Original Article

Chemical interaction of stains on polymethylmethacrylate used for maxillofacial prosthesis: A spectroscopic analysis

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BACKGROUND: Acrylic maxillofacial prosthesis made in our country fades quickly, and the effect of stains on polymer has not been documented yet. **AIM:** 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. **MATERIALS AND METHODS:** Wax cubes (2 cm x 2 cm) were made, flasked and dewaxed. The dewaxed mold was packed with stained heat cure acrylic resin (Acrylan-H). To the monomer the following stains were added - stains used for fabric painting, glass paint, acrylic emulsion, cotton dye, and hosiery dye. They were grouped into II, III, IV, V and VI, respectively. Group I, without stain, was control. Scrapings were taken from each group and subjected to infrared spectroscopy. **RESULTS:** The spectrograph of glass paint, acrylic emulsion, and hosiery dye showed changes, while stains used for fabric painting and cotton dye did not produce much change in the spectrograph. **CONCLUSION:** Glass paint, acrylic emulsion and hosiery dye belong to the organic group of dyes, while stains used for fabric painting and cotton dye belong to group of inorganic dyes. As inorganic dye can retain the shade for a longer period, it is better to use an inorganic group of dyes.

Key words: Stains, maxillofacial prosthesis, dyes, spectroscopy, infrared spectrum, PMMA, polymer

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INTRODUCTION

In recent years, maxillofacial prosthodontics has been playing an epicentric role in restoring extra oral and intraoral defects. The primary purpose of such a maxillofacial prosthesis is to restore the normal as well as anatomical contours of the face and maxilla, to allow the patient to perform routine functions such as mastication and speech, to as great an extent as possible. Though silicon prosthesis has an excellent reproduction detail, such as means of contour of the structure and surface texture, acrylic resin has been successfully employed for all types of maxillofacial defects,[1] owing to its economic advantage. Since the success of maxillofacial prosthesis is primarily dependent on the shade matching with the skin, achieving this is a Herculean task. It has been the ultimate challenge for maxillofacial prosthodontists, as human skin is a multi-layered structure composed of epidermis, hypodermis and subcutaneous tissue.[1]

Acrylic prosthesis can be stained either by intrinsic, extrinsic or a combination of the two techniques.[1] Dry earth pigments, rayon, fiber flocking, artist's paints, Kaolin and liquid cosmetics are widely used to stain the acrylic prosthesis.[2] The addition of stains to acrylic prosthesis can alter the physical property and weathering can alter the color stability.[2-4] The most common reason for refabrication of facial prosthesis is degradation of color and physical property.[1,3,4]

There are two types of pigments used to stain acrylic prosthesis - organic stains and inorganic stains. Inorganic pigments have ionic bond. Therefore, these molecules are stable and retain stains for a longer period.[3]

Organic colorants have double and triple bond, which is responsible for imparting the color, but they are relatively less stable.[3] Inorganic stains, when added to acrylic resin, can remain as such without reacting with the polymer. On the other hand, if organic stains are added, it can alter the structure of polymer. A study was conducted to evaluate the effect of stains on PMMA at the molecular level, by using infrared spectroscopy.

MATERIALS AND METHODS

Pink color heat cure acrylic denture base resin (Acrylan-H) was selected for the study. Stains used were glass paint, acrylic emulsion, cotton dye, hosiery dye, and stains used for fabric painting. Thirty cubes measuring 2 cm x 2 cm were made in wax. These cubes were invested and dewaxed. Stains were added to the monomer. Acrylic powder and stained monomer were mixed in a ratio of 3 : 1 by volume,[5] packed into the mold in dough stage and subjected to heat curing. The acrylic blocks were divided into Groups II, III, IV, V, and VI. Group I served as the control, with no stains. The grouping of samples is given in Table 1.

Scrapings were taken from each group and mixed with potassium bromide. They were made into pellets and subjected to infrared spectroscopy. The principle behind infra red 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 a spectrograph with percentage of transmittance in y-axis and wave number in x-axis.

