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THE RELATIONSHIP BETWEEN THE DEGREE OF CONVERSION IN DENTAL DIMETHACRYLATE POLYMERS DETERMINED BY INFRARED SPECTROSCOPY AND POLYMERIZATION SHRINKAGE

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Theoretical background

- The degree of conversion (DC) is the most useful parameter in the characterization of dental composite restorative materials based on dimethacrylates.
- If the DC is insufficient, the physicochemical and mechanical properties of the composite can significantly deteriorate. Inadequate curing also decreases the biocompatibility of the material, due to an increase in free monomer content, which tends to leach from the composite matrix.
- DC depends on i) the monomer chemical structure, ii) initiation method, iii) initiation type, iv) sample thickness, v) irradiation lamp, and vi) filler type and content.
- The most popular techniques used for the DC determination include i) Fourier transform infrared spectroscopy (FTIR), ii) Raman spectroscopy, iii) solid-state nuclear magnetic resonance (ssNMR), and iv) differential scanning calorimetry (DSC)
- The DC determination method that uses FTIR is the most common, simple, and gives the most reliable Results.

FTIR method

- It is based on the monitoring of changes in the absorption intensity of several bands resulting from vibrations of the C=C double bond, present in the methacrylate group.
- The intensity of these bands decreases due to polymerization.
- The band located at 1637 cm^{-1} is the most resolved and intense and thus is the most commonly used for DC determination.
- To comply with the Beer-Lambert law, the C=C absorption intensity has to be related to the absorption intensity of an internal standard – the band whose absorption intensity does not alter due to the polymerization.
- The band corresponding to the skeletal stretching vibrations of the C-C bonds in the aromatic ring, located at 1608 cm^{-1}, usually serves as an internal standard.
- If the system lacks an aromatic ring, the band corresponding to the C=O stretching vibrations, located within 1715 and 1720 cm^{-1}, can be used.
- However, this method produces underestimated DC values, and therefore it is recognized as less reliable compared to that using an aromatic internal standard.

Polymerization shrinkage method – alternative to FTIR

- It is based on measuring differences in the monomer and polymer densities resulting from the polymerization shrinkage and calculating its theoretical value (DC_S).
- The calculation of the DC uses the literature information that the molar volume of one mole of the methacrylate group decreases by 22.5 cm^3 due to polymerization, in the course of which van der Waals forces that occur between monomer molecules turn into covalent bonds that constitute crosslinks of hardened composite matrix.
- This method has already been applied in the survey on the DC of dimethacrylate systems, however, its reliability has not yet been established.

Methods

Seven Bis-GMA/TEGDMA mixtures were prepared. The Bis-GMA weight fraction ranged from 20 to 80 % and increased by 10 % each time. TEGDMA content decrea proportionally.

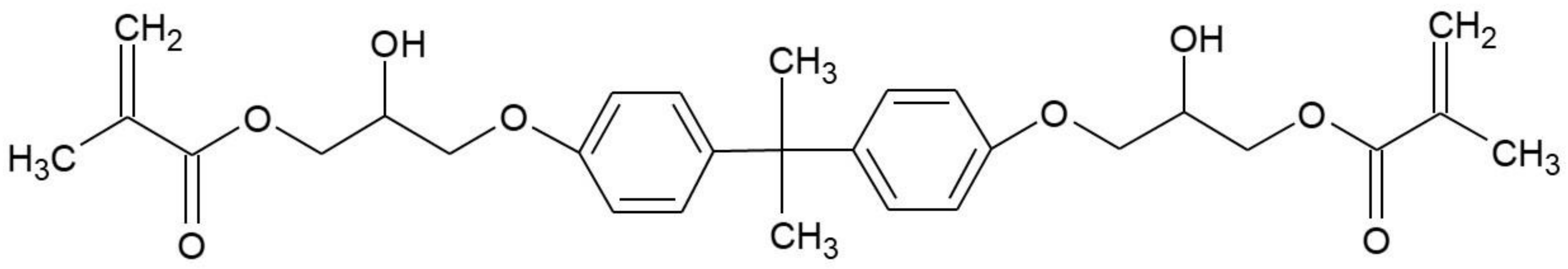


Figure 1. Chemical structure of Bis-GMA.

