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Characteristics of Ethoxylated-BisGMA as Base Resin of Restorative Composite

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Abstract

The characteristics of Ethoxylated-BisGMA (E-GMA) composite were investigated to find out its possibility as an alternative to Bis-GMA. Even though Bis-GMA has been most commonly used as a major matrix for the restorative composites, Bis-GMA has an inherent problem of huge viscosity. In this study, the properties of E-GMA composite were investigated and compared with those of Bis-GMA composite. The E-GMA composite exhibited much better physical-chemical properties than Bis-GMA/TEGDMA (70wt%/30wt%) composite; for example, deeper depth of cure, higher degree-of-conversion (DC), lower polymerization shrinkage, and lower water sorption. From these experimental results, it might be suggested that E-GMA could be used as a promising alternative to the most widely used material of Bis-GMA.

Keywords

Ethoxylated-BisGMA; Restorative; Composite; Bis-GMA

Introduction

Resin composites, which are composed of a resin matrix and inorganic fillers, are extensively used in dental restorative treatment. Restorative dentistry has faced problems brought by the inherent volumetric shrinkage, marginal gap formation, discoloration, and post-operative sensitivity. The most common monomer in commercially available dental resin composite is Bisphenol-A-glycidyldimethacrylate (Bis-GMA), which was developed by Bowen in 1962 to improve the physical properties of acrylic resin [Bowen, 1963]. Bis-GMA monomer has a stiff central phenyl ring core and the two pendant hydroxyl-groups, which are slightly hydrophilic and responsible for the high water sorption [Kalachandra *et al.* ,1991] and the extremely high viscosity due to its strong hydrogen bonding [Cook 1992, Kalachandra *et al.* 1997]. The high viscosity of Bis-GMA necessitates diluent such as TEGDMA to achieve high filler loading for a better physical properties of the composite. However, a diluent monomer (e.g., TEGDMA) leads to higher water uptake and higher polymerization shrinkage. The stress generated by volumetric shrinkage at the tooth-restoration interface creates marginal gaps, which adversely influence the longevity of a resin composite restoration. In order to avoid the adverse effects of curing shrinkage by the diluent comonomer such as TEGDMA, in this study, ethoxylated-BisGMA (E-GMA) was employed as a base resin matrix in place of Bis-GMA. The E-GMA is structurally analogous to Bis-GMA with a stiff central phenyl ring core. However, the E-GMA does not have the two pendant hydroxyl groups which cause the strong hydrogen bonding. Therefore, the E-GMA has low viscosities to eliminate the use of the diluent monomer [Kawaguchi *et al.*, 1997; Labella *et al.*, 1996].

In this experiment, the properties of the E-GMA composite were determined and compared with those of the Bis-GMA/TEGDMA (70wt%/30wt%) composite. To compare depth of cure, degree of conversion, the polymerization volumetric shrinkage, water uptake, flexural strength, and diametral tensile strength, the specimens of E-GMA composite and Bis-GMA/ TEGDMA(70wt%/30wt%) composite were fabricated according to ISO 4049 specification and polymerized by irradiating with visible light (Monitex LD-105, Taiwan).

Materials and Methods

Materials

The chemicals for the preparation of the composites were used as received from manufacturers (Aldrich Chemical Co. Inc.,USA); Bis-GMA as a base resin, TEGDMA as a diluent, E-GMA as an alternative base resin, the photo-initiator Camphorquinone(CQ), N,N-dimethylamino ethyl methacrylate (DMAEMA) as a co-initiator, an accelerator, visible light stabilizer, oxygen inhibitor or polymerization inhibitor Hydroquinone(HQ). The γ- methacryloxy propyltrimethoxysilane(γ-MPS) treated silica (Sukgyung AT, 0.05 μm) and barium glass (Sukgyung

AT, 1 ㎛) were used as an inorganic fillers.

Methods

Specimens preparation : The specimens of E-GMA composites, which were loaded with 70wt% silanated fillers (20wt% silica and 80wt% barium glass), the mixed monomer comprising of Bis-GMA and TEGDMA (70/30 wt/wt) as control were prepared.

Measurement of Depth-of-cure : Specimen discs with 6.0mm in thickness and 4.0mm in diameter were prepared and the depth of polymerization of the composite was measured according to ISO 4049 standard specification.

Measurement of Degree-of-conversion(DC) : The degree of photopolymerization conversion of specimens was measured by FTIR spectroscopy (FTLA 2000-104, ABB Inc.). The specimens were placed between two polyethylene films, pressed to form a very thin film and the absorbance peaks of the un-cured specimens were obtained. The specimens were then light-cured for 40 seconds using a dental light source with an irradiance of circa 800mW/cm^2 (Monitex LD-105, Taiwan) and the Spectra were obtained by 64 scans at a resolution of 4cm^{-1} for the cured specimens. Degree-of-conversion (DC%) was determined from the ratio of absorbance intensities of aliphatic cabon-carbon double bonds (C=C peak at 1635cm^{-1}) before and after curing of the specimen, with the aromatic ring of the monomer C·=C bonds (peak at 1608cm^{-1}) used as a internal reference. From this ratio, the degree-of-conversion was calculated by standard baseline techniques [Ferracane *et al.*,1984].

