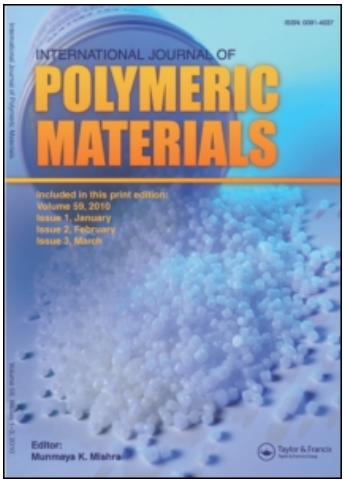

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Porosity, Microstructure and Thermal Stability of Microwave-cured Polymeric Denture Molds

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The relevance of controlling the chemical structure, thermal stability, composition and the porosity, of microwave-cured polymeric denture-molds is a key parameter if some degree of control of the corresponding adhesion among components is to be achieved. Different microwave-cured only polymer blends (Epoxy resin + Hardener) for producing denture molds were characterized by different techniques and compared to microwave-cured composites, also used for producing denture molds (Epoxy resin + Hardener + Alumina). In both cases the porosity was characterized by SEM, and the best material (in terms of porosity) was then subjected also to thermal and structural characterization. The results show the lowest porosity for the 90% Epoxy resin + 10% Hardener blend. The morphology shows a homogeneous surface with irregular particles smaller than five microns and voids-free. Also, the optimum temperature 100.8°C for microwave-cured denture molds was achieved with only a 0.64% loss of the original mass.

Keywords: Denture molds; microwave-cure; epoxy resin blends properties

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INTRODUCTION

Different polymer blends have been employed for fabricating denture molds, and their preparation procedure has drawn the attention of both applied and pure researchers in the area of dentistry for at least the past two decades [11, 12]. For manufacturing the molds, a wide variety of processing techniques have been employed, including extrusion, injection and compression [16]. Because of easy handling and low cost, the compression method as well as a block molecular architecture have been prefered for producing dental materials, because that particular molecular structures being most adequate for blending, which in turn produces good and aesthetic denture bases.

Some investigations have shown that is in principle possible to control a number of parameters for achieving a low porosity, such as: content and particle size distribution of both filler and soft matrix phase. The discrete phase (filler) is formed by particles of rather complicated structures, and from 20 to 40% weight content in the blends [13]. Optical microscopy of such blends shows surfaces formed by different structures (spherical, elongated, *etc.*) due to the components partial miscibility as well as voids that produce the most detrimental porosity [1].

For manufacturing artificial denture molds and removal prosthesis, a variety of materials have been tested, being poly(methylmethacrylate) (PMMA) the most common one. Its polymerization (by addition reaction) begins with an initiator (benzoil peroxide), which produces free radicals that generate chain reactions. In general, the acrylic polymerization is carried out in metallic flasks, with a previous casting of the resin (by compression). The main curing methods of dental resins include: 1) hot water or hot air, 2) hot stream, 3) visible light, and 4) microwave energy [15].

In the conventional method for to curing the acrylic resin used for the molds (hot water), either two procedures are followed: 1) a long method, where the especimen is held from 8 to 10 hours in hot water at 70°C, 2) a short method, holding the mold for half and hour at 70°C in hot water first, and then at 100°C for one hour. Both procedures assure a good polymerization and low porosity. The thermal reaction up to 60°C generate free radicals and the exothermic reaction at 100.8°C is reached. Nevertheless the cured resin contains a percentage

of residual monomer and low dimensional stability. On the other hand, when microwave energy is utilized, these free radicals are incorpored to the denture mold and a complete polymerization is reached [3, 5].

For microwave irradiation a microwave oven with two operating modes: LOW at 90 and HIGH at 500 watts and the use of a not-metallic denture flask to avoid the reflexion of electromagnetic waves are recommended. The conventional method consist in curing in the LOW mode for twelve minutes, first and then for two minutes in the HIGH mode. Finally to let set the mold in room conditions for 30 minutes [2]. Several results show that porosity reduction depends on the adequated handling of both mode and irradiating times. For the case of PMMA resins cured by microwave energy. However, large voids, measuring up to 5 mm in diameter either on the surface of the sample or just below it have been found whereas porosity-free molds have been produced by using non-polymeric materials [1]. The porosity present in the mold is key for producing a denture with good resistance to staining, calculus deposition, and adherent substances.

