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Preparation of base materials for prosthetic socket fabrication

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The properties and performance of the matrix material are key factors for obtaining comfortable and wearable prosthetic sockets. However, there are only a few reported studies on prosthetic socket materials, especially on the preparation of the base material. Methyl methacrylate monomers were used to synthesize prepolymers *via* bulk polymerization with different initiator contents, and the prepolymer was modified to generate base materials for prosthetic socket fabrication. The performance of the different base materials was investigated, as well as the effect of the inhibitor content on the curing time and storage stability. The experiments and subsequent investigations indicate that a prepolymer synthesized with an initiator content of 0.30 % and a base material prepared with an inhibitor content of 1.25 % exhibited the best storage stability and the most suitable post-curing time, and therefore showed the most favourable properties for manufacturing wearable prosthetic sockets.

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1. Introduction

A prosthesis is an artificial limb that is produced and assembled in order to restore the body's form and function, and to compensate for the disability caused by limb amputation. For the more than 200 million amputees in China, receiving a prosthesis is an important step for their rehabilitation and reintegration into society. The prosthetic socket which connects the stump with the prosthesis is a critical part of a prosthesis and determines its performance. It may contain a prosthetic stump to transfer the force between the stump and the prosthesis, and to connect the stump with the prosthesis [1-5]. The basic requirements for a prosthetic socket are the ability to bear loads, to control the prosthesis, and to suspend the prosthesis. The prosthetic socket material must not only exhibit a good processing performance so that a variety of desirable shapes can easily be formed, which can make the socket production process more controllable and adjustable and the sockets more compatible with human anatomy and movement mechanics, but also needs to show a high strength, a light weight and must be comfortable for the patient use [6-13]. However, studies on prosthetic socket materials are rarely reported.

Modified poly(methyl methacrylate) (PMMA)-based fibre composites are the main materials used for the production of prosthetic sockets. The composite materials are generally synthesized in a two-step process: the first step is to use methyl methacrylate (MMA) monomers to synthesize prepolymers and then generate a modified matrix material, and the second step is to combine the fibre material and the prepolymer matrix *via* a proper processing technology to eventually prepare the prosthetic sockets. The properties and performance of the matrix material are key factors for obtaining comfortable and wearable prosthetic sockets. However, there are only a few reported studies on the preparation of the base material. In this study, MMA and benzoyl peroxide (BPO) were used to synthesize the prepolymer which was then modified to prepare different matrix materials for prosthetic sockets. The resulting matrix material was investigated by gel chromatography, differential scanning calorimetry (DSC) and Fourier transform infrared spectrometry (FTIR) in order to better understand the properties of the base materials.

2. Material and methods

2.1 Material

MMA, BPO, nitrogen and N dimethyl aniline were all obtained from Tianjin Fucheng Chemical Reagent Factory. MMA was purified by vacuum distillation, prior to the experiments.

2.2 Methods

2.2.1 Polymerization

A four-necked flask equipped with an electric stirrer, a thermometer, a reflux condenser and a nitrogen inlet was used as the polymerization reactor. MMA, BPO, dicyclohexyl phthalate ester and phenyl salicylate were added into the flask to initiate the polymerization reaction at 70 °C in a protective nitrogen atmosphere. The initiator content was varied from 0.10 %, 0.30 %, 0.50 %, 0.75 %, 1.00 % were used to get the prepolymer of 1#-5#.

2.2.2 Preparation of the base materials

After the prepolymer cooled down to room temperature, a predetermined amount of N, N-dimethylaniline, saccharin and a polymerization inhibitor were added to the solution which was then stirred until mixed evenly. The different inhibitor contents used in the experiments were 0.50 %, 1.00 %, 1.25 %, 1.50 % and 2.00 %, in order to investigate the influence of the inhibitor content on the properties of the resulting matrix materials.

2.2.3 Curing reaction at room temperature

The curing agent was added to the obtained matrix materials, and then the curing reaction with the fibre material was performed in a vacuum chamber. This process was used to simulate a realistic fabrication process for fiber-MMA prosthetic sockets.