$$DC(\%) = 100 - \frac{[Abs(aliphatic\ C=C)/Abs(aromatic\ C=C)]_{after\ cure}}{[Abs(aliphatic\ C=C)/Abs(aromatic\ C=C)]_{before\ cure}} \times 100 \qquad (1)$$

Measurement of Polymerization Shrinkage: Specimen with 25mm(length)×2mm(width)×2mm(height) was fabricated and volumetric shrinkage measurements were performed by density kit (SMK-103, SHIMADZU) at 23.0±0.1ºC. The volumes of the specimen before polymerization and after polymerization were determined by;

$$V = \frac{(M_{air} - M_{water})}{\rho_w} \qquad (2)$$

and then polymerization shrinkage was obtained by;

$$V_{after\ polymerization} / V_{after\ polymerization} \times 100 \qquad (3)$$

where V, M_{air}, M_{water}, and ρ_w , are specimen volume(cm^3), specimen weight in air(g), specimen weight in water(g), and density(g/cm^3), respectively.

Measurement of Water Sorption(W_{sp}) : Specimen discs with 1.0mm in thickness and 15.0mm∅ in diameter were fabricated, and *water sorption* of the composite was measured according to ISO 4049 standard specification. Water sorption was calculated using the equation;

$$W_{sp} = \frac{(m_2 - m_3)}{V} \qquad (4)$$

where W_{sp}, m_2, m_3, and V are water sorption(μg/mm^3), weight of specimen immersed in water for 7 days(μg), weight of retreated specimen(μg), and volume of specimens(mm^3), respectively.

Measurement of FS and DTS: For determining the flexural strength (FS), specimen with 25mm (length) ×2mm (width) ×2mm(height) was fabricated. Flexural strength (FS) was measured by pressing the center of the specimen with Universal Testing Machine (UTM, LR10K, Lloyd instruments) at a cross-head speed of 1.0mm/min according to ISO 4049 specification. The flexural strength of specimen was given by

$$FS = \frac{3Fl}{2b \cdot h^2} \qquad (5)$$

where *FS*, *F*, , *b* and *h* are flexural strength (MPa), maximum load(N), distance between supports(mm), specimen width(mm), and specimen height(mm), respectively. For measuring the diametral tensile strength (DTS) by compression with UTM(LR10K, Lloyd instruments) at a cross-head speed of 1.0mm/min, specimen discs with 4.0mm in height and 8.0mm in diameter were fabricated. The diametral tensile strength (DTS) was given by;

$$DTS = \frac{2P}{\pi DT} \qquad (6)$$

where *DTS*, *D*, *T* and *p* are diametral tensile strength(MPa), specimen diameter(mm), specimen thickness(mm), and maximum load(N), respectively.

Results and Discussions

TABLE 1. THE MEASURED PROPERTIES OF ETHOXYLATED-BISGMA COMPOSITE AND BIS-GMA/TEGDMA (70WT%/30WT%) COMPOSITE LOADED WITH 70WT% SILANATED FILLERS

Resin composite	**Bis-GMA/TEGDMA (70wt/30wt)**	**Ethoxylated-BisGMA**
Depth of cure	5.2mm	6.0mm
Degree of conversion(%)	66	73
Polymerization shrinkage(%)	7.0± 0.4	2.4± 0.4
Water sorption(μg/mm^3)	4.1± 0.2	1.0± 0.4

Ethoxylated-BisGMA (E-GMA) composite was prepared and compared with Bis-GMA/TEGDMA (70wt%/30wt%) to find out whether it might be an alternative to Bis-GMA. For comparison, Bis-GMA/ TEGDMA (70wt%/30wt%), which was most commonly found in commercial, was fabricated and its properties was measured as control. The properties were summarized in Table 1.

Depth of Cure: Photo-cured resin composites have been used widely for restoration of teeth because they are easy to handle and have improved esthetics and enhanced mechanical properties relative to chemical-cured composites. However, major clinical problems caused by photo-cured resin composites are related to the limited curing depth and the lower rate of polymerization conversion deep within the resin composite [Arikawa *et al*, 2004]. This decrease in the polymerization conversion of the resin composite occurs because the photo-energy of visible light passing through the resin composite does not penetrate the resin composite sufficiently to reach the cavity floor and to activate the photo-initiator, such as Camphorquinone, CQ [Asmussen, 1982; Chung *et a.l*, 1988; Kawaguchi *et al.*, 1994]. This is because scattering of visible light occurs at the resin-silica interface [Inokoshi *et al.*, 1996; Azzopardi *et al.*, 2009]. The experimental value of depth-of-cure of the E-GMA composite is 6.0mm, which is deeper than that of Bis-GMA/TEGDMA (70wt%/30wt%) composite. Also, it is much more deeper than the minimum value of depth-of-cure 1.5mm specified in KP ISO4049.

