Effect of polyimide addition on mechanical properties of PMMA-based denture material

An YANG1,2*, Dan ZHAO1,2*, Yaqin WU1,2 and Chun XU1,2

1 Department of Prosthodontics, Ninth People’s Hospital, Shanghai Jiao Tong University School of Medicine, Shanghai 200011, China
2 Shanghai Key Laboratory of Stomatolgy, Shanghai 200011, China
Corresponding author, Chun XU; E-mail: imxuchun@163.com

The aim of the study was to evaluate the effect of modifying polymethyl methacrylate (PMMA) denture base material with polyimide (PI) on its flexural property and biocompatibility. Low molecular weight (1,500 g/mol) PI was synthesized and small amount of PI (0.4, 0.6, 0.8 and 1 wt%) was dispersed into the PMMA matrix. Three-point bending tests, scanning electron microscopy and thermal cycling were used to measure the mechanical properties, while MTT assay was used to evaluate the biocompatibility of the denture base material. The results showed that 0.6% addition of PI significantly increased flexural strength of PMMA denture base material by 13.5%, compared with the control group (p<0.05). Even after 5,000 hydrothermal cycling the reinforce effect still existed. However, when the PI content further increased, flexural strength of the denture base material decreased due to particle agglomeration. The MTT assay confirmed that the addition of PI did not change the biocompatibility of the PMMA denture base material. The present study suggested that blending polyimide in the proper proportion can be a potential method to strengthen the PMMA-based denture base material.

Keywords: Polyimide, PMMA, Denture base

INTRODUCTION

Polymethyl methacrylate (PMMA) is the leading material for denture base today. PMMA shows good performances in esthetics, biocompatibility and stability in the oral environment1). However, the insufficient strength of PMMA, which might result in fractures of dentures during functioning2,3), still need further improvement. Studies have shown that 68% of PMMA dentures broke within a few years4).

Metal wires and cast metal plates have been used to improve the strength of PMMA denture base, but due to the poor bonding between metal parts and resin, the improvement on mechanical properties was not satisfying5,6).

Another way to strengthen acrylic resin materials was adding various organic and inorganic fillers, such as polyester fiber, polyethylene fiber, carbon fiber, sapphire whiskers, silica or glass particles etc. However, this method has various drawbacks including poor esthetics, tissue irritation, difficulties in handling and polishing, and questionable bonding of the fibers with the resin7). For these reasons, the success of fiber reinforcement remains limited8,9).

In recent years, nanoparticles and nanofibers have been considered as new potential filler for strengthening dental composites due to the large surface area and good stress transferring features10). Many investigations have focused on nanoparticle addition to strengthen PMMA, such as addition of nanosilica11), carbon nanotube12) or TiO2 and SiO2 nanoparticles13), and some of them have shown progress. But on the other hand, decreased mechanical properties of PMMA resulted from nanoparticle addition have also been reported14,15).

Polyimide (PI) is a macromolecule polymer material, owning the collective advantages of excellent thermal stability, mechanical properties and chemical resistance. Meanwhile, polyimides have also been used to improve the thermal or mechanical properties of different matrices16-19). The best known polyimides are those obtained through polymerization of monomer reactants (PMR), which has low cost and simple process20,21).

In this study, a self-synthesized polyimide was blended into PMMA-based denture materials. To make the polyimide better dispersed into the matrix, low molecular weight (1,500 g/mol) and small amount of PI was adopted. Three-point bending tests, scanning electron microscopy and thermal cycling were used to measure the mechanical properties, while MTT assay was used to evaluate the biocompatibility of the denture base material. The results showed that 0.6% addition of PI significantly increased flexural strength of PMMA denture base material by 13.5%, compared with the control group (p<0.05). Even after 5,000 hydrothermal cycling the reinforce effect still existed. However, when the PI content further increased, flexural strength of the denture base material decreased due to particle agglomeration. The MTT assay confirmed that the addition of PI did not change the biocompatibility of the PMMA denture base material. The present study suggested that blending polyimide in the proper proportion can be a potential method to strengthen the PMMA-based denture base material.

MATERIALS AND METHODS

Materials

Type 2 denture base resin powder and liquid were purchased from Second Medical Zhangjiang Biological Material (Shanghai, China). The monomers used in the polyimide polymerization, 4,4'-oxydiphthalic anhydride (ODPA), 4,4'-oxydianiline (ODA), p-phenylenediamine (PPD) and 5-norbornene-2,3-dicarboxylic anhydride (NA), were purchased from Sinopharm Chemical Reagent (Shanghai, China). All raw materials were pulverized before use.