2.3 Characterization

2.3.1 Fourier transform infrared spectroscopy (FTIR) analysis

The matrix material was mixed with KBr to produce pellets which were then investigated in a Shimadzu Iffinity-21 Fourier transform infrared spectrometer at a resolution of 4 cm^{-1} and a scanning number was 16.

2.3.2 Determination of molecular weight and its distribution by gel chromatography (GPC)

Gel chromatography (Waters Corporation) measurements were performed to obtain the molecular weight and the weight distribution of the matrix materials. Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1.0 mL min^{-1}. The polymer molecules were separated into GPC columns according to their molecule size, then the molecular weight and molecular weight distribution were determined.

2.3.3 Differential Scanning Calorimetry (DSC)

A Shimadzu DSC-60 DSC facility was used to characterize the phase-temperature change of the matrix material in a protective argon atmosphere. The sample weight was between 5 and 8 mg, the air flow rate was adjusted to 30 mL min^{-1} and the temperature for the experiments ranged from -100 °C to 1,000 °C. The sample was firstly heated to 200 °C then kept at this temperature for 3 min. Afterwards, the sample was quenched to -100 °C and kept at this temperature for 3 min. Then, the sample was annealed at a rate of 20 °C min^{-1} during measurements. After the formation of a thin film, the sample was placed into a desiccant vessel to prevent an influence of moisture on the DSC curve. About 5 mg of the sample were used to perform the DSC test. During the measurement the temperature was decreased from -50 °C to -250 °C at a rate of 10 °C min^{-1}.

2.3.4 Determination of the curing time and storage stability of the base material

The base material was stored for 20 weeks. The conformational change of base material was observed and the change in volume recorded. The curing time was measured directly.

3. Results and discussion

3.1 FTIR spectra of the base material synthesized with different initiator contents

Fig. 1 compares the FTIR spectra of the obtained base materials #1, #3 and #5. The observed C = O stretching vibration linked to the peak at 1,730 cm^{-1} and the C-C-O-C stretching vibrations at 1,150 cm^{-1}, 1190 cm^{-1}, 1,240 cm^{-1} and 1,268 cm^{-1} were similar to the characteristic bands of MMA. The characteristic peaks at 1,450 cm^{-1}, 1,600 cm^{-1}, 1,760 cm^{-1} and 1,790 cm^{-1} can be attributed to amines and ether groups originating from the modification of the PMMA-based prosthetic socket materials. In all the three samples, no obvious difference in the FTIR spectra was observed, indicating that the initiator content had little influence on the chemical composition of the prepared base materials [14-19].

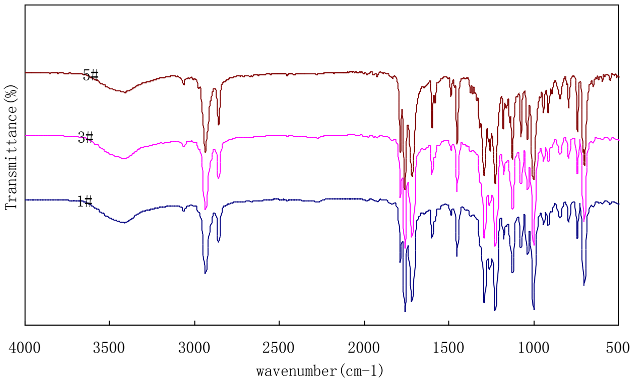

Fig. 1. FTIR spectra of the base materials #1, #3 and #5.

3.2 Molecular weight distribution and glass transition temperature of the base materials

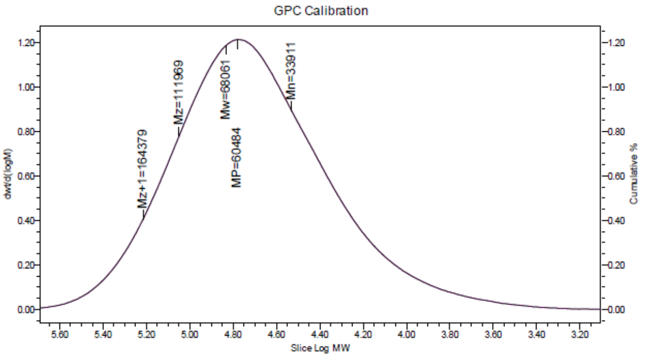

Fig. 2. Molecular weight distribution of the base materials #3.