The-degree-of-conversion(DC) : As polymerization progresses, the diffusion rate of the propagating free radicals undergoes a rapid decline. Thus, monomer conversion is not complete and, at the end of the reaction, part of the monomers remains as pendant double bonds or unreacted monomers trapped in the polymeric matrix [Noronha *et al.*, 2010]. The degree-of-conversion in composite resin greatly affects the physical properties of the restorative materials. The presence of unreacted molecules, or poorly polymerized resin has several undesirable features. The mechanical strength and hardness of the resin reduced and unreacted components may be leached out from the restoration, causing irritation and secondary carries. As shown in Table 1, the E-GMA composite presented much higher degree-of-conversion (73% conversion) than that (66% conversion) of Bis-GMA/TEGDMA (70wt%/30wt%). It is likely that Bis-GMA, which has strong intermolecula interaction due to the hydrogen bonding, was presented in a composition of 70wt%, along with the fact that the very flexible aliphatic TEGDMA molecule was only 30wt% presented in this composition, might be accounted for decreased mobility and, therefore, low conversion. However, the E-GMA containing material has a much lower viscosity than Bis-GMA. The low viscosity incurs high mobility and, therefore, high conversion. Also, the flexible ether linkages present in the E-GMA molecule facilitate conversion. The E-GMA is a less viscous molecule than Bis-GMA and, thus, has more degrees of freedom. Consequently, it shows a greater conversion rate. The diluent TEGDMA(MW:286 g/mol) has very low viscosity of 0.0086 Pa·s and Bis-GMA(MW: 512 g/mol) shows huge viscosity of 574 Pa·s which is about 60,000 times higher than that of TEGDMA. The diluent TEGDMA interferes the hydrogen bonding between Bis-GMA in the mixture of Bis-GMA/TEGDMA (70wt%/30wt%). It also can act as lubricant in the mixture [White, 1987]. Therefore, the sharp decline of the mixture viscosity might be due to not only disruption of intermolecula association (intermolecular hydrogen bonding) but also lubrication of TEGDMA. However, the E-GMA showed a low viscosity of 3.7 Pa·s, which might be attributed to "no hydrogen bonding between molecules". As expected from the viscosity, degree of conversion of the E-GMA was 73% and much higher than that of Bis-GMA/TEGDMA (70wt%/30wt%) as shown in Table 1.

Volumetric Shrinkage: One of the major drawbacks, especially in dental restorative materials (dental composites) is their polymerization shrinkage which may lead to marginal gaps and secondary caries in the restored teeth. Shrinkage is the result of matrix-phase polymerization of composites and is a major drawback in dental resin-monomers. The polymerization of resin is accompanied by the volumetric shrinkage. As the polymerization proceeds, van der Waals distances are changed to covalent bond distance which results in volumetric shrinkage. The degree of shrinkage is represented by the number of covalent bonds formed, which is the extent of the polymerization reaction. Another reason for the volumetric shrinkage is that the molecular distance between the polymer chains becomes smaller than that between the monomers [Van Krevelen, 1990]. Since the stresses generated from polymerization shrinkage cause defects of debonding at the tooth-restorative interface [Dickens *et al.*, 2005; Santos *et al.*, 2002], reducing or eliminating the polymerization shrinkage is one of the most important issues for dental composite. As shown in

Table 1, the composite with the E-GMA presented much smaller volumetric shrinkage (2.4% shrinkage) than that(7.0% shrinkage) of Bis-GMA/TEGDMA (70wt%/30wt%). Much smaller volumetric shrinkage of the E-GMA might be one of the most prominent characteristics as an alternative to Bis-GMA.

***Water Sorption*:** Water sorption is reduced by the use of more hydrophobic monomer, preventing the hygroscopic expansion. Water sorption might be accounted for the adverse effects such as discoloration and subsequent swelling of restorative materials. The E-GMA monomer is obtained by the ethoxylation of hydroxyl group(-OH) contained in Bis-GMA, which leads to a more hydrophobic molecule, and consequently the material becomes less susceptible to the sorption of liquids. As shown in Table 1, the E-GMA composite exhibited significantly lower water uptake than Bis-GMA/TEGDMA (70wt%/30wt%). It might be attributed to molecular structure; Bis-GMA has two hydroxyl groups (-OH) and, therefore, it has higher affinity to water molecules, resulting in higher water uptake (4.0μg/mm^3). In contrast to that, the E-GMA monomer has "no hydroxyl groups (-OH)", therefore, lower water uptake (1.0μg/mm^3). The experimental value of lower water uptake of the E-GMA might be a good characteristic as a resin matrix.

***FS and DTS* :** Regarding the mechanical properties as shown in Table 2, flexural strength was nearly same values within the limitations of this study. A little bit greater diametral tensile strength was exhibited by Bis-GMA/TEGDMA (70wt%/30wt%) than the E-GMA containing composite. It is expected that TEGDMA molecule behaves as a crosslinking agent [Sideridou *et al.*, 2003], even though TEGDMA molecule is used as a diluent and its degree of conversion is lower than that of the E-GMA composite.