*Authors who contributed equally to this work.
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Synthesis of polyimide
Three structurally similar polyimides of low molecular weight (1,500 g/mol) were synthesized from ODPA, ODA, PPD and NA. The monomer ratio was calculated according to the set molecular weight. The equation of the polyimide synthesis and the structural formula of the PI product are shown in Fig. 1.

The monomer was completely dissolved in alcohol and then mixed with an input of nitrogen. The reaction mixture was further stirred for 8 h at room temperature to yield the polyimide prepolymer solution. Subsequently, the solution was heated in a vacuum oven at 80°C for 3 h and then at 150°C for 3 h to synthesize the polyimide. All polyimide products were dried and pulverized.

Characterization of the polyimide product
The target polyimide compound was pulverized and prepared as KBr samples, and then characterized by Fourier transform infrared spectroscopy (FT-IR). The characteristic absorbance bands for polyimide were observed with the Fourier transform infrared spectroscope (IS10, Thermo Fisher Scientific, Waltham, MA, USA).

Preparation of standardized specimens
The polyimide product was ground into fine powder and blended into PMMA powder. The blended powder was mixed with mono-MMA liquid at a powder/liquid mass ratio of 2:1. The mixture was pressed into the mold and then heated at 100°C for 1 h until the resin polymerized. The modified composites were thus obtained.

The modified composites were divided into 4 groups according to different amounts of polyimide addition at 0.4, 0.6, 0.8 and 1 wt%. Unmodified PMMA-based denture resin was prepared in the same way but without addition of polyimide as the control group.

Testing of the flexural properties and thermal cycling
Flexural strength was evaluated according to the ISO 20795-1:2013. Specimens with a size of 64×10×3.3 mm were prepared using a slicing machine (IsoMet 4000, Buehler, Chicago, IL, USA) and then polished with buffing wheel. Before the test, all the specimens were kept in a water bath of 37°C for 48 h. Three-point bending tests were carried out to fracture the specimens with a span of 50 mm and a crosshead speed of 5 mm/min on a universal testing machine (EZ-20, LLOYD, Steyning, UK), which was calibrated prior to each testing session. The bending data were recorded as flexural strength, flexural modulus and rupture elongation. Sample size was set as five with reference to similar published studies.

What is more, the group of specimens with best flexural strength was then arranged to thermal cycling. With reference to ISO 11405:2015, the samples, together with the control group, were exposed to thermal cycles between 5 and 55°C for 1 min for 5,000 cycles as an accelerated test of deterioration.

Scanning electron microscopy
To observe the properties of flexural section surface of the specimens, the fractured surfaces of the specimens were gold coated by an ion sputter and then observed with a scanning electron microscope (Nova NanoSEM NPE218, FEI, Eindhoven, Netherlands). An accelerating voltage of 5 kV was used during scanning.

MTT assay
Specimen preparation and extraction was undertaken in accordance to ISO 10993-12:2012. The specimens were incubated with dulbecco’s modified eagle medium (DMEM) (Gibco, Thermo Fisher Scientific) for 24 h at 37°C, with the ratio between the surface of the sample and the volume of the added medium being 1.25 cm²/mL. Human gingival fibroblast cells were seeded in 96-well tissue culture plates (at a concentration of 10⁴ cells/well) and then incubated at 37°C in a 5% carbon dioxide atmosphere. After 24 h, the culture medium was aspirated and replaced with 100 μL of specimen extractions, and incubated for 72 h at 37°C. The number of living cells after incubation were measured with 3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide (MTT) assays (Sigma, Sigma-Aldrich, St. Louis, MO, USA). The positive control was dimethyl sulfoxide (DMSO), and the negative control was DMEM.

Statistical analysis
Data on flexural properties and MTT assay were statistically analyzed by SPSS software (version 19, IBM, New York, NY, USA). Analysis of variance (ANOVA) and Turkey’s post hoc method were used to compare the differences among groups of materials (p<0.05).
RESULTS

The polyimide product

The result of FT-IR analysis was shown in Fig. 2. Typical characteristic imide absorbance bands were located at 1,778 cm\(^{-1}\) (symmetric C=O stretching vibration), 1,716 cm\(^{-1}\) (asymmetric C=O stretching vibration), 743 cm\(^{-1}\) (deformation of imide ring band of OC–N–CO vibration), and 1,365 cm\(^{-1}\) (C–N–C stretching vibration). No characteristic bands at 1,650 cm\(^{-1}\) and 1,550 cm\(^{-1}\), which result from C=O and N–H bending of the amide group, were observed. This result indicates complete imidisation of the polymer.