Fortunately, novel composite materials based on improved physical properties, have diminished the processing time and the cost of polymer-based molds. For example, the control of thermal conductivity of some composites can be obtained by embedding metal fillers in the soft matrix. For the case of poly(methylmethacrylate), whose thermal conductivity is low, when metal fillers (10 microns average size) are added (from 5 to 25 percentage), the thermal conductivity is increased approximately 4 fold, as well as the compressive strength. However the tensile strength and the water absorption decrease and the material becomes opaque [4].

In terms of spectroscopy, it is possible to figure out the segregation properties of these blends. According to the literature, the Infrared band contributions of Epoxy resins spand over three important regions: $2975-2830\,cm^{-1}$, $1610-1440\,cm^{-1}$ and $950-810\,cm^{-1}$ [11–13]. For the case of Aluminum oxide is possible to detect important bands at 1334, 1300, 1150, 740, 600, 494 and $453\,cm^{-1}$ [8].

On the other hand, almost all organic solid materials have low melting temperature as compared to inorganic materials. By the TGA technique it is possible to obtain information on their thermal

stability, degradation temperature, components contribution in the case of copolymers, as well as determining volatiles, additives and solvents [14]. By DSC it is possible to gather information on: enthalpy changes, glass transistion as well as melting and crystalization temperatures. By using both techniques, the composition of the blends through the glass temperature, as indicator of the phase separation degree, is in principle possible to obtain [6].

Accordingly, in the present work (Epoxy resin + Hardener) and (Epoxy resin + Hardener + Alumina) blends, employed for fabrication denture molds were prepared by different microwave treatments and the porosity was observed by SEM. The best blend was then studied by FT-Infrared spectroscopy to evaluate the chemical structure. Thermal stability was studied by the DSC and TGA techniques.

EXPERIMENTAL

a) Molds Preparation

Five (Epoxy resin + Hardener) and five (Epoxy resin + Hardener + Alumina) (PLASTIMUNDO^{TM}) blends with different compositions were prepared, as described in Table I.

Each processed blend was let for 24 hours to set and then subjected to microwave energy by either one of two procedures: 1) LOW mode (90 watts) for 12 minutes and 2) HIGH mode (500 watts) for 2 minutes. To compare the efficience of microwave energy as a polymerization

TABLE I Blend composition

Sample	*Epoxy resin* (%)	*Hardener* (%)	*Aluminum oxide* %
1	97	3	
2	95	5	
3	93	7	
4	90	10	
5	87	13	
6	85	10	5
7	80	10	10
8	75	10	15
9	70	10	20
10	65	10	25

method, two additional procedures were followed: 3) to process and let set for 24 hours in room conditions and 4) to irradiate in the LOW mode (90 watts) for 12 minutes directly, without setting.

A microwave house hold oven machine, with a maximum power of 500 watts, and two modes at 90 (LOW) and 500 (HIGH) watts, was utilized and to avoid sticking problems to the mold after irradiating, Ioxamide and magnesium stereate were employed as lubricants.

b) Morphology Characterization

The resulting materials were prepared by ultramicrotomy in a microtome model MT 600-XL (RMC) which produces very thin and uniform cuts with diamond knives. The pyramid-shaped cuts were vacuum-coated with carbon to diminish charging effects [10] and the surfaces were observed by scanning electron microscopy (SEM) in a JEOL-JSM-5200 machine, in secondary electrons mode at 25 KeV.

c) Spectroscopy Characterization

FT-Infrared experiments were carried out in a FT-IR NICOLET bench, model 910. The resolution of the equipment is $4\,cm^{-1}$, with a spectral range from 100 to $3400\,cm^{-1}$. All measurements were realized both parallel and perpendicular to the surface of the samples.

d) Thermal Characterization

The samples with a weight of 20 mg, were evaluated in a thermobalance Dupont 910, attached to a 2100 system (Thermal Analysis Instruments), under N_2 atmosphere and a heat speed of 10°C/min in the temperature range from 20 to 500°C. The melting temperature and the fusion heat were evaluated by a Dupont 910 Differential Scanning Calorimeter (DSC) under N_2 atmosphere and a heat speed of 10°C/min in the same temperature range.