TABLE 2. MECHANICAL STRENGTH OF BIS-GMA/ TEGDMA (70WT%/30WT%) AND ETHOXYLATED-BISGMA COMPOSITE RESIN LOADED WITH 70WT% SILANATED FILLERS.

Resin composite	Bis-GMA/TEGDMA (70wt/30wt)	Ethoxylated-BisGMA
Flexural strength(Mpa)	105± 3.2	103± 4.5
Diametral tensile strength(Mpa)	36± 1.2	32± 2.4

Conclusions

In this work, the specimens of Ethoxylated-BisGMA (the E-GMA) composite and Bis-GMA/TEGDMA (70wt%/ 30wt%) composite were fabricated, and their properties were determined and compared. Their mechanical strength such as flexural strength and diametral tensile strength showed nearly same values. However, the physical-chemical properties of E-GMA composite such as Depth of cure, Degree-of-conversion(DC), polymerization shrinkage and water sorption were 6mm, 73%, 2.4% and 1.0μg/mm^3, which were much superior to those (5.2mm, 66%, 7.0%, 4.1μg/mm^3) of Bis-GMA/TEGDMA (70wt%/30wt%) composite. From these experimental results, it might be suggested that Ethoxylated-BisGMA monomer could be a promising alternative resin to the most widely being used base material Bis-GMA.

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Synthesis of Tic Thin Films by CVD from Toluene and Titanium Tetrachloride with Nickel as Catalyst

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Abstract

Titanium Carbide TiC_x was deposited onto quartz substrates by the chemical vapour deposition (CVD) method. TiC_x thin films were obtained from titanium tetrachloride ($TiCl_4$) and toluene ($C_6H_5CH_3$) as carbon source. Deposits were carried out in the range of substrate temperatures from 300 to 1100 °C, with a source gas molar ratio ($C_6H_5CH_3/TiCl_4 + C_6H_5CH_3$) of 0.8. There was two deposit processes; the first was to carry out without nickel as catalyst and the second with nickel as catalyst.

Results showed that the effect of nickel as catalyst is very relevant to obtain TiC_x. $TiC_{0.87}$ thin films, 0.5 μm thickness, were obtained for deposition temperatures above 900°C using nickel as catalyst. In this case a cubic structure, with a lattice parameter of 4.327 Å and a hardness of 2900 Vickers, was obtained at 1100°C. whilst for substrate temperatures between 300 to 900°C with nickel as catalyst amorphous carbon samples were obtained. For the samples prepared without the presence of the nickel as catalyst only C amorphous thin films were obtained for all deposit temperatures.

Keywords

Titanium Carbides; CVD; Nickel Catalyst; Cubic Structure; Lattice Parameter; Microhardness

Introduction

Carbon and elements from the group IV form the transition metal carbides. From this group TiC_x, which assumes the NaCl crystal structure fcc, is a typical example. TiC_x has a wide range of composition, from $TiC_{0.47}$ to $TiC_{1.0}$, where the complement $1-x$ corresponds to vacancies. Titanium carbide, TiC, is known as one of the hardest carbides with a hardness of 1900 kg/mm^2 at $TiC_{0.8}$. Since it possesses a remarkable thermal and chemical stabilities, its melting temperature is 3067 °C and it is not affected by acids or aqueous alkalis, titanium carbide is therefore of great industrial interest, i.e. as first-wall coating for fusion reactors and coating for tools and bearings. TiC also can be used as decorative thin films. There are several techniques to prepare titanium carbide coatings such as ion plating (IP), sputtering, plasma enjanced chemical vapour deposition (PECVD), reactive ion beam-assisted electron beam – physical vapor deposition (RIBA, EB-PVD), by laser igniting self-propagating high-temperature synthesis LISHS, by self—propagating high-temperature synthesis SHS. Thermal CVD technique has shown to be an effective mean to obtain TiC high purity and defect free films.

Commercial processes involve chemical vapour deposition from hydrogen, methane and titanium tetrachloride at 1200 °C. In this work TiC_x films were deposited on silica quartz by thermal CVD with and without nickel as catalyst. The relation between deposition conditions and the properties like hardness, structure and non–stoichiometry of TiC_x films, was investigated. In addition, preferred orientation, lattice parameter and deposition rate of the TiC_x films were also determined.

