Effect of the addition of bio-polymer lignin on the Transverse and Impact strength of the autopolymerizing acrylic resin.

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Summary:

Background: Acrylic resin dentures are susceptible to fracture; it is unresolved problem in prosthodontics. The repair procedure should be simple, strong, and accurate. This study evaluated the transverse and impact strength of autopolymerizing acrylic resin, the repair material was modified with kraft lignin as a new enforcement material and compared with the commercially available self cured acrylic resin.

Materials and Methods: The addition of kraft lignin to the acrylic resin were done in percentages of 0.25%, 0.5%, 0.75%, 1.0%, 1.25%, and 1.5% (wt%). Seventy specimens were made according to the ADA specification No 12 for transverse strength using three point bending test and Impact strength test was conducted following the procedure given by the ISO 179 with Charpy Type Impact testing instrument.

Results: Mean transverse strength of experimental specimens where increased only in 0.25wt% addition of lignin (61.3400 Mpa) then results tend to decrease, and no statistical differences found between the control and any one of the modified groups. The impact strength increased more than the control in the groups 0.25, 0.50, 0.75,and 1.0wt%,13.9700, 15.5900, 35.2100, 33.6900 Kj/m^2 respectively, then has been decreased at 1.50wt% until reach value of the control (9.2525 Kj/m^2).Highly significant difference was found at 0.5, 0.75 and 1.0wt% ($p<0.05$).

Conclusions: The autopolymerizing acrylic resin exhibited significantly higher impact strength as a result of addition the biopolymer lignin. The transverse strength of the modified specimens was decreased after increasing the weight percent addition of lignin.

Key words: Autopolymerizing acrylic resin, KL (kraft lignin), transverse strength, impact strength.

Introduction:

Loss of teeth is a matter of great concern to a majority of people, and their replacement by artificial substitutes, such as dentures, is vital to the continuance of normal life. Acrylic resin dentures are susceptible to fracture (1). The fracture of dentures may be due to the mechanical properties of the acrylic resin or may be due to a multiplicity of factors leading to failure of the denture base material. Generally, various modifications of PMMA have been tested to improve the existing material; these modifications include chemical modification to produce rubber graft copolymer high impact resins (2).

One of the first dental uses of the self-curing resins, based on methyl methacrylate, was as a repair material for artificial dentures. The self curing resins appear to offer advantages the heat-curing type for use in repairing dentures by: quickly making repair, no heating equipment is needed to process, and no external heat need to apply for polymerization (3; 4).

Satisfactory repairs must have adequate strength be easily and rapidly completed, retain its dimensional accuracy and restore the original strength of the denture so as to avoid further fracture, but this is not always possible. (1).

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Lignin in polymers:-Lignin is a polymeric material that has active groups; it is used to improve many physical, mechanical and thermal properties for polymers through many studies done by researchers in this field. A polymer blends consisting of hydroxyl propyl lignin and poly (methyl methacrylate) was prepared by injection moulding and by solution casting. The addition produced an increase in modulus and a decrease in ultimate properties (5).

Kraft lignin was also tested as specific filler for rubber, which leads to an increase of hardness and improvement of abrasion resistance (6).

In 2005, Mansur et al confirmed the high potential application of lignin as a nontoxic natural polymer binder to be used as three dimensional scaffold template for biomedical applications (7).

It was suggested that lignin is expected to improve toughening properties, the connectivity in the network, adding stiffening groups to the matrix, inducing plasticity, enhanced photoresistance and thermal stability(8).

Finally, the characterization of lignin, one of the most abundant plant constituent has recently been the subject of much interest, due to its complex and varied structure and diverse molecular weight. Nevertheless, by means of powerful analytical methods, the characterization of lignin has been achieved.

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Objectives of the study: Evaluate some mechanical properties of the modified PMMA as transverse strength, impact strength via commercial available cold cure acrylic denture base material.

Materials and Methods

The study was carried out in the Department of Prosthodontics, College of Dentistry, University of Baghdad.

The materials used in this study include: self curing polymethyl methacrylate (powder and liquid-Major, Italy), alkali kraft lignin (powder- Aldrich company) which was used as reinforced material.