RESULTS AND DISCUSSION

The lowest porosity of the whole set of samples prepared was found in the 90% Epoxy resin + 10% Hardener blend, which was cured by

mixing and setting for 24 hours and to cure in the LOW mode (90 watts) for twelve minutes. The corresponding morphology shows a rather good homogeneity, where both polymeric phases, *i.e.*, the Epoxy resin (gray region) and the Hardener (light region) can be observed in the micrograph of Figure 1. Moreover, there exist polymeric particles smaller than 5 microns and no voids were detected (Fig. 1), which allow to assure that not adhesion of bacteria when implanting the denture in patients will be likely to take place. A Hardener content below 10%, produces the presence of voids and several irregular particles can be observed (Fig. 2).

The effect of the Alumina content in the blends, aimed to improve the porosity was not as clear as thought. For example in the 85% Epoxy resin + 10% Hardener + 5% Alumina, the morphology consists of some irregular voids smaller than 10 microns, average size, and many irregular particles (Fig. 3). When the alumina content is increased, the porosity increases accordingly, and was possible to observe voids up to 200 microns in diameter and inhomogeneous surfaces.

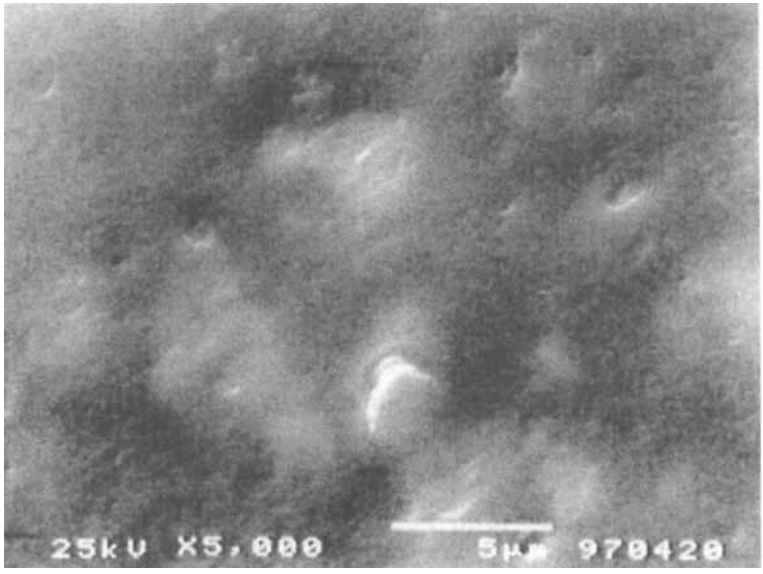


FIGURE 1 SEM Micrograph of the 90% Epoxy resin + 10% Hardener blend, cured by method 1.

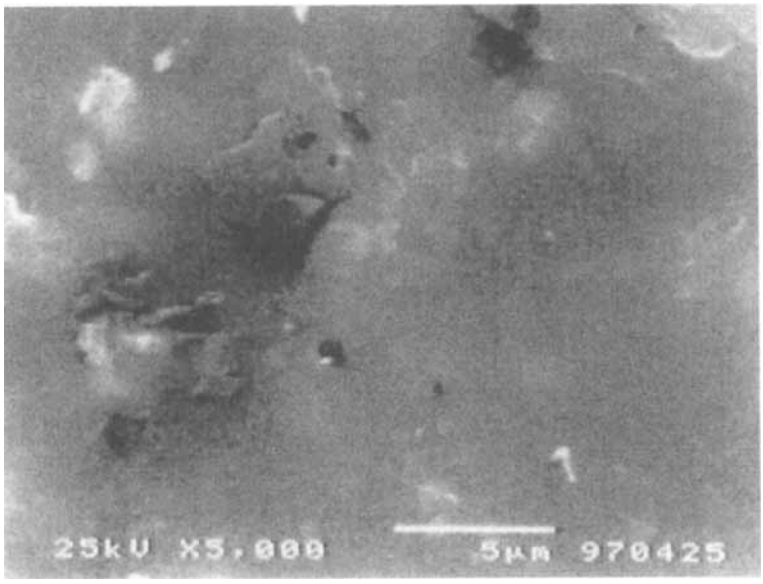


FIGURE 2 SEM Micrograph of the 93% Epoxy resin + 7% Hardener blend, cured by method 1.

