



The percolation theory in studying the morphology of polymer networks formed by photopolymerization of dental dimethacrylates



Monika Krasowska*, Izabela M. Barszczewska-Rybarek

Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland

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ABSTRACT

Atomic force microscopy (AFM), percolation parameters (the percolation probability (P) and the length of percolation path (L)) are used to characterize the morphology of dimethacrylate polymer networks. They are produced from dimethacrylates, popular in restorative dentistry, by photoinduced homo- and copolymerizations. The combination of the material morphology visualization tool and the advanced calculation methodology, based on the theory of percolation, delivers new data regarding the structure of polymer networks and their mechanical performance. Extending the knowledge of fracture propagation and its mechanism is of special interest. The results show that the percolation path, which is related to a fracture path, propagates through hydrogen bonds and thus through physical crosslinks. The copolymerization of monomers, which are able to form strong hydrogen bonds, promotes the morphology. The fracture generates bigger spanning clusters, which indicate a more homogeneous structure of the dimethacrylate polymer network.

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1. Introduction

Much research in recent years has focused on densely crosslinked networks obtained by the polymerization of dimethacrylates which are widely applied in dentistry, such as dental composites, pit and fissure sealants, cements as well as dental adhesives [1–6].

The kinetics of such multifunctional monomer polymerization has been well explored. It exhibits anomalous reaction behaviors, including autoacceleration and autodeceleration, unequal functional group reactivity, reaction–diffusion controlled termination and limited functional group conversion due to hindered mobility of methacrylate groups. Additionally, one of the most important characteristics of this process is the formation of highly crosslinked microgels, their agglomeration into clusters and their connections in the less cross-linked matrix. They arise due to a varied reactivity of groups involved in the process of free radical polymerization: the monomer double bonds and side bonds (the remaining unreacted double bonds of multifunctional monomer molecules which are already incorporated into the polymer chain). At the beginning of the process, at low conversion, the reactivity of side bonds far exceeds the reactivity of monomeric bonds, mainly due to the close proximity of side bonds and the radical chain end. This leads to the formation of loops in the chains and the formation of microgel particles (highly crosslinked polymer regions with a high degree of cyclization, suspended in a

* Corresponding author.

E-mail address: Monika.Krasowska@polsl.pl (M. Krasowska).

less crosslinked matrix). As the conversion increases, side bonds inside the microgel particles are readily available and less reactive, because of the screening effect. The monomeric double bond reactivity equals the side bond reactivity or even exceeds it, and a less crosslinked matrix is formed. In the final network there are strongly crosslinked microgel agglomerates and, later formed, less crosslinked areas, giving rise to spatial heterogeneity of the polymer network [4–10]. Recent research on these polymers suggests that their strongly heterogeneous morphology affects their mechanical properties [5,11–18].

The structural heterogeneity of dimethacrylate polymer networks is commonly visualized by means of atomic force microscopy [15,16,18–20] or scanning electron microscopy [17,18]. Other experimental techniques widely used for this purpose are a dynamic-mechanical analysis [6,12,19,21], infrared spectroscopy [11,19–22] and solid state NMR [13]. X-ray powder diffraction is also used and delivers interesting results [14,15]. Simple solvent extraction of a soluble fraction, followed by the collection of a gel fraction on a filter of a specified pore size make it possible to determine micro- and/or macrogel fraction [23]. However, the methodology providing quantitative information about morphological species is still deficient.

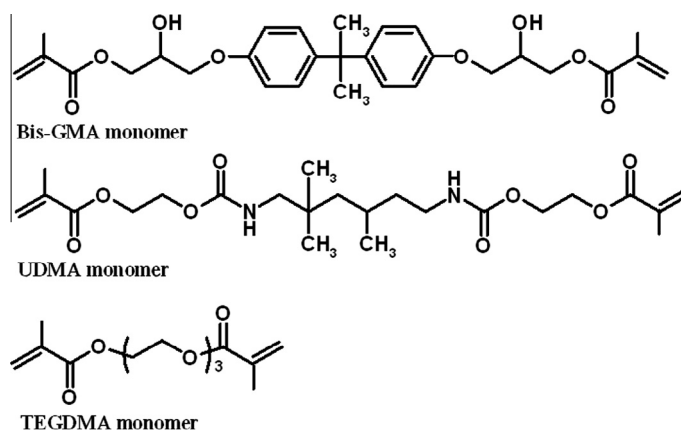
This paper presents the application of the percolation theory in studying the AFM morphology of dimethacrylate polymer networks. For this purpose, three popular dental monomers: Bis-GMA, TEGDMA and UDMA [1–4] were used for producing a family of homo- and copolymer networks (Scheme 1). The selection of three structurally different dimethacrylates enabled the building of a relatively simple model system, composed of three homopolymers and two copolymers with a wide range of various structures and properties. The bisphenol A diglycidyl ether methacrylate (Bis-GMA) molecule, which has a stiff bisphenol A core and two pendant hydroxyl groups, being able to form strong hydrogen bonds, is the largest and has the lowest concentration of double bonds. The urethane-dimethacrylate (UDMA) molecule, with its flexible aliphatic core and two urethane links is also able to form hydrogen bonds. However, it is smaller in size and therefore has a higher concentration of double bonds. Triethylene glycol dimethacrylate (TEGDMA) does not contain proton donors for hydrogen bonds and additionally, it is the smallest and has the highest concentration of double bonds (Table 1).

The concept of this work has been developed on the basis of our previous studies performed with the same research objectives. Those results showed good correlations between the physico-mechanical properties and the variety of fractal dimensions of AFM images of fractured poly(dimethacrylate) surfaces [16,18].

Research based on the percolation theory may benefit the development of modern testing methods and it will allow the advanced interpretation of polymeric material properties. Percolation is a process in which a set of initially independent objects suddenly forms a larger structure by means of connecting, bonding, chemical reactions, etc. [24–27]. The following step involves a gradual increase of the concentration of microscopic bonds accompanied by a sudden change of macroscopic parameters. It occurs when a rapid transition with long-range consistency appears or disappears in the system. The parameter at which it occurs is called the percolation threshold (p_c) [24,27]. Apart from the application of percolation theory to the research of conductive polymeric systems for which percolation threshold is usually determined [28,29], the percolation theory may constitute a valuable tool to study compositionally heterogeneous polymer blends or block copolymers in terms of their phase-separated morphologies [30,31].

The combination of the popular tool of visualization of the material morphology with the advanced calculation methodology is supposed to deliver new data regarding polymer networks and to extend the description of the nature of their physico-mechanical properties.

Correlating the percolation studies with the mechanical tests would be beneficial in defining the role of morphology in the mechanical behavior of dimethacrylate networks. It could consequently lead to the development of a reliable method for identifying the cause of dimethacrylate-based dental material failures under stress. A percolation theory could thus become one of the key elements in testing materials based on dimethacrylate polymer networks.



Scheme 1. Structure of dimethacrylate monomers studied.

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