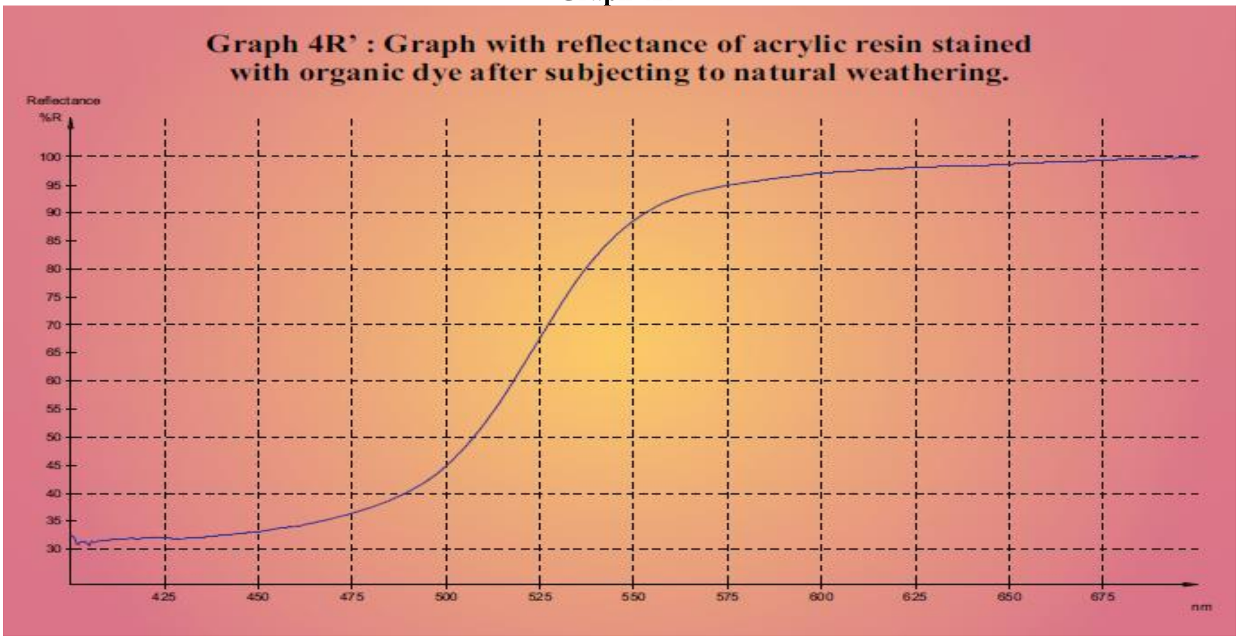
Graph 4A



Graph 4R



Graph 4R'



On comparing the spectrograph readings, the following inference were observed – The main polymer chain (functional groups - carbonyl and vinyl) does not show much change, which is evident in the comparison between graph 1 (control) with and graph 5 (organic dye).

The addition of acrylic emulsion, glass paint to acrylic resin produce changes in the main polymer chain which are significant and evident in the comparison between graph 1 (control) with graph 4(acrylic emulsion) and graph 3(glass paint) respectably. The addition of fabric paint to acrylic resin does not produce much change in the spectrograph which is evident in the comparison between graph 1 (control) with graph 2 (fabric paint). Infrared (IR) frequency distribution of PMMA stained with various stains is listed in table III.

Table 3: IR frequency (cm $^{-1}$) absorption of PMMA stained with various dyes

Control	Fabric Paint	Glass Paint	Acrylic Emulsion	Organic Dye
		3547	3900	
3444	3622	3442	3625	3443
3003	3004	2955	2997	3007
2889	2884	2905	2836	2883
		2841	2528	
1733	1733	1733	1732	1733
		1626	1639	
1487	1488	1452	1482	1489
			1449	
			1272	
1245	1245	1246	1242	1245
		1065	1193	
1140			1148	
			1061	
			1019	
986	989	987	992	988
		914	879	
841	842	842	810	842
			703	
752	752	752	751	751
600	598	599	537	596
483	480	481	467	483
		410		

Discussions

PMMA is widely used to fabricate prosthesis for restoring maxillofacial defects[14], in developing countries like India, because of its advantages of being easy method of fabrication, easy to stain both by intrinsic and extrinsic methods and the fact that it is economical[5,6,7,9]. The stains generally used for staining the maxillofacial prosthesis is burnt siena, and black and white colors used for fabric painting. Studies on staining of maxillofacial prosthesis are mainly focused on silicone prosthesis. There is no scientific documentation on the effect of stains on PMMA. The stains used for staining acrylic prosthesis are organic and inorganic agents. The accepted coloring agents for PMMA which are biocompatible are – 1. Chromium oxide, green hydrates chromium sesquioxide (color index no. 1292). 2. Cosmetic red oxide, purified iron oxide.3. D and C red which is (1-10, nitro-p-tolylazol-z-napthol).4.Napthol red (5-nito-o-toludine).5 Hansa yellow (4-chloro-2-nitroaniline). 6. Haliogen blue copper phthalocyanine blue. 7. Montery red x-2277. These colors belong to organic and inorganic groups[15,16].