Experimental

The experimental system was a typical hot–wall reactor, figure 1. The reactor chamber consisted of a horizontal silica tube, 100 cm length and 2 cm diameter, placed into a furnace. $TiCl_4$ (*l*) (99.99%) and $C_6H_5CH_3$ (*l*) (99.99%) were used as source reactant materials and helium as carrier gas. $TiCl_4$ (*g*) was introduced into the silica tube by bubbling 200 sccm of helium (99.99%) through a glass flask of $TiCl_4$ (l) at 80 °C. The $C_6H_5CH_3$ (g) was introduced into the silica tube by bubbling 40 sccm of helium (99.99%) through a glass flask of $C_6H_5CH_3$ (l) under a temperature of 30 °C. The molar ratio of the reactants $TiCl_4$ (g) and $C_6H_5CH_3$ (g), m_c = [$C_6H_5CH_3$/ ($TiCl_4$ + $C_6H_5CH_3$)], was 0.8. Nickel, which was used as catalyst, was placed in 1 cm^2 area sheets alternating with the quartz substrates, figure 1. Deposition temperatures (T_{DEP}) ranged from 300 °C to 1100 °C, with a deposition time of 45 min. Under similar conditions, deposits were carried out with and without nickel as catalyst. For crystalline samples, preferred orientation and lattice parameters were investigated by X–ray diffraction (XRD) using a Siemens D 500 diffractometer, Cu$K\alpha$ radiation with λ = 1.5406 Å. The thickness of the films was measured with a Dektak IIA equipment. The stoichiometry of the samples was determined by EDS with a Pentafet microprobe linked to a Leica–Cambridge Stereoscan 440 electron microscope. Microhardness measurements on the deposits were carried out with a Matsuzawa Seiki MXT30-UL ultra microhardness tester equipped with a Knoop indenter, suitable for measurement of extremely thin plates that are hard to be measured by the ordinary Vickers hardness testers. The deposition rate was calculated from a linear relationship between the thickness of deposits and deposition time.

Results and Discussion

Nickel as Catalyst

Nickel belongs to a transition metals family in which the elements are very efficient catalysts. Ni is widely used in the laboratory and industry in a umber of liquid–phase and gas–phase processes involving organic compounds. Transition elements are distinguished of main group elements having partly filled d or f shells. The main transition group, or *d*–block elements have partially filled the d shell. Nickel metal ion has, on average, 9.4 valence shell orbitals, –*s*, p_x, p_y, p_z, d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz}– to accommodate its valence electrons to form hybrid molecular orbitals bonded to other groups. These valence orbitals inherent to nickel metal give the capacity to form both sigma (σ) and pi (Π) bonds with other moieties or ligands. This is an ability to form those bonds, one of them is the key factor imparting catalytic properties to the nickel metal and its complexes.

In this work, the reaction between titanium tetrachloride and toluene to obtain titanium carbide may be described as

$$7\ TiCl_4 + C_6H_5CH_3 + Ni\ (catalyst) \rightarrow 7\ TiC + 8\ HCl + 10\ Cl_2$$

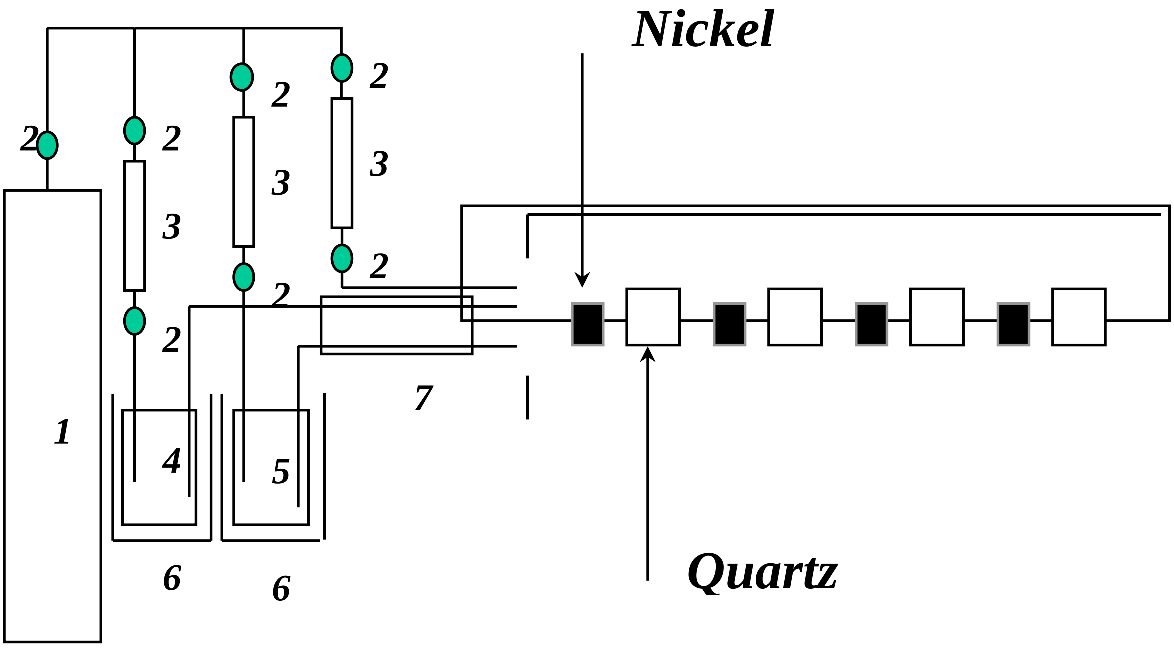

FIGURE 1. SCHEMATIC DIAGRAM OF THE CVD APPARATUS: 1) HE (g), 2) VALVE, 3) FLOW METER, 4) $TiCl_4$ RESERVOIR, 5) $C_6H_5CH_3$ RESERVOIR, 6) CONSTANT TEMPERATURE BATH, 7) RIBBON HEATER, 8) HORIZONTAL SILICA TUBE AND 9) FURNACE.