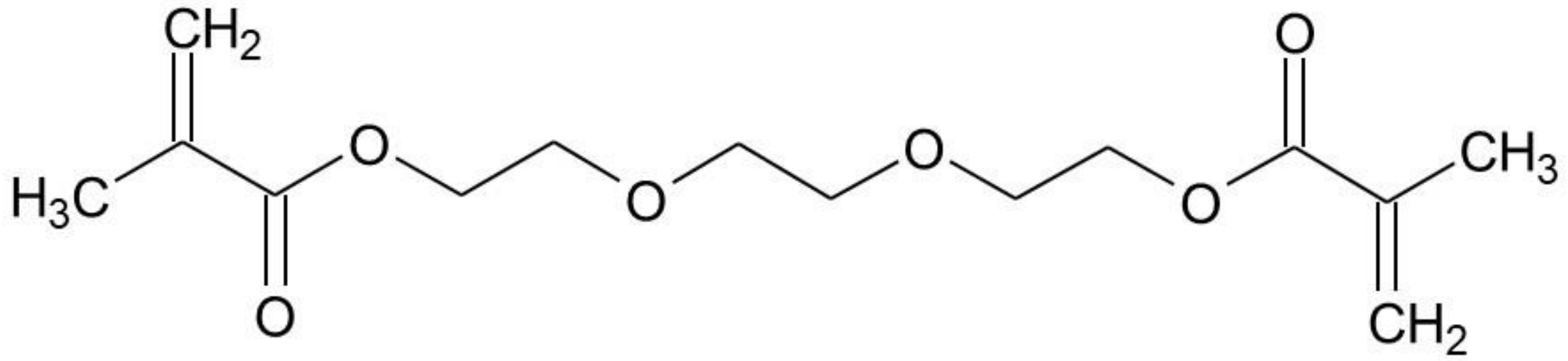


Figure 2. Chemical structure of TEGDMA.

The mixtures were admixed with the 0.4 wt.% CQ and 1 wt. % DMAEMA that was a photoinitiating system, composed of respectively, initiator/and accelerator.

The mixtures were admixed with the 0.4 wt.% CQ and 1 wt.% DMAEMA that was a photoinitiating system, composed of respectively, initiator/and accelerator. Thus prepared compositions were introduced into silicon molds with a diameter of 15 cm and 5 cm thick, covered with PET film to prevent oxygen inhibition, and irradiated with the UV-VIS lamp for 1h, from a distance of 15 cm.

Methods

FT IR method

FTIR spectra were recorded with the use of a spectrometer, with 128 scans at resolutions of 1cm^{-1}. Monomers and polymers were tested as KBr pellets. A thin layer of a monomer was placed between two KBr pellets, whereas a polymer was ground into a fine powder with a grain size smaller than 25 µm, mixed with KBr powder, and pressed into a pellet.

The DC_{IR} was calculated with the use of the following equation:

$$DC_{IR}(\%) = \left(\frac{\left(\frac{A_{C=C}}{A_{Ar}}\right)_{polymer}}{\left(\frac{A_{C=C}}{A_{Ar}}\right)_{monomer}} \right) \times 100,$$

where $A_{C=C}$ is the absorption intensity of the band resulting from the carbon-carbon double bond stretching vibrations, located at 1637 cm^{-1}, and A_{Ar} is the absorption intensity of the internal standard – the band resulting from the skeletal stretching vibrations of the carbon-carbon bonds in the aromatic rings, located at 1608 cm^{-1}.

Polymerization shrinkage method

Densities of monomers (d_m) were measured with the use of a 1 mL pyknometer, according to the ISO 1675 standard [18]. Densities of polymers (d_p) were determined with the use of an analytical balance equipped with a density determination kit, that uses the Archimedes' principle.

The experimental (S) and theoretical polymerization shrinkages (S_{theor}) was calculated with the use of the following equations:

$$S(\%) = \left(1 - \frac{d_m}{d_p}\right) \times 100,$$

$$S_{theor}(\%) = \left(1 - \frac{\frac{MW}{d_m} - 2 \times 22.5}{\frac{MW}{d_m}}\right) \times 100,$$

where d_m is the density of a monomer mixture, d_p is the density of the corresponding polymer, MW is the molecular weight of a monomer mixture, 2 is the number of double bonds in the monomer molecular, and 22.5 is the volumetric contraction of one mole of the methacrylates group due to its polymerization.