The biocompatibility of the colors used in our country to stain maxillofacial prosthesis requires a detailed evaluation[17,18]. It is the duty of the maxillofacial prosthodontist to find a stain, which is safe as well as economical. As a first approach, the effect of stains on the PMMA at a molecular level was taken for the study.

Infrared spectroscopy is an effective tool for studying the chemical interaction of the polymers. J.W Stansbury and dickens S.H used Infrared spectroscopy to study the polymerization kinetics of acrylic and to evaluate the double bond conversion in composite resins. Infrared spectroscopy is used in this present study to evaluate the effect of stains on PMMA[7,9].

The spectrograph of PMMA has three regions 1. From 785 cm^{-1} and below, it corresponds to main chain of the polymer. 2. From 3040-1655 cm$^{-1,}$ it corresponds to the terminal double bond of PMMA. The functional group (C=0. $CH=CH_2$) is the finger print region. Infrared absorption of functional group related to PMMA is given in table II[7].

On comparing the spectrograph readings, the following inference were observed – The main polymer chain (functional groups - carbonyl and vinyl) does not show much change, which is evident in the comparison between graph 1 (control) with and graph 5 (organic dye).

The addition of acrylic emulsion, glass paint to acrylic resin produce changes in the main polymer chain which are significant and evident in the comparison between graph 1 (control) with graph 4(acrylic emulsion) and graph 3(glass paint) respectably. The addition of fabric paint to acrylic resin does not produce much change in the spectrograph which is evident in the comparison between graph 1 (control) with graph 2 (fabric paint).

Infrared (IR) frequency distribution of PMMA stained with various stains is listed in table III[9].

Ideally, the PMMA-colorant combination should not only allow satisfactory esthetics to be achieved clinically, but also to maintain the esthetics indefinitely, or at least until tissue changes in structure, color, or esthetics necessitate re-fabrication of the prosthesis. The color also should be stable over time and aging.

Two types of colorants are available, inorganic and organic. The inorganic colorants are metallic oxides. These molecules are very stable as a result of their ionic bonds. These inorganic compounds are commonly used in products such as paints and tend to be very stable. Presence of double and triple bonds impart color to the organic colorant molecule. These bonds tend to be relatively reactive, and colorants are less stable. A common example of the use of organic colorants is in textiles.

Fabric paint is a form of inorganic colorant. Judging from least change in values of absorbance that is 0.8 and 0.95 before and after subjecting the acrylic resin-fabric paint combination to natural weathering respectably, suggest that the colorant is most stable. On the contrary organic dye and glass paint are least stable of all the four stains tested with before absorbance numerical as 0.45 and 0.23 for organic dye and glass paint and after absorbance numerical as 1.0 and 0.9 respectably. Therefore increased absorbance numerical before and after subjecting to natural weathering suggests degradation of color over time.

Conclusion

Chemically non-reactive and a more color stable PMMA-stain combination over time will result in a maxillofacial prosthesis which is more durable[19,20,21,22]. Even though a number of colorants are commercially available but most of them are not stable at molecular level and to environmental conditions, leaving the clinician with a limited choice [23,24,25,26]. It was in this context that the present study was designed so as to find out a stain material most suitable for coloring maxillofacial prosthesis. The four most commonly used commercially available stains used in this in- vitro study are: 1) Fabric paint, 2) Glass paint, 3) Acrylic emulsion, and 4) Organic dye.

This experiment was carried out on PMMA-stain combination specimens measuring 2 cm x 2 cm in length and breadth, 3 mm in thickness. The acrylic blocks were divided into two categories. Scrapings from first category were subjected to spectroscopy to determine the interaction of the four PMMA-stain combinations at molecular level. And scrapings from second category were tested with spectrophotometer after being subjected to weathering. The comparison between the graphs obtained was made using absorbance variance. On analyzing the results obtained from the present study, the following conclusions were drawn:

1. The addition of colors to PMMA for staining definitely produces changes in the structure of the PMMA at the molecular level.
2. The addition of inorganic group stains like fabric paint to acrylic resin does produce change but which are insignificant.
3. The addition of organic group stains like the acrylic emulsion, glass paint and organic dye to the acrylic resin produce changes at the molecular level which are significant.
4. Inorganic coloring agent (fabric paint) was the most color stable over time whereas the organic colorants (glass paint, acrylic emulsion, organic dye) were the least color stable.

Conflict of Interested: None
Source of Support: Nil

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