RESULTS

PMMA has C-C main chain and a pendant methyl, hydrogen and carboxymethyl group and a terminal double bond with functional group of C = O and CH = CH_2 infrared absorption of functional group related to PMMA is given in Table 2.[6]

Graph 1 is the spectrograph of the control group. Graph 2 is the spectrograph of acrylic resin stained with fabric color used for paintings (conventional stain for MFP). Group 3 is the spectrograph of acrylic resin stained with glass paint. Graph 4 is the spectrograph of acrylic resin stained with acrylic emulsion. Graph 5 is the spectrograph of acrylic resin stained with cotton dye. Graph 6 is the spectrograph of acrylic stained with hosiery dye. Infrared (IR) frequency distribution of PMMA, stained with the various stains, is listed in Table 3.

Table 1: Grouping of the samples and the stains used

Group number	Type of stain material
I	No stain (control)
II	Fabric paint (conventional)
III	Glass paint
IV	Acrylic emulsion
V	Cotton dye
VI	Hosiery dye

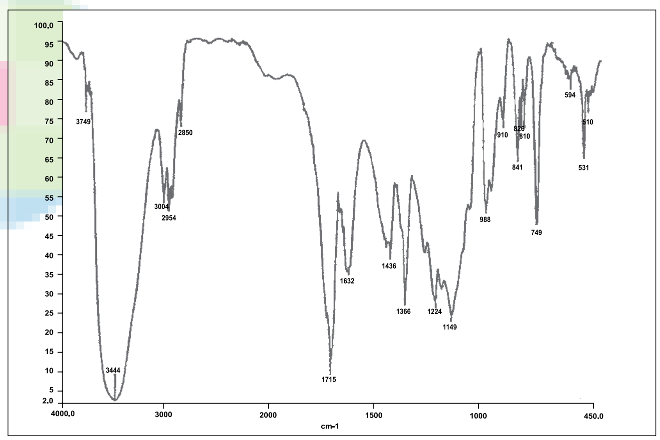
Table 2: IR frequency absorption of functional group related to PMMA

Group	Frequency cm^{-1}
-C = O (Carbonyl group)	1740
-CH = CH_2 (Vinyl Group)	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=3

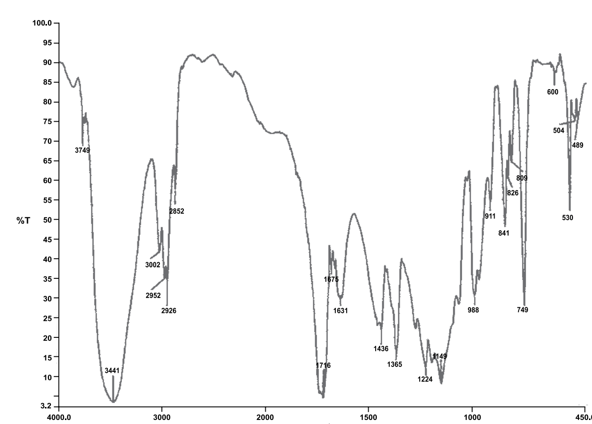
DISCUSSION

PMMA is widely used to fabricate prosthesis for restoring maxillofacial defects, in developing countries like India, because of its advantages of being an easy method of fabrication, easy to stain both by intrinsic and extrinsic methods and the fact that it is economical. 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 used in our country on PMMA. The stains used for staining acrylic prosthesis are of organic and inorganic agents. The accepted coloring agents for PMMA which do not produce unwanted changes on the tissue are[7] 1) Chromium oxide, green hydrated 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-nitro-o-toludine)