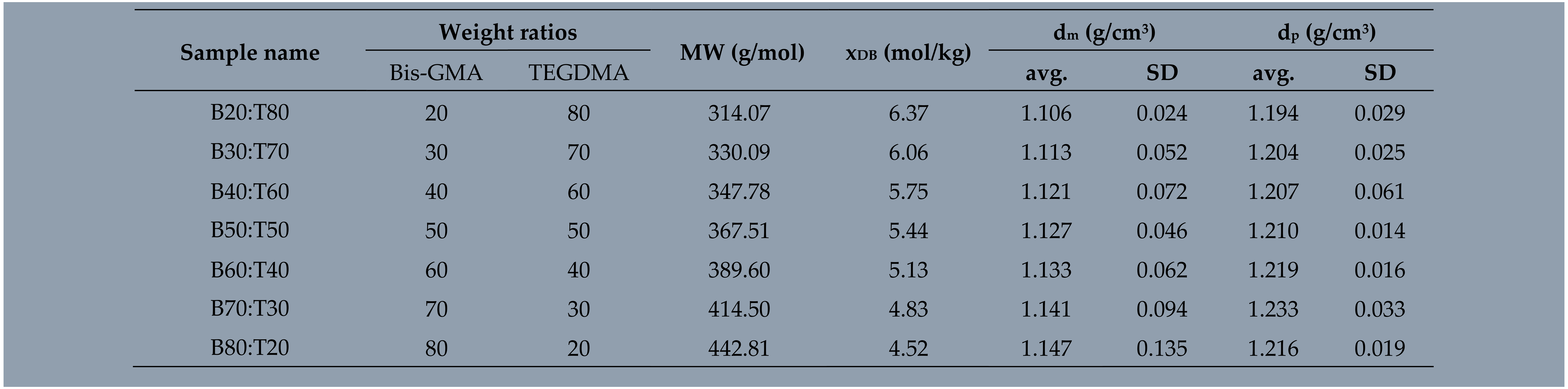
The DC_S was calculated according to the following equation:

$$DC_S(\%) = \frac{S}{S_{theor}} \times 100,$$

where S is the experimental polymerization shrinkage, and S_{theor} is the theoretical polymerization shrinkage.

Results

Table 1. Sample names, their chemical compositions and properties: MW – molecular weight, x_{DB} – concentration of double bonds, d_m – density of uncured samples, and d_p – density of cured samples..



Sample name	Weight ratios		MW (g/mol)	x_{DB} (mol/kg)	d_m (g/cm^3)		d_p (g/cm^3)	
	Bis-GMA	TEGDMA			avg.	SD	avg.	SD
B20:T80	20	80	314.07	6.37	1.106	0.024	1.194	0.029
B30:T70	30	70	330.09	6.06	1.113	0.052	1.204	0.025
B40:T60	40	60	347.78	5.75	1.121	0.072	1.207	0.061
B50:T50	50	50	367.51	5.44	1.127	0.046	1.210	0.014
B60:T40	60	40	389.60	5.13	1.133	0.062	1.219	0.016
B70:T30	70	30	414.50	4.83	1.141	0.094	1.233	0.033
B80:T20	80	20	442.81	4.52	1.147	0.135	1.216	0.019

- The x_{DB} values ranged from 4.52 to 6.37 mol/kg. Its value decreased as the Bis-GMA content increased. As the x_{DB} value informs about the theoretical crosslink density of the dimethacrylate polymer network, it can be said that the greater the Bis-GMA concentration in the monomer mixture, the lower the crosslink density in the resulting polymer network.
- The densities of monomer mixtures (d_m) ranged from 1.106 to 1.147 g/cm^3. The d_m value increased as the Bis-GMA content increased.
- Polymerization resulted in tighter packing, which was reflected in higher densities of cured materials compared to the densities of their uncured counterparts (on average by 7.5%). The polymer densities (d_p) ranged from 1.194 to 1.233 g/cm^3. Its value increased with the increase of the Bis-GMA content up to 70 wt.% and then decreased.