Scanning electron microscopy analysis

The SEM micrographs of the fracture surfaces of the specimens after the three-point bending test were showed in Fig. 3. Figure 3A showed the surface of the...
control group specimen, which has a smooth section. Figure 3C showed the surface of the specimen added with 0.6% PI, revealing a good dispersion of PI. In comparison to the smooth fracture surface of the control specimen, the specimen with addition of PI showed rough fracture surface with numerous curved and stretched steps, which implied that PI particles could deflect the cracks and the composites had higher fracture energy than the unfilled PMMA resin. Figure 3E showed the surface of the sample added with 1% PI, from which agglomeration of PI particles could be observed.

The flexural properties

Table 1 showed the flexural strength and the flexural modulus of the specimens tested. The flexural strength of the control group was 87.95±5.01 MPa, and those of the samples with the PI addition ranged from 89.55 to 99.84 MPa. The group of 0.6 wt% PI addition had the highest flexural strength (99.84±3.07 MPa) and was significantly different from the control group (p<0.05). The flexural modulus of the samples ranged from 2,928.2 to 3,390.7 MPa and there was no significant difference in the flexural modulus among all the groups (p>0.05). Table 2 showed that after thermal cycling, flexural strength in both the control group and the 0.6 wt% PI

<table>
<thead>
<tr>
<th>Group</th>
<th>Flexural strength</th>
<th>Flexural modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>Control</td>
<td>87.95</td>
<td>5.01</td>
</tr>
<tr>
<td>0.4% PI</td>
<td>91.12</td>
<td>3.73</td>
</tr>
<tr>
<td>0.6% PI</td>
<td>99.84</td>
<td>3.07</td>
</tr>
<tr>
<td>0.8% PI</td>
<td>89.65</td>
<td>5.55</td>
</tr>
<tr>
<td>1.0% PI</td>
<td>89.55</td>
<td>3.61</td>
</tr>
</tbody>
</table>

In the significance column, different letters label the statistical significance of between-group differences.

Table 2 Descriptive statistics of flexural strength (MPa) and flexural modulus (MPa) after thermal cycling

<table>
<thead>
<tr>
<th>Group</th>
<th>Flexural strength</th>
<th>Flexural modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>SD</td>
</tr>
<tr>
<td>Control</td>
<td>70.44</td>
<td>2.09</td>
</tr>
<tr>
<td>0.6% PI</td>
<td>77.84</td>
<td>4.14</td>
</tr>
</tbody>
</table>

In the significance column, different letters label the statistical significance of between-group differences.

Table 3 Descriptive statistics of MTT results

<table>
<thead>
<tr>
<th>Group</th>
<th>Cell viability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Negative control</td>
<td>82.50</td>
</tr>
<tr>
<td>Positive control</td>
<td>4.98</td>
</tr>
<tr>
<td>Group control</td>
<td>76.90</td>
</tr>
<tr>
<td>0.4% PI</td>
<td>69.22</td>
</tr>
<tr>
<td>0.6% PI</td>
<td>69.28</td>
</tr>
<tr>
<td>0.8% PI</td>
<td>68.44</td>
</tr>
<tr>
<td>1.0% PI</td>
<td>69.54</td>
</tr>
</tbody>
</table>

In the significance column, different letters label the statistical significance of between-group differences.
addition group decreased, but the latter still showed a significantly higher flexural strength than the former ($p<0.05$).

**MTT assay**

The results of the cytotoxicity test using the MTT assay are presented in Table 3. The percentage of viable cells in the negative control was 82.50%, while that in the control group without PI addition was 76.90%, and those in groups with PI addition ranged from 68.44 to 69.54%. There was no significant difference in the percentage of viable cells among the control group without PI addition and all the PI added groups ($p>0.05$).

**DISCUSSION**

This study was designed to investigate the potential of modifying denture base material with polyimide. PMR type polyimide was selected as experimental material because it was easy to produce and its linear molecular structure could insert in the matrix as a reinforcement agent. 1,500 g/mol molecular weight of the polyimide was adopted to get small particles which could be dispersed in the matrix.