The presence of HCl and gas chloride as reaction products were detected by conventional methods, however it is necessary to carry out a detailed study about the kinetic of the reaction to elucidate the role of the nickel as catalyst in this process. This work is in progress.

Structure and Film Composition

1) Without Nickel

X–ray diffraction patterns of TiC thin films deposited on fused quartz substrates of 1 cm^2, at different temperatures, 300 °C to 600°C, without the nickel presence, are shown in figure 2. These patterns showed only broad curves, characteristic of graphitic amorphous carbon.

Figure 3 shows the X–ray diffraction patterns of TiC films, which were deposited at substrate temperatures of 700 °C to 1100°C without nickel as catalist. This patterns also showed the amorphous character of the TiC films.

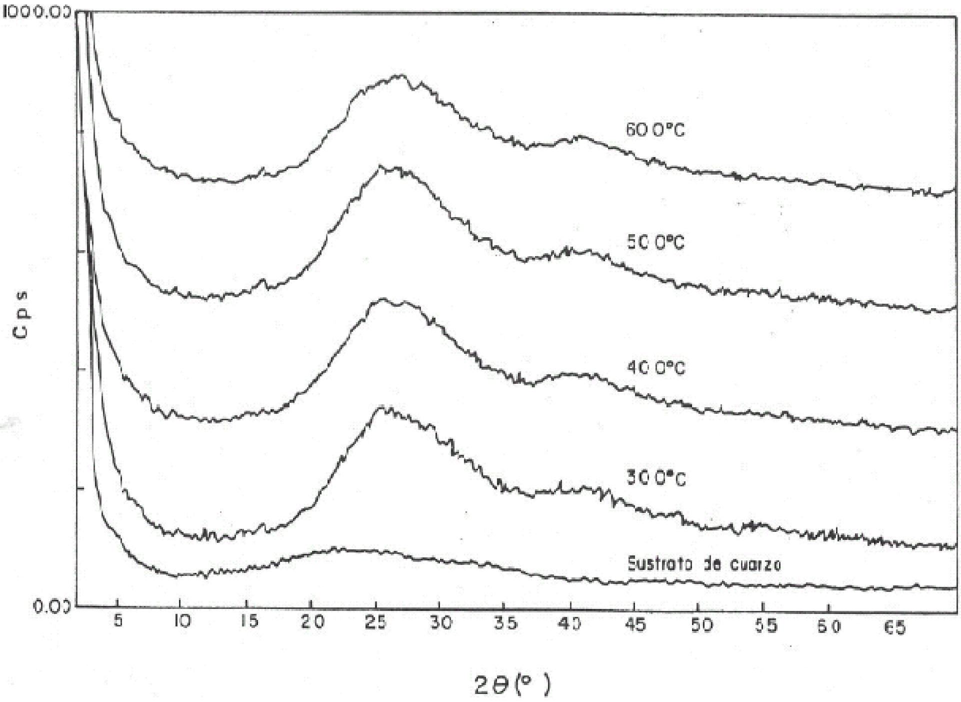

FIGURE 2. X-RAY DIFFRACTOGRAMS PATTERN OF THE AMORPHOUS CARBON THIN FILMS PREPARED AT DIFFERENTS TEMPERATURES WITHOUT NICKEL AS CATALYST.

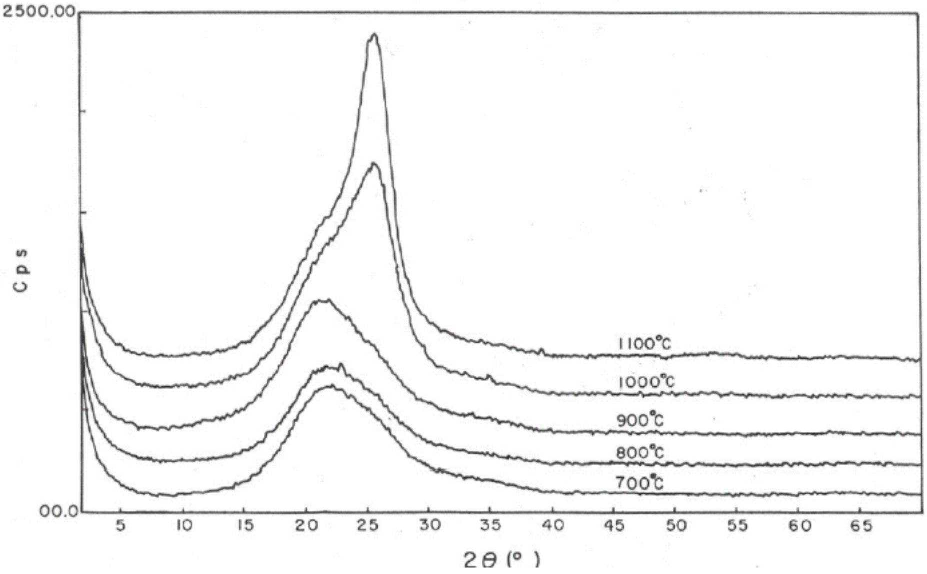

FIGURE 3. XRD ANALYSIS OF THE AMORPHOUS CARBON THIN FILMS PREPARED AT DIFFERENTS TEMPERATURES WITHOUT NICKEL AS CATALYST.