Table 1. Molecular weight distribution and glass transition temperature of the base materials for different initiator contents. Mn = number - average molecular weight, Mw =weight-average molecular weight.

	Initiator content (%)	Mn	Mw	Mw/Mn	T_g(°C)
#1	0.10	36,780	69,326	1.8849	110
#2	0.30	35,098	63,530	1.8101	109
#3	0.50	33,911	60,484	1.7836	110
#4	0.75	32,176	56,927	1.7692	110
#5	1.00	30,125	52,031	1.7272	109

Fig. 2 and Table 1 shows the molecular weight distributions and glass transition temperatures of the base material for different initiator contents. In the free radical polymerization process, a change of the initiator content will lead to a change of the concentration of the free radicals, which has a great influence on the initiation rate of the prepolymer synthesis as well as the conversion rate of the polymerization reaction. *Ceteris paribus*, the molecular weight distribution and glass transition temperature of the modified base materials were measured for different initiator contents. As shown in Table 1, the molecular weight decreased and its distribution became narrower with increasing initiator content. The main reason was that the higher initiator concentration led to increased production of free radicals, and consequently, to a comparatively smaller molecular weight. However, during prepolymer synthesis, an excessive amount of free radicals generated by high initiator content would cause an automatic acceleration or even an implosion phenomenon. Further experiments indicated that the addition of dicyclohexyl phthalate esters could help to eliminate the reaction heat and prevent the implosion [20-23]. Fig. 3 shows that the initiator content did not cause an obvious change of the glass transition temperature of the base materials, and the observed glass transition temperature of all base materials was approx. 110 °C.

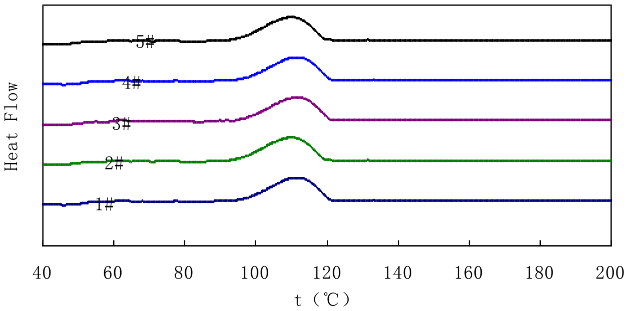

Fig. 3. Results of the DSC measurements performed on the base materials.

3.3 Storage stability and curing performance of the base materials

The storage stability and curing time of the base material are important factors for the future performance of prosthetic sockets, and are essential to the post composite curing process with the fibre material. The prepolymer material is susceptible to external environmental conditions, especially changes in temperature, and is prone to self-polymerization. Consequently, if the storage time is too short, the unstable matrix will not work as desired. Besides, the curing time should be in the range of 25 to 40 min for preparing the prosthetic sockets. If the curing time is too short, the solidification heat is difficult to be released, so that bubbles may form in the composites. On the other hand, if the curing time is too long, the final shaping of the prosthetic socket will be affected. Again *ceteris paribus*, both the curing time of the prepolymer for different initiator contents and the storage stability of the base material in the absence of inhibitors were measured. In addition, the influence of the inhibitor content on the curing time and stable storage time was investigated for a constant initiator content of 0.30 %.

Fig. 4 shows the curing time of the prepolymer for different initiator contents and Fig. 5 shows the stable storage time of the base material in the absence of an inhibitor. Both figures indicate that a higher initiator content can reduce the curing time of the base material and a content of 0.30 % can be considered a relatively suitable initiator content. Furthermore, a higher initiator content also reduces the storage stability, with the longest storage time being less than one month, which means that the matrix material is relatively unstable in the absence of an inhibitor.