Graph 1: IR spectrograph of the control group



Graph 2: IR spectrograph of PMMA stained with fabric paint

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

Control	Conventional	Glass paint	Acrylic emulsion	Cotton dye	Hosiery dye
3749	3749		3748	3749	
				3834	
3444	3441		3421	3442	3442
3004	3002			3001	
2954	2952	2954	2921	2955	2922
2850	2852	2851	2852	2851	2851
	2926		1630		
1715	1716	1734	1453	1734	1733
1632	1631				
1675	1623		1623	1623	
1436	1436	1456		1456	1456
1366	1665			1388	1388
1224	1224			1271	
1149	1149	1149	1118	1148	1149
988	988	985		988	986
910	911				
841	841	840		841	841
826	826			877	
810	809	810		810	
749	749	753	749	715	
750	749				
599	600	601	593	599	594
531	530			528	
510	504	505			
	489			485	

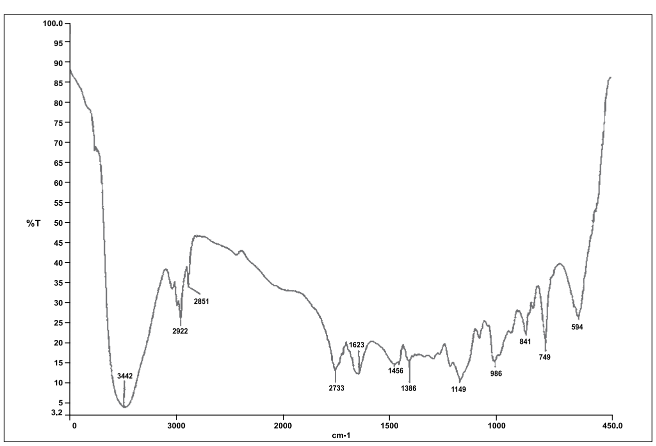
5) Hansa yellow (4-chloro-2-nitroaniline) 6) Heliogen blue copper phthalocyanine blue 7) Montery red x-2277. These colors belong to organic and inorganic groups.

The biocompatibility of the colors used in our country to stain maxillofacial prostheses requires a detailed evaluation. 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.

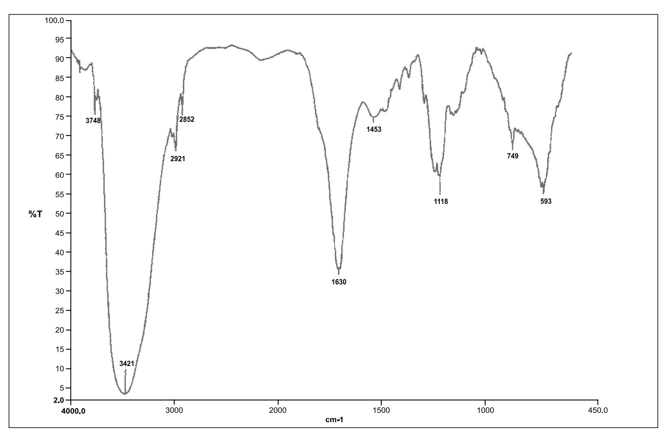
Infrared spectroscopy is an effective tool for studying the chemical interaction of polymers.[6,8] used IR spectroscopy to study the polymerization kinetics of acrylic.[9] J. W. Stansbury used infrared spectroscopy to evaluate the double bond conversion in composite resins. Infrared spectroscopy is used in this present study to evaluate the effect of stains on PMMA.

On comparing the spectrograph reading in Table 2, the following inference were observed - addition of oil paint used for fabric painting and cotton dye to PMMA does not produce much change, while addition of glass paint, acrylic emulsion, cotton dye and hosiery dye produces changes which are evident in the spectrograph [Graphs 1-6].