2) With Nickel

Figures 4 and 5 shows the X-ray diffractograms of the TiC films prepared at 300-600^{0}C, 700-900^{0}C temperature intervals's with nickel as catalyst respectively, it is clearly observed that this TiC films are amorphous. X–ray diffraction patterns of the samples prepared at, 1000 and 1100 ºC, using nickel as catalyst during the deposit process, are showed in figure 6. XRD patterns exhibited intense peaks at 35.94, 42.71 and 60.45 2θ degrees, for the two deposition temperatures. These strong reflections are associated to the *fcc* structure of the TiC phase. The lattice parameter *a* of TiC was calculated from the *d* spacing using the most intense peaks. Results indicated that these carbides are cubic with a cell parameter a = 4.3270 Å, which matches well the standard JCPDS 6–1614, also similar to the value a = 4.3285 Å which was reported for the bulk standard, this *a* value is also consistent to that reported by Norton and Lewis.

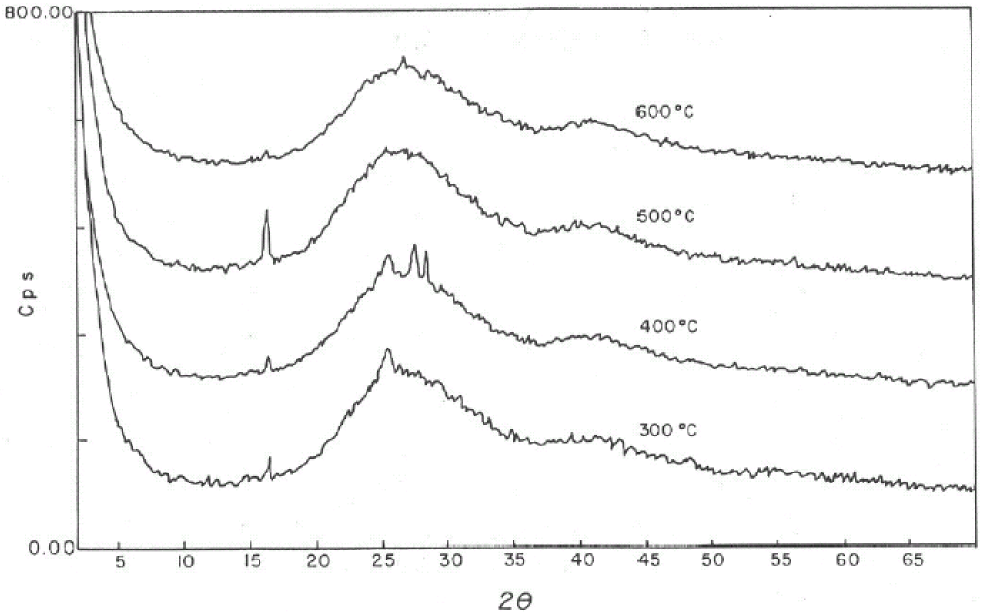

FIGURE 4. X-RAY DIFFRACTOGRAMS OF AMORPHOUS CARBON THIN FILMS PREPARED AT DIFFERENTS TEMPERATURES WITH NICKEL AS CATALYST.