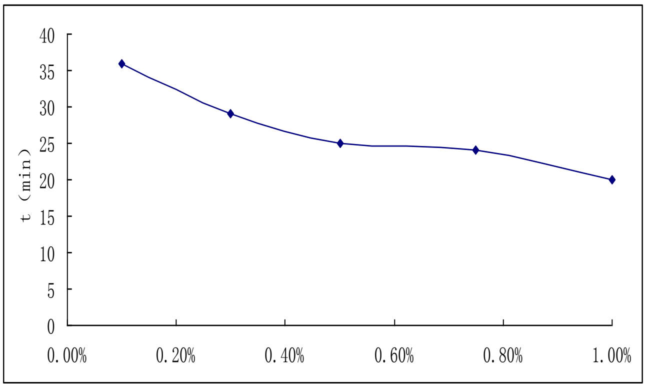

Fig. 4. Curing time of the prepolymer for different initiator contents.

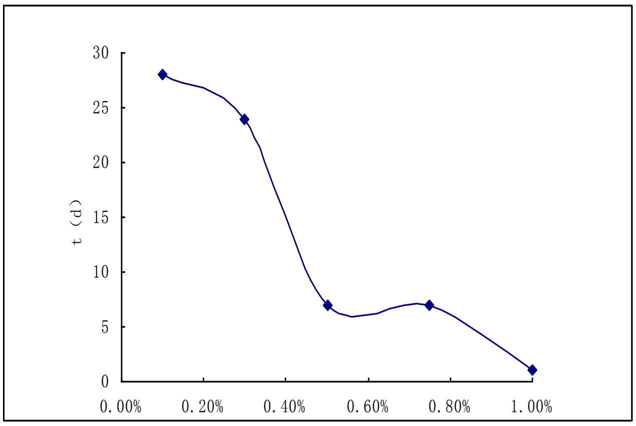

Fig. 5. Storage stability of the prepolymer for different initiator contents.

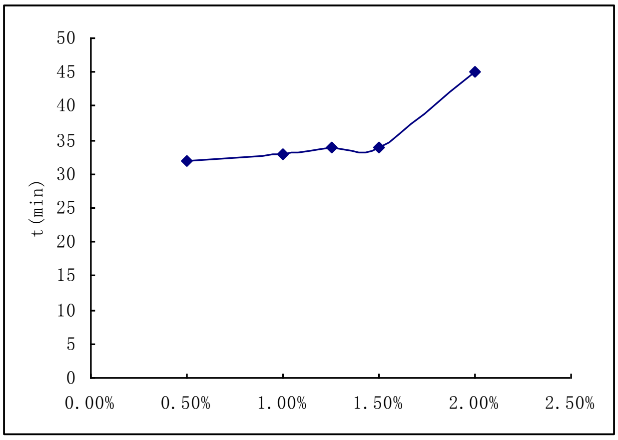

Fig. 6. Curing time of the base material for different initiator contents.

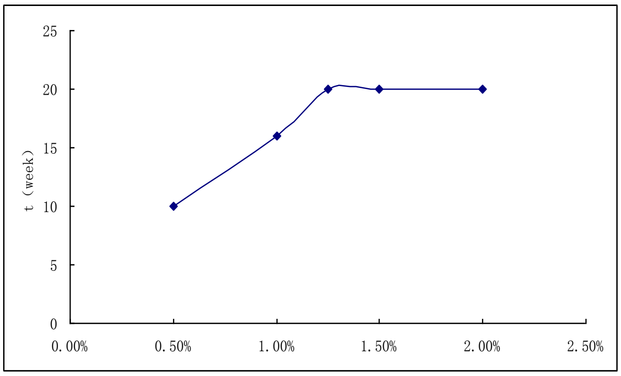

Fig. 7. Storage stability of the base material for different initiator contents.

Ceterus paribus, for inhibitor contents below 1.50 %, the curing time did not significantly change, as seen in Fig. 6. However, when the inhibitor content was increased to 2.00 %, the required curing time apparently increased. The results presented in Fig. 7 demonstrate that the addition of an inhibitor can enhance the storage stability of the base materials, with the storage stability of the base material meeting the manufacturing requirements for inhibitor contents greater than 1.25 %.