By using the HIGH mode (500 watts) and by irradiating for two minutes the samples with Alumina [method 2], it was not possible to reduce the porosity, because no complete polymerization was obtained done. The morphologies in these cases show the presence of several low contrast, regions corresponding to alumina material and large voids (Fig. 4).

After evaluating both types of blends and having determined the lowest porosity composition, *i.e.*, 90% Epoxy resin + 10% Hardener, the efficience of method 1 was clear, since when the materials were subjected to methods 3 and 4, the presence of several irregular particles (not fixed to the matrix) and incomplete polymerization were found, when method 3 was utilized (Fig. 5), whereas for the blend processed in the LOW mode (90 watts) without setting [method 4], the resulting surface is inhomogeneous, with considerable crazes surrounded by light zones (Fig. 6).

The best procedure for obtaining a good polymerization and thus a good homogeneity in the molds, was also determined when the blends were characterized by spectroscopy. In Table II, the chemical structure

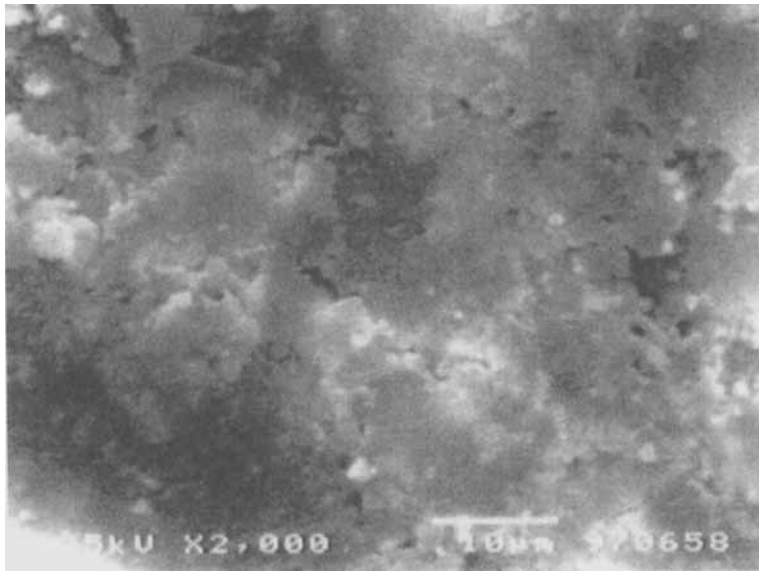


FIGURE 3 SEM Micrograph of the 85% Epoxy resin + 10% Hardener + 5% Aluminum oxide blend, cured by method 1.

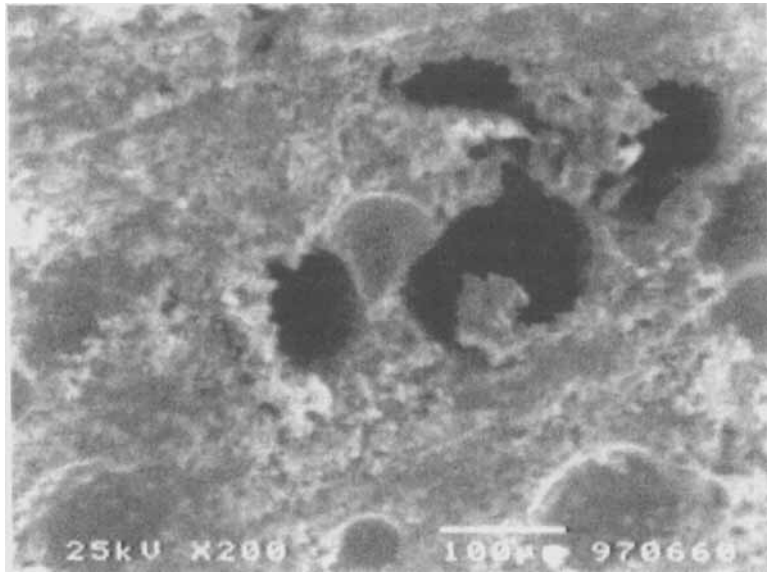


FIGURE 4 SEM Micrograph of the 85% Epoxy resin + 10% Hardener + 5% Aluminum oxide blend, cured by method 2.