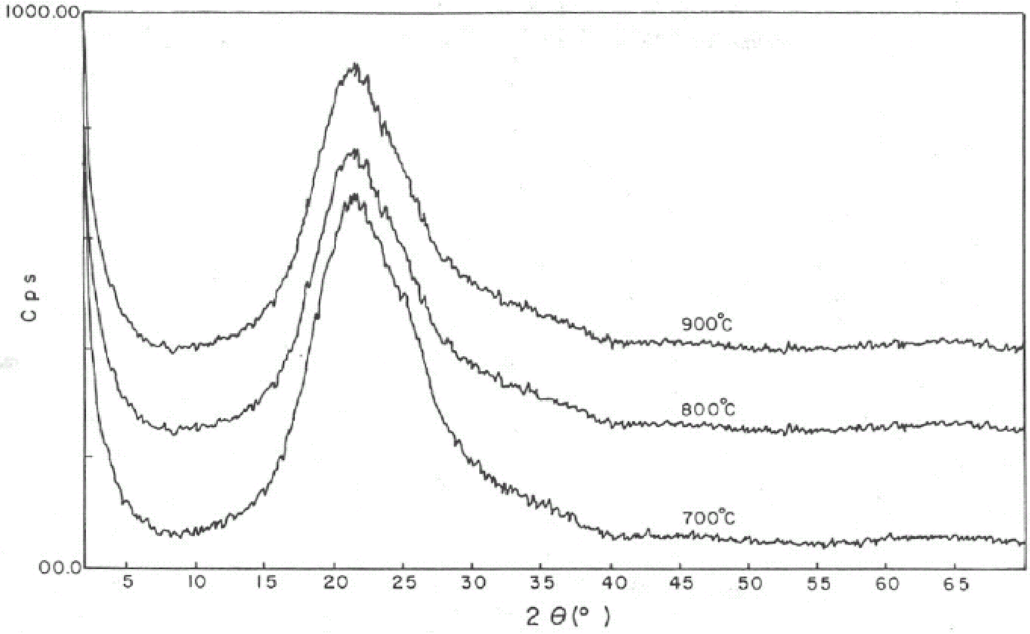

FIGURE 5. X-RAY DIFFRACTOGRAMS OF AMORPHOUS CARBON THIN FILMS PREPARED AT DIFFERENTS TEMPERATURES WITH NICKEL AS CATALYST.

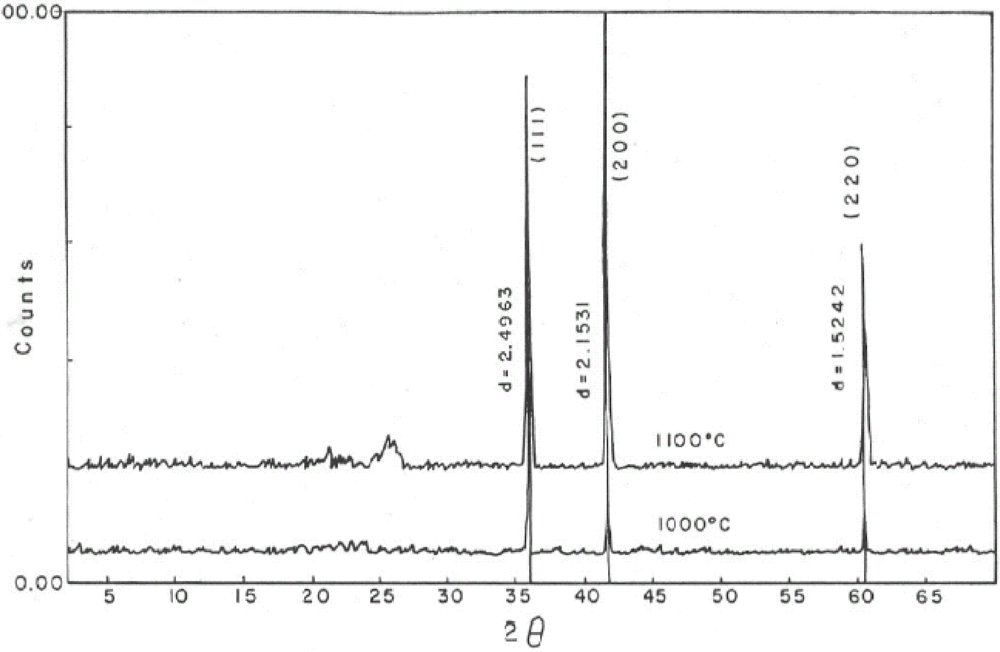

FIGURE 6. X-RAY DIFFRACTOGRAMS OF TiC THIN FILMS PREPARED AT 1000 AND 1100ºC WITH NICKEL AS CATALYST.

The composition ratio x (x =C/Ti) obtained by EDS resulted to be approximately the same value for the two deposit temperatures, x = 0.87. This result is consistent with the study realized by Guinier on TiC obtained by ARE; however these authors concluded that for high values of the molar fraction (> 0.7) x and a are independent of deposition temperature, in this temperature range.

The crystallite size, which were estimated from the full width at half maximum peak using the Scherrer equation, was 230 nm.

3) *Microhardness*

With the use of the indenter Knoop it is possible to measure an indentation length min. of 0.01microm or 100nm. We have TiC films with thickness > 500nm, for that reason, we can be sure that the hardness measurements are of the TiC thin films. For the hardness measurements a load of 50g was used.

TABLE I. MICROHARDNESS FOR CRYSTALLINE TIC FILMS AS A FUNCTION OF THE SUBSTRATE TEMPERATURE.

Substrate Temperature (º C)	**Microhardness (50 g load)** (Vickers)
1000	2500
1 100	2900

The microhardness of TiC film shows a marked dependence on the substrate temperature. Microhardness results of the crystalline TiC films which were deposited in the range temperature 1000–1100 ºC are summarized in table I.

These results are similar to those which were reported by Bunshah´s group on ARE deposited films.

Conclusions

Thermal CVD of toluene and titanium tetrachloride were carried out at deposition temperature range 300 – 1100 ºC on quartz substrates using helium as carrier gas.

Deposits were obtained with and without nickel as catalyst. Below 900 ºC, X–ray diffraction revealed that the films prepared with nickel as catalyst are of amorphous carbon, whilst those films deposited betwen 300 to 1100 ºC without nickel as catalyst all exhibited amorphous carbon.

$TiC_{0.87}$ films with *fcc* structure and lattice parameter of 4.3270 Å were obtained using nickel as catalyst and substrate temperatures of 1000-1100 ºC. This films exhibited 2500 and 2900 microhardness vickers respectively.

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