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Shrinkage/stress reduction and mechanical properties improvement in restorative composites formulated with thio-urethane oligomers

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Abstract

Thio-urethane oligomers (TUs) have been shown to favorably modify methacrylate networks to reduce stress and significantly increase fracture toughness. Since those are very desirable features in dental applications, the objective of this work was to characterize restorative composites formulated with the addition of TUs. TUs were synthesized by combining thiols - pentaerythritol tetra-3-mercaptopropionate (PETMP) or trimethylol-tris-3-mercaptopropionate (TMP) - with isocyanates - 1,6-Hexanediol-diisocyanate (HDDI) (aliphatic) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic) or dicyclohexylmethane 4,4'-Diisocyanate (HMDI) (cyclic), at 1:2 isocyanate:thiol, leaving pendant thiols. 20 wt% TU were added to BisGMA-TEGDMA (70–30%). To this organic matrix, 70 wt% silanated inorganic fillers were added. Near-IR was used to follow methacrylate conversion and rate of polymerization ($R_{p_{max}}$). Mechanical properties were evaluated in three-point bending (ISO 4049) for flexural strength/modulus (FS/FM) and toughness (T), and notched specimens (ASTM Standard E399-90) for fracture toughness (K_{IC}). Polymerization stress (PS) was measured on the Bioman. Volumetric shrinkage (VS) was measured with the bonded disk technique. Glass transition temperature (T_g) and heterogeneity of network were obtained with dynamic mechanical analysis. The addition of TUs led to an increase in mechanical properties (except for T_g and FS). Fracture toughness ranged from 1.6–1.94 MPa.m^{1/2} for TU-modified groups, an increase of 33–61% in relation to the control (1.21±0.1 MPa.m^{1/2}). Toughness showed a two-fold increase in relation to the control: from 0.91 MPa to values ranging from 1.70–1.95 MPa. Flexural modulus was statistically higher for the TU-modified groups. The T_g , as expected, decreased for all TU groups due to the greater flexibility imparted to the network (which also explains the increase in toughness and fracture toughness). Narrower tan-delta peaks suggest more homogeneous networks for the TU-modified materials,

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though differences were marked only for TMP_AL. Degree of conversion was not affected by the addition of TUs. VS was similar for all groups, with one exception where VS dropped (PETMP-cyclic). Finally, PS showed a reduction of 23–57% for TU-modified groups (6.7 ± 1.3 to 11.9 ± 1.0 MPa) in relation to the control (15.56 ± 1.4 MPa). The addition of thio-urethane oligomers was able to reduce polymerization stress by up to 57% while increasing fracture toughness by up to 61%.

Graphical Abstract

Keywords

composite resin; thio-urethane oligomers; polymerization stress; volumetric shrinkage; mechanical strength; dynamic mechanical analysis

1. Introduction

Methacrylate-based composite resins have been extensively used since the advent of adhesive Dentistry nearly 60 years ago. The success of this technique is partially due to its conservative nature, especially when compared to amalgam preparations that require a lot larger tooth preparations. However, composites undergo relatively fast hydrolytic and enzymatic degradation in the oral environment, and some by-products have been shown to pose cytotoxicity concerns [1]. In addition, long-term clinical studies have shown that the average life span of a composite restoration is about 5–10 years, with failures mostly related to secondary caries and fracture [2].

In vitro properties of the composite are important predictors of clinical behavior [3]. For example, high degree of conversion imparts greater chemical stability to a polymeric material and has been correlated with decreased wear [4], while mechanical properties, particularly fracture toughness, have been correlated with clinical longevity [3]. In addition, it has been demonstrated that volumetric shrinkage and the resulting polymerization stress influence gap formation at the bonded interface [5]. Even though a definitive link has not been established to date between gap formation and clinical outcomes, the reduction in polymerization stress continues to be an important issue in restorative dentistry.

The use of two types of thio-urethane oligomers as additives has been shown to effectively improve methacrylate-based composites, due to chain-transfer reactions that delay polymer vitrification, at the same time increasing the limiting conversion, reducing polymerization

stress and forming more homogeneous structures [6]. Toughness and fracture toughness increases have been well documented in those networks, and suggested for applications where impact resistance is needed [7]. In the specific case of oligomer additives, the high molecular weight is expected to provide lower volumetric shrinkage [8