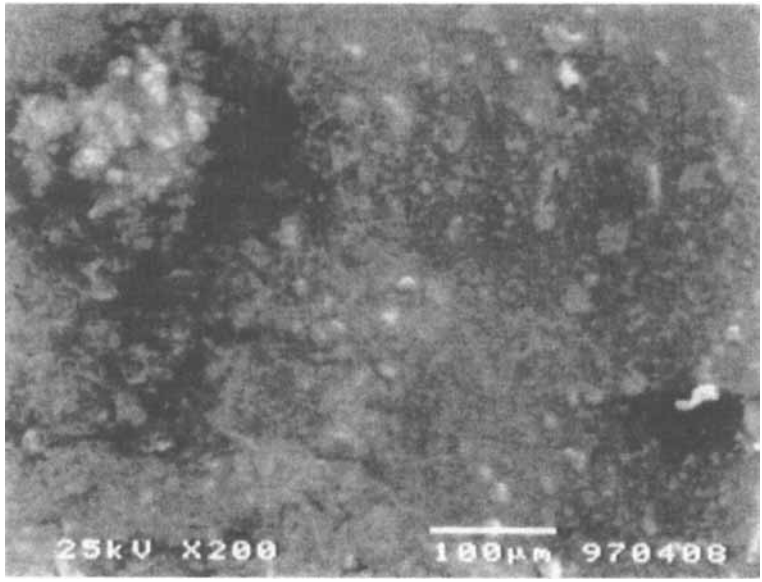


FIGURE 5 SEM Micrograph of the 90% Epoxy-resin + 10% Hardener blend, cured by method 3.