The sample group with 0.6 wt% addition of PI showed the highest flexural strength, which was significantly increased by 13.5% comparing with that of the control group ($p<0.05$). Possible explanations for this strengthen effect could be: (1) the PI particles that were strongly adhered to the matrix enhanced the flexural strength, (2) the PI particles that were not strongly adhered to the resin could debond during the load application, which distributed the stress across the matrix cracks, increasing the resistance to fracture. However, when the PI addition further increased, flexural strength of the sample decreased. Such results may be explained by the degree of particle agglomeration. As the SEM micrographs showed, in the sample with 0.6 wt% PI addition, the PI particles with diameters of less than 1 μm were uniformly dispersed and adhered to the PMMA matrix. When stress occurs, the debonding of the PI/PMMA interface relieves the load application, which distributed the stress across the matrix cracks, increasing the resistance to fracture. In specimens with 1 wt% PI addition, agglomeration was observed in the SEM micrograph. Large agglomerates could result in structural defects, which may fracture under stress and transmit the stress to the matrix. Other possible causative factors for the decrease in strength could be a reduction in the cross section of the PMMA matrix; an increase in the amount of filler particles which increases the stress concentration. Similar results were also found in researches on reinforcing PMMA with nanotube or nanofiber. The addition of 0.5% multiwalled carbon nanotubes (MWCNTs) increased the flexural strength of PMMA by an average of 9.3, but 2% addition of MWCNTs resulted in a 11.4% decrease in flexural strength due to the poor dispersion of MWCNTs. Compared with researches of the similar kind, the 13.5% increase in flexural strength of PMMA by addition of PI in this study could be satisfying.

Flexural strength is one of the essential characteristics for denture base materials, so 0.6 wt% was considered as the optimum PI addition level to enhance the mechanical properties of the PMMA denture base material. Besides flexural strength, there are still other critical characteristics, such as physical and chemical durability, and biocompatibility to be addressed for a denture base material.

In this study, hydrothermal cycling was adopted to provide an indication of how would the material perform in the oral cavities. ISO 11045:2015 suggests that thermal cycling should continue for 500 cycles, which represent less than 2 months usage in the mouth. The number of cycles used in this study was 5,000, which could represent usage in the mouth for more than 1 year. As the result of flexural tests showed, both groups showed significant decrease in flexural strength after thermal cycling, with the group with PI addition decreased even more. For a composite denture material, the thermal expansion difference between the resin base and the filler would lead to internal stresses. Also, the water absorption could change the dimensional and mechanical properties of acrylic resin denture base through the formation of microcracks. Thus, addition of filler might have more reduction on the strength of the denture material after wearing in the mouth for a period of time. Although the hydrothermal cycling decreased the flexural strength of the samples, group with PI addition still had significantly higher flexural strength than the control group ($p<0.05$), suggesting that the reinforcement effect of PI will exist even after usage in oral cavities.

Cytotoxicity testing through MTT assay was used to evaluate the biocompatibility of the denture base material. With reference to ISO 10993-5:2009 biological evaluation of medical devices, if viability of the test group is reduced to <70% of the blank, it has a cytotoxic potential. The result of this study suggests that the groups with PI had similar level of cytotoxicity to the control group. All the groups had lower percentage of viable cells than the negative control, the possible reason might be that unconverted monomer had slightly toxic to the cells. Since the denture base is a kind of surface-contacting device rather than external communication device or implant device, this result could be acceptable. The observed level of biocompatibility with human gingival fibroblasts indicated potential for the use of this material in the oral cavity.

The results above suggested that the hypothesis, PI addition would improve the flexural strength of the PMMA denture base material and keep its biocompatibility, could be accepted.

There are also limitations of this study. Firstly, just one type of denture base material was adopted. However, this PMMA-based material may represent commercial denture materials to a great extent, because currently most of them are PMMA-based. Future research should test the effects of PI addition on more physical and chemical properties in more PMMA-based denture materials. Secondly, the specimens were tested at the
dry condition, while denture base materials are usually used at a wet condition. Although we have tried to reduce the experimental error by keeping the specimens in a water bath before testing of the flexural properties, the error could not be eliminated. So in future research, mechanical testing at wet condition might be adopted.

CONCLUSION

Addition of 0.6 wt% PI into PMMA matrix significantly increased the flexural strength of PMMA-based denture base material, and the reinforce effect existed after hydrothermal cycling. PI addition did not change the biocompatibility of the PMMA-based denture base material. Blending polyimide in the proper proportion can be a potential method to strengthen the PMMA-based denture base material.

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