Lignin was blended with ordinary PMMA powder and proceed in conventional flasking method to give the appropriate test specimens. The powder of kraft lignin was incorporated into the powder PMMA at concentrations of 0%(control) 0.25%, 0.50%, 0.75%, 1.0%, 1.25%, and 1.50% (wt%). A total of 70 specimens (35 for each test) were fabricated. 5 specimens for each of the experimental as well as control groups.

Mould preparation:- Moulds were prepared by using either wax pattern blocks or machined stainless steel standards according to the required measurements of the adopted specimens. Metal specimens of dimension 65×10×2.5 mm were prepared for transverse strength test and wax blocks of (55mm **x** 10mm **x** 10mm) dimensions were prepared for impact strength test. Each block was fixed on a flat glass plate; stone slurry according to the mixing ratio was prepared and poured into the lower half of a dental flask. The glass plate was then turned over and the wax block immersed in the stone slurry. The investing stone was left for one hour to set, and then the glass plate was removed. The set stone was coated with separating medium (alginate solution) and subsequent steps of conventional flasking technique including investing, wax elimination and packing was followed.

P/L ratio of acrylic was 2.5g: 1.0ml w/v according to a pilot study, and the polymer and monomer were mixed for 45 seconds and the mixture was left at room temperature in a closed jar to reach the required dough stage. Each flask was packed with resin once it reached the dough stage; the two halves of the flask were closed together and placed under press (Hydrofix press-Germany) with slow application of pressure to allow even flow of the dough through out the mould space, left for 15 minutes, then released. The flasks were left clamped for 45 minutes till complete curing. The flasks were opened and acrylic specimens were carefully retrieved. Excess flash was trimmed and the test specimens finished and polished.

All the tested specimens were conditioned in distilled water at 37° C for 48 hours before they were tested according to ADA specification No- 12 (9).

Transverse strength:- The three-point transverse tests (flexural or bending) were conducted in accordance with ADA specification No.12.

$$S = \frac{3FI}{2bd^2}$$

S= Transverse strength (N/mm^2) =MPa
F= the maximum load in Newton=N
I= the supporting width in mm. =50
b= the width of the test specimen in mm.
d= the height of the test specimen in mm.

Impact Strength Test::- Charpy impact strength of unnotched specimens was adopted, the impact energy absorbed in breaking an unnotched specimen, according to ISO 179- 1982.

The specimen was supported horizontally at its ends and strucked in its middle by a 2 joules, free swinging, pendulum which is released from a fixed height. And digital display to show the impact energy. A pendulum of testing capacity was used. Some samples offered resistance to the shock, and not fracture therefore; five joules pendulum was used.

$$\text{Impact strength} = \frac{A}{X.Y} \times 10^3$$

A = is the impact energy in joules.
X = is the width dimension, in millimeters, of the test specimen.
Y = is the height dimension y, in millimeters, of the test specimen.

Statistical Analysis:- Statistical analyses were done by using SPSS version 16 (statistical package for social science).The statistical analysis includes the following:

1. Arithmetic mean and standard deviation
2. Descriptive and statistical tables.

The results were analyzed by analysis of variance (ANOVA); test to examine the significant difference between the groups. Further exploration of statistical significance of difference in mean between each group and control were assessed by Dunnett t test multiple comparisons. Post Hoc analysis for each test variable.

Results:

The transverse strength of the specimens as a function of different kraft lignin (KL) content of modified acrylic resin expressed as mean and standard deviation shown in Table (1). Addition of 0.25% KL, give the highest effect (61.340 MPa). Then the results showed a decreasing effect. Applying ANOVA test revealed highly significant differences between groups (0.00)

Acrylic resin containing KL of 1.0 wt% and above possess lower values of transverse strength compared with that of the unmodified acrylic (38.2475MPa), more statistical investigation was done by applying multiple comparison Dunnett t-tests between the control and each group of the experimental materials. The results in Table (2) represents no significant differences between the control and all groups at ($p < 0.05$).

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Table (1): Mean standard deviation and ANOVA test results of Transverse strength related to lignin wt%.

Lignin (wt %)	Mean(Mpa) Transverse strength	Std. Deviation	ANOVA	
			Between Groups	
0.00	56.1475	7.68010	**Sum of Squares**	1841.788
0.25	61.3400	1.33492	**df**	6.000
0.50	53.6025	10.05859	**Mean Square**	306.965
0.75	52.5400	6.84599	**F**	7.762
1.00	48.4900	4.64071	**Sig.**	0.000
1.25	38.4050	4.07631		
1.50	38.2475	5.46457		

Table (2): Multiple comparison of transverse strength test results.