4. Conclusions

This study showed that the fabrication process for the base material for prosthetic sockets differs compared to that of ordinary poly(methyl methacrylate) fabrication since a prepolymer and a subsequent modification are required to realize an ideal performance. The experiments and subsequent investigations indicate that a prepolymer synthesized with an initiator content of 0.30 % and a base material prepared with an inhibitor content of 1.25 % exhibited the best storage stability and the most suitable post-curing time, and therefore showed the most favourable properties for manufacturing wearable prosthetic sockets.

References

[1] O. Ciobanu, Rev. Med. Chir. Soc. Med. Nat. Iasi, **116**(2), 642 (2012).
[2] R. D. Alley, T. William, J. Matthew, E. David, Journal of Rehabilitation Research and Development, **48**(6), 679 (2011).
[3] S. Gerzeli, A. Torbica, G. Fattore, Eur. J. Health Econ., **10**(1), 47 (2009).
[4] B. Silver-Thorn, T. Current, B. Kuhse, Prosthet. Orthot. Int., **36**(4), 435 (2012).
[5] N. P. Fey, G. K. Klute, R. R. Neptune, J. Biomech. Eng., **134**(11), 1 (2012).
[6] K. Postema, H. J. Hermens, J. de Vries, et al. Prosthet Orthot Int, **21**(1), 17 (1997).

[7] E. J. Rouse, L. J. Hargrove, M. A. Peshkin, et al. Conf Proc IEEE Eng Med Biol Soc, 2011, 8179 (2011).

[8] J. B. Barr, C. J. Wutzke, A. J. Threlkeld, Physiother Theory Pract, **28**(5), 407 (2012).

[9] L. L. McNealy, S. A. Gard, Prosthet Orthot Int, **32**(1), 111 (2008).

[10] L. F. Yeung, A. K. Leung, M. Zhang, et al. Gait Posture, **35**(2), 328 (2012).

[11] D. Pailler, P. Sautreuil, J. B. Piera, et al. Ann Readapt Med Phys, **47**(6), 374 (2004).

[12] R. Hirons, Preparing our Paralympians: research and development at Ossur, UK. Interview by Sarah A. Curran, Prosthet Orthot Int, **36**(3), 366 (2012).

[13] B. J. Hafner, J. E. Sanders, J. M. Czerniecki, et al. J Rehabil Res Dev, **39**(1), 1 (2002).

[14] M. A. Gauthier, Z. Zhang, X. X. Zhu, ACS Appl Mater Interf, **1**(4), 824 (2009).

[15] Huanqin Chen, Chunbao Huang, Huifang Shen, Kai Zhang, Polymer Materials Science and Engineering, **29**(2), 141 (2014).

[16] Yu Li, Pengyu Liu, Zheng Wei, Yuansheng Wang, Hongwei Yu, Polymer Materials Science and Engineering, **29**(2), 5 (2014).

[17] M. Mravljak, M. Sernek, Drvna Industrija, **62**(1), 19 (2011).

[18] J. Jaruchattada, A. Fuongfuchat, C. Pattamaprom, Journal of Applied Polymer Science, **123**(4), 2344 (2012).

[19] Qingli Du, Zhongjie Du, Ming Li, Xiaowei Sun, Chen Zhang, Wei Zou, Polymer Materials Science and Engineering, **29**(3), 31 (2013).

[20] Min Cai, Yan Jing, Hongyan Shi, Renguo Song, Hongwen Zhang, Mengchao Zhao, Polymer Materials Science and Engineering, **29**(5), 23 (2013).

[21] R. Bai, Z. B. Wei, F. A. Zhang, Acta Polymerica Sinica, (7), 849 (2013).

[22] J. Cai, T. Chen, G. Z. Wang, et al. Adv. Mater. Res, 476-478, 2188 (2012).

[23] Fameng Sun, Zhibo Wei, Faai Zhang, Polymer Materials Science and Engineering, **30**(6), 29 (2014).

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