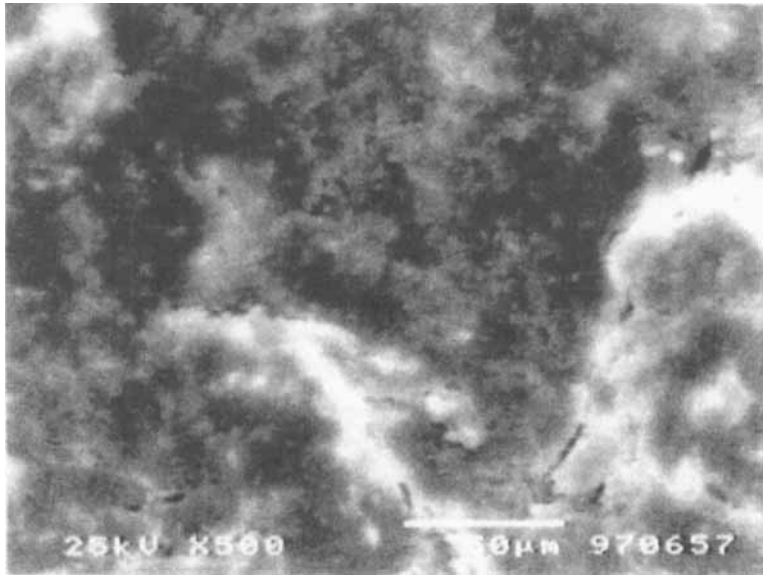


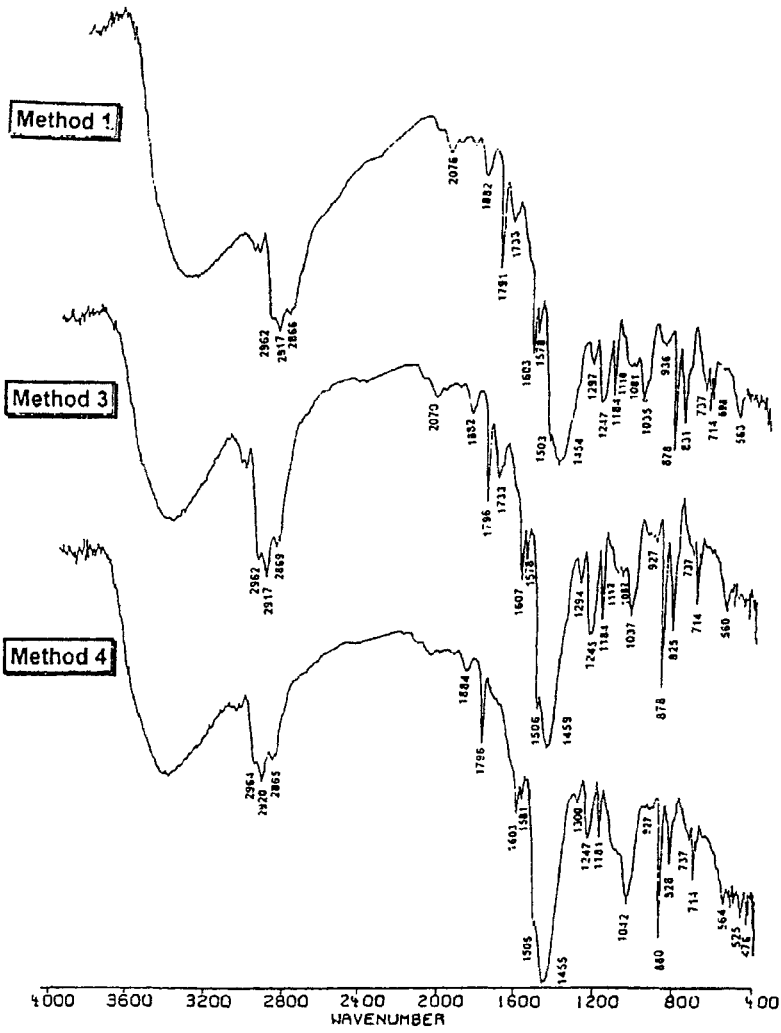
FIGURE 6 SEM Micrograph of the 90% Epoxy-resin + 10% Hardener blend, cured by method 4.

of the less porous blends, cured by different methods are described. In this table it is possible to observe the most important bonds for achieving a complete polymerization (that is the less porous molds) and the structural changes, show in Graph 1.

Structural changes were followed by FT-Infrared spectroscopy. The band at 698 cm^{-1} corresponding to γ_w(CH) aromatic vibration, was not present when methods 3 and 4 were utilized, that is no completed polymerization was obtained. Moreover, the contributions at 2076 cm^{-1}, corresponding to ν(C=O), 1733 cm^{-1}, corresponding to ν(C=O), 1110 and 1081 cm^{-1}, corresponding to δ(CH) [in-plane] aromatic and the 698 cm^{-1} band corresponding to γ_w(CH) aromatic vibrations, when the blend was prepared by method 4, were not detected. This suggest that the CH and C=O bonds are not strongly completed yet.

TABLE II FT-Infrared bands of the 90% Epoxy-resin + 10% Hardener blends, processed by different methods

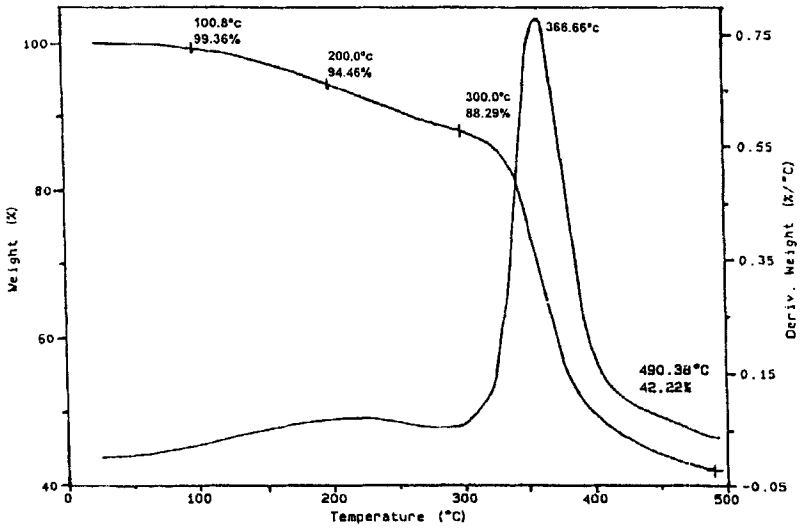
Wavenumber (cm^{-1})			
Method 1	*Method* 3	*Method* 4	*Assignment*
2962	2962	2964	ν(CH)
2917	2917	2920	
2866	2869	2865	
2076	2070		ν(C=O)
1882	1882	1884	
1791	1796	1796	
1733	1733		
1603	1607	1603	ν(C—C) aromatic
1578	1578	1581	ν(C=O)
1503	1506	1506	ν(C=C) aromatic
1454	1459	1455	$\delta(CH_2)$
1297	1294	1300	ν(CO)
1247	1245	1247	
1184	1184	1181	δ(CH)
1110	1112		[inplane]
1081	1082		aromatic
1035	1037	1042	
936	927	927	δ(CH)
878	878	880	[out-of-plane]
831	825	828	aromatic
737	737	737	$\delta(CH_2)$
714	714	714	γ_w(CH)
698			aromatic
563	560	564	δ(C=O) [out-of-plane]