	Dunnett t Test Transverse Strength (Mpa)			
(I) Lignin	(J) Control	Mean Difference (I-J)	Std. Error	Sig.
0.25	0.00	5.19250	4.44669	N S
0.50	0.00	-2.54500	4.44669	N S
0.75	0.00	-3.60750	4.44669	N S
1.00	0.00	-7.65750	4.44669	N S
1.25	0.00	-17.74250	4.44669	N S
1.50	0.00	-17.90000	4.44669	N S

Impact strength test:-The mean values and standard deviation related to impact strength of the modified self cured acrylic resin samples were evaluated and presented in (Table-3). However, it was found that the impact strength of different samples were increased until 0.75wt %(35.21 kj/m^2) which is the more pronounced effect, followed by 1.0wt% content (33.69 kj/m^2), then the impact strength tends to decrease with increasing KL percentage. ANOVA analysis (Table-4) revealed highly significant differences between the mean values were observed for the measured groups. Applying multiple comparisons Dunnett t test between the control and experimental groups revealed that highly significant differences were found in the 0.50, 0.75, and 1.0 wt% of lignin.

Table (3): Mean, standard deviation and ANOVA test results of Impact strength related to lignin wt%.

Lignin (wt %)	Mean (KJ/m^2)	Std. Deviation	ANOVA	
0.00	9.2525	2.96813	**Between Groups**	
0.25	13.9700	1.50800	**Sum of Squares**	2969.429
0.50	15.5900	0.78681	**df**	6.000
0.75	35.2100	4.03492	**Mean Square**	494.905
1.00	33.6900	4.42150	**F**	56.680
1.25	12.2025	2.84921	**Sig.**	0.000
1.50	9.6550	2.33862		

Table (4): Multiple comparison of Impact strength test results.

	Dunnett t Test Impact Strength (Kj/m^2)			
(I) Lignin	(J) control	Mean Difference (I-J)	Std. Error	Sig.
0.25	0.00	4.71750	2.08944	0.072
0.50	0.00	6.33750*	2.08944	0.015
0.75	0.00	25.95750*	2.08944	0.000
1.00	0.00	24.43750*	2.08944	0.000
1.25	0.00	2.95000	2.08944	0.281
1.50	0.00	0.40250	2.08944	0.799

Discussion

This study has been carried out for evaluating the effect of bio-polymer lignin, which is a natural product in plants, non-toxic and non-degradable. Addition of lignin to the self curing acrylic resin repair material has been studied here. However, no studies have been reported on such application. Natural polymers generally exhibit a larger amount of variation of functional groups and linkages. The effect of KL addition is a complex interplay between reinforcement and plasticization. The level of improvement depends on the size of the lignin molecules and cross- linked density of the matrix polymer. Using lignin in many studies has received a considerable amount of attention. The application found limited positive to negative effects on mechanical properties. Mechanical property improvement or no property deterioration was obtained up to certain lignin load (8). Many factors affect the properties of polymers, including the chemical composition of chain its degree of polymerization, and the number of branches and/ or cross-links between polymer chains. (10).Method for converting lignin which is non-degradable biopolymer (11) to a useful thermoplastic, with synthetic thermoplastic polymer, PMMA. During the polymerization process, formation of some sort of crosslinked polymer may occur (12).

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Transverse strength:-In order to investigate the effectiveness of modifiers or fillers in acrylic resins, various mechanical tests can be performed. The commonly used method is transverse strength and impact strength (13; 14). The sample preparation followed the ADA specification No. 12 to test the transverse strength, which was tested using 3-piont bending test. The popularity of transverse bend test, as a method of evaluation has obviously been influenced by desire to make a test condition approximate in service conditions as closely as possible. The evaluation is based on a three point loading system, since it reflects the loading arrangement in the clinical situation. It was carried out using Instron Universal testing machine.Results showed that there was no statistical difference between the control and any of the modified materials used, when applying multiple compression t test Table-2.