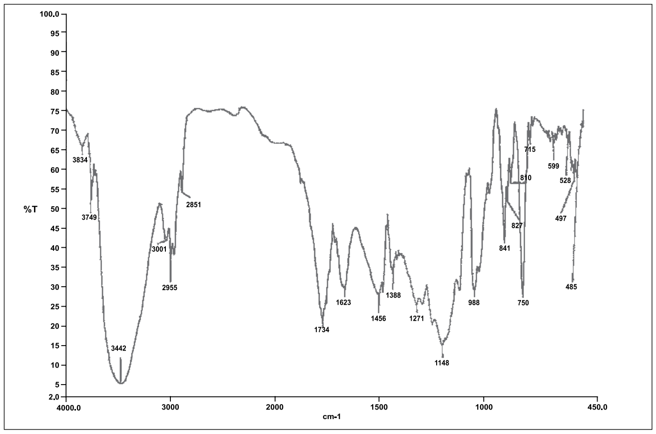
The spectrograph of PMMA has three regions 1) From 785 cm^{-1} and below, it corresponds to main chain of the polymer 2). From 3040-1655 cm^{-1}, it corresponds to carbonyl group (C = O) 3) 1740 cm^{-1}, it corresponds to the terminal double bond of PMAA. The functional



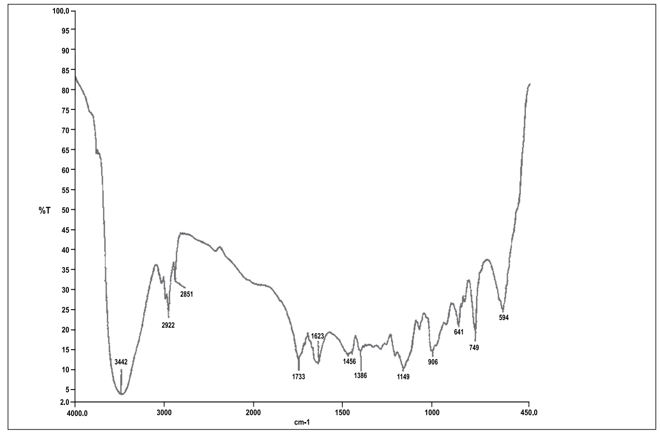
Graph 3: IR spectrograph of PMMA stained with glass paint



Graph 4: IR spectrograph of PMMA stained with acrylic emulsion



Graph 5: IR spectrograph of PMMA stained with cotton dye



Graph 6: IR spectrograph of PMMA stained with hosiery dye

group (C=O, $CH=CH_2$) is the finger print region.

The addition of cotton dye and colors used for fabric painting to acrylic does not produce changes in the polymer chain. The main polymer chain, functional group-carbonyl and vinyl group, does not show much change, which is evident in the comparison between Graph 1 (control) with Graph 2 (fabric paint) and Graph 5 (cotton dye).

The addition of acrylic emulsion to acrylic resin produces changes in the main polymer chain, which is evident in the comparison between Graph I (control) and Graph 4 (acrylic emulsion).

The addition of hosiery dye to the acrylic resin does not produce any change in finger print main carbon chain polymer but the intensity of the peak is less when compared with the control group, which is evident in the comparison between Graph 1 (control) and Graph 6 (hosiery dye).

The addition of oil color used for fabric painting cotton dye and hosiery dye does not produce much of a change in the spectrograph and they belong to the group of inorganic dyes. The addition of glass paint, acrylic emulsion to the acrylic resin produces changes in the molecular level, and they belong to the group of organic dyes.

CONCLUSION

1. The addition of dye to the PMMA for staining definitely produces changes in the structure of the PMMA at the molecular level.
2. The addition of colors used for fabric painting, cotton dye and hosiery dye does not produce many changes; the colors and dye belong to inorganic group dye.
3. The addition of acrylic emulsion to the acrylic resin produces changes in the molecular level, as it belongs to organic dye.
4. The addition of glass paint to the acrylic resin produce changes in the resin at the molecular level, as they belong to organic dye.
5. A detailed evaluation of the physical property of the resin due to addition of stain should be done.

A detailed evaluation of the effect of weathering in the color change of MFP should be done

A detailed evaluation of the effect of various colors and edible dyes on the tissues should be done, so that they can be used safely for staining maxillofacial prosthesis.

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