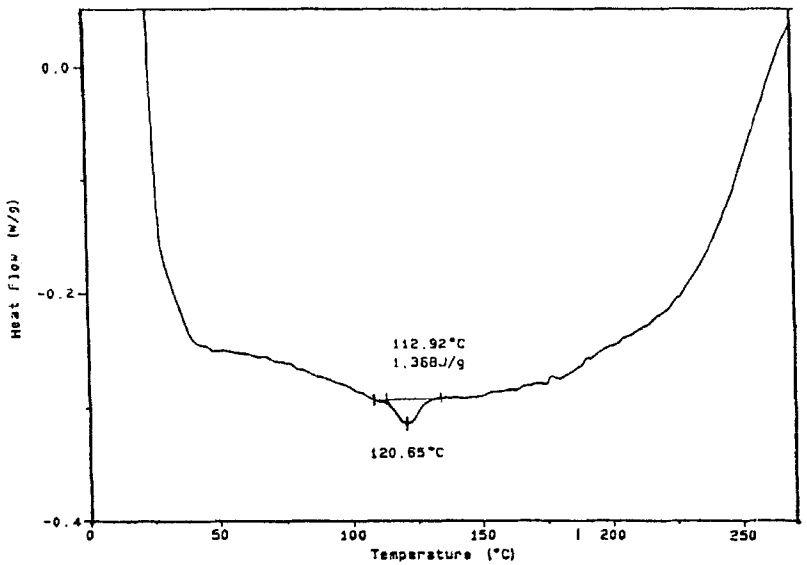
GRAPH 1 FT-Infrared spectra of the 90% Epoxy-resin + 10% Hardener blends, cured by methods 1, 3 and 4.

On the other hand, the most intense bands at 1506, 1455, 1247, 880 and 828 cm^{-1} can serve as indicators to determined the best method for manufacturing of good denture molds.

Finally, Graph 2 shows the thermal behaviour of the best blend, where a 0.7% of loss mass when the optimum temperature (100.8°C) is



GRAPH 2 Plot of Weight (%) *vs* Temperature of the 90% Epoxy-resin + 10% Hardener blend, cured by method 1.



GRAPH 3 Plot of Heat Flow *vs* Temperature of the 90% Epoxy resin + 10% Hardener blend, cured by method 1.

reached was found whereas, a loss of 11.8% for 300.0°C, was also observed. This ensures a minimum mass loss (0.7%) when a new denture will be prepared by using this mold. On the other hand, at 120.6°C the glass transition temperature (T_g) was found with 1.36 (J/g) of Heat Flow ratio (Graph 3), which is related to the C—H bonds corresponding to the 2964–2865 cm^{-1} region. That is, the use of microwave energy produce, at the very same time bonds destruction and chain crosslinking, with the result of a better temperature stability.

CONCLUSIONS

The influence of the Hardener content on the porosity degree of the Epoxy resin + Hardener blends, allows to propose the most adequated proportion of Hardener as well as the best preparation procedure as well as the most adequated power in the microwave oven for manufacturing good denture molds.

The porosity was not improved when the Alumina was added. Nevertheless, the lowest porosity was achieved by the 90% Epoxy resin + 10% Hardener blend, which was processed and set for 24 hours, and irradiated in the LOW mode (90 watts) for twelve minutes. The morphology shows a very good homogeneity with some irregular polymeric particles.

By using FT-Infrared spectroscopy it was possible to detect the most important molecular bonds participating in the polymerization of the best artificial denture mold, which correspond to the 1506, 1455, 1247, 880 and 828 cm^{-1} bands, as well as to determine the best manufacturing method. On the other hand, the evaluation of the good adhesion between the polymeric components was checked out by using both TGA and DSC techniques, which show that the blend is stable at high temperatures, with only a mass loss of 11.8% up to 300.0°C, and a glass transition temperature of 120.6°C.

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