The effect of lignin on the mean transverse strengths of cold cure acrylic resin was a slight increase, which was not significant for all weight percentages. 0.25wt% of KL increased the transverse strength of the resin slightly.

Results in the present study may be attributed to the higher plastisizing effect of the lignin. Because of long chain and cross linking occurs among the chain; may lead to mechanical properties reduction (15). Mechanical grinding is one of the actions that lead polymerized chain to breakdown through grinding. This process is similar to other types of degradation in which the effects of outer forces as accumulated heat formed mechanical effects, which can cause stress on certain points that if exceeds a certain limit will lead to breakdown of polymeric chain. It can be seen that the mechanical effect are converted to chemical effect in the polymers (16). During finishing and polishing of samples, the use of carbide or diamond finishing burs. Their use is thought to weaken the surface through the formation of micro creaks or to degrade the matrix through the generation of heat (10). The transverse strength of a autopolymerized resin was not significantly increased. Values for transverse strengths of most specimens were close, and the results were then decreased when increasing the wt% when lignin-reinforced specimens were compared with the control group. This may be related that at higher loading in polymer the compatibility maybe decreased between the PMMA and kraft lignin of high molecular weight, which may act as poor compatibilizer (17). As a result, in adequate compatibility between the two polymers, may lead to weakening the molecular interaction between the two resins, consequently decreasing the mechanical properties. In addition to that, different types of lignin are produced commercially; the reactivity of industrial lignin is much lower than that of phenolic resin because of their low phenolic hydoxyl content high ring substitution and steric hindrance (18). This explains the relatively low values obtained for the transverse strength measurement in groups of high lignin content. However, lignin particles which did not dissolves act as inclusion bodies, and each particle actually caused a micro fracture that weakened the resulting resin. This is in accordance with the findings of Wool (11) who reported that the flexural strength of vinyl ester improved for lower lignin fractions.

Impact strength:-Is a measure of the energy absorbed by the material before fracture (19). Impact test is designed to test the resistance of material to the sudden application of a load. A standard bar specimens is subjected to an impulse load provided by a heavy pendulum. Although the test is empirical, it provides a useful means of comparing impact resistance of a range of materials (20). However, depending on the loading configuration (Izod or Charpy), the specimen's dimensions and the presence of notches and their geometry, this test can result in different values of impact strength (13).

The result showed in Table (3) of impact strength revealed that it was raising with increasing kraft lignin contents up to 0.75 wt% (35.2100 kJ/m^2). The results demonstrated that there are a highly significant difference between groups of lignin (P=0.000) in ANOVA test Table (3), when applying Post-Hoc (Dunnett t-test) multiple comparison Table (4),There were significant mean difference between 0.50wt% group and control group (6.33750 Kj/m^2) ,and highly significant differences in 0.75wt% , 1.0 wt% and control group (P=0.000). Reduction of impact strength in 1.25 wt% and more maybe related to the high molecular weight of lignin, this may act as bad compatibilizer, lead to decrease the adhesion between PMMA matrix and lignin, or aggregates of lignin particles which act as stress concentration and reduce strength. This agreed with Uzun et al (21) who studies the effect of fiber reinforcements and reported that changes in the impact strength and transverse strength should be due to difference stress distribution, fiber structure, volume fraction and adherence to the matrix. This reduction could be the result of cross-linking and void spaces because if thick specimen dimensions that may act as stress concentration points in that polymer matrix and these decrease interfacial bonding, agreed with the results of Karacaer et al (19).

The impact strength of this study showed a plasticization effect with the addition of kraft lignin, plasticization is known to have a beneficial effect on the fracture properties of polymer. It is common practice to add plasticizers to these polymers to improve their fracture properties, as PMMA broke with sharp fracture. Many materials as high strength acrylic resins, it is not possible to discuss the mechanisms of reinforcement of individual acrylic resins as most manufacturers of denture base materials are reluctant to reveal the exact constituents of the products, or the mechanisms of reinforcement used (2;22). According to the structure of kraft lignin, cross-linking may occurred, and high concentrations of cross-linking agents are avoided, because their observed effect in reducing

tensile strength and impact resistance, this was also reported by Price (23).

On conclusion, the present work a new reinforcing system for PMMA has been developed based on lignin biopolymer. It is a convenient method to develop products with desirable high impact properties, with low percentages so as not to deteriorate the other properties.

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