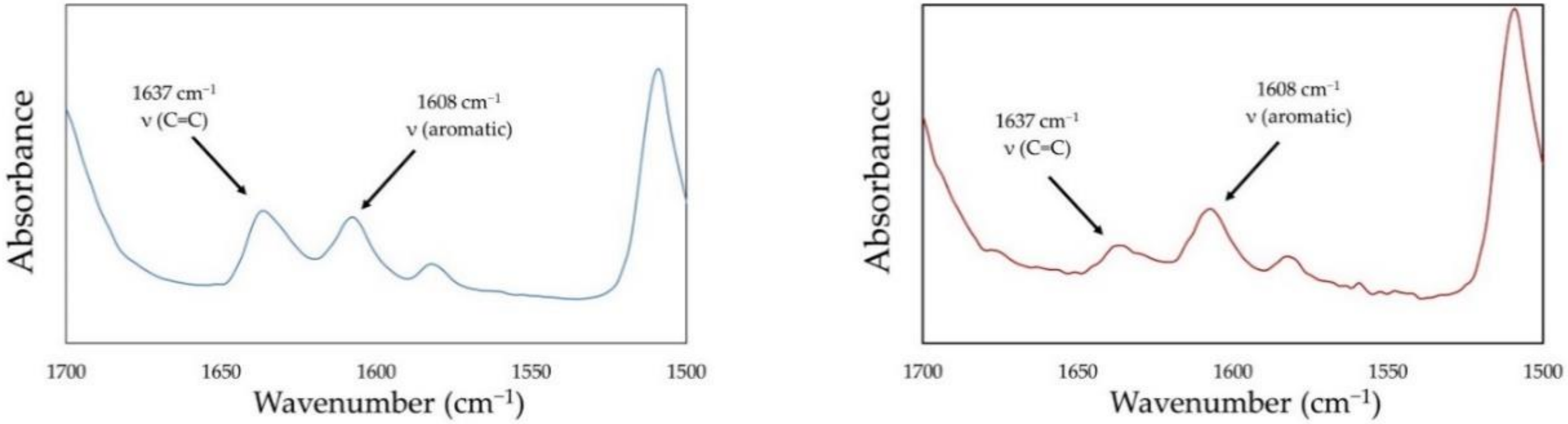
Results

Table 2. The theoretical (S_{theor}) and experimental polymerization shrinkage (S) as well as degree of conversion, calculated from the polymerization shrinkage (DC_S) and absorption intensity (DC_{IR}).

Sample name	S_{theor} (%)	S (%)		DC_S (%)		DC_{IR} (%)	
		avg.	SD	avg.	SD	avg.	SD
B20:T80	15.85	7.39	0.45	46.64	2.32	55.30	5.23
B30:T70	15.17	7.55	0.52	49.81	2.56	60.47	4.78
B40:T60	14.49	7.21	0.41	49.75	2.31	61.01	5.23
B50:T50	13.80	6.89	0.46	49.88	3.04	63.97	3.56
B60:T40	13.09	7.11	0.39	54.33	4.34	64.87	4.87
B70:T30	12.38	7.57	0.55	61.23	3.45	72.83	5.44
B80:T20	11.66	5.44	0.25	46.68	2.98	61.34	5.34

- The S values ranged from 5.44 to 7.57 %. They showed no clear trend throughout the studied series.
- The S_{theor} values ranged from 11.66 to 15.85 % and decreased with the increase in the Bis-GMA content. This relationship resulted from a decreasing concentration of double bonds in this order, since the lower the concentration of double bonds, the lower the volumetric contraction can occur.
- The DC_S values ranged from 46.68 to 61.23 %. It can be seen that the DC_S increased with the increasing Bis-GMA content up to 70 wt.% and then decreased.

Results



(**a**) (**b**)

Figure 3. The representative FTIR spectra of the B80:T20 composition in its uncured (a) and cured (b) forms.

- DC_{IR} values ranged from 55.30 to 61.34 %. As can be seen from Table 2, the DC_{IR} values were higher than the corresponding DC_S values.
- Nevertheless, it is worth noting that a similar tendency was observed in both methods.
- The DC_{IR} values increased as the Bis-GMA content increased up to 70 % and then decreased when the Bis-GMA content exceeded 70 %.
- The DC_S values were lower, in comparison to the DC_{IR} values on average by 18%.

Results

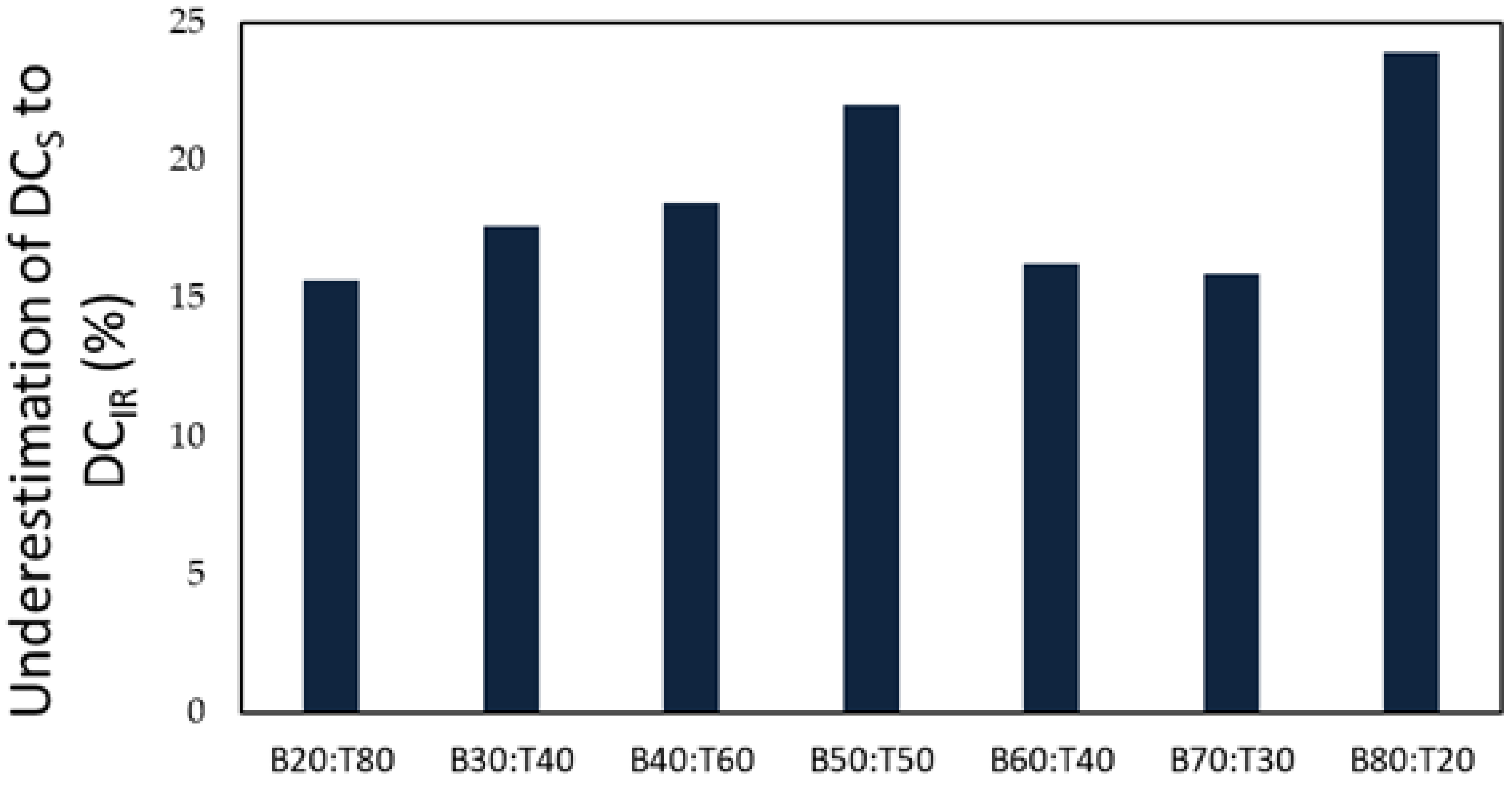


Figure 4. The percentage of underestimation of the DC$_S$ values to the DC$_{IR}$ values.

- The underestimation of the DC$_S$ values to the DC$_{IR}$ values can be explained by the fact that the volumetric contraction does not only depend on the concentration of double bonds, but other factors, too, play an essential role in this phenomenon.
- By increasing the Bis-GMA content, its molecular features increase their impact on the ability to tight packing. It probably resulted in lower d$_p$ values than expected.
- The increase in the Bis-GMA content caused an increase in the viscosity of the monomer mixture, which might increase the inaccuracy of the d$_p$ measurement (the higher the viscosity, the higher the air trapping probability that decreases density).
- The literature shows that the DC$_{IR}$ values calculated with the use of the carbonyl internal standard (instead of the aromatic one) are also underestimated – by approximately 23%.

Conclusions

The methodology of the degree of conversion determination in dimethacrylate polymers based on the measurements of the polymerization shrinkage can be a valuable alternative to the methodology based on the FTIR measurements. It produces underestimated results compared to the methodology using an aromatic internal standard. However, the results achieved with the use of the carbonyl internal standard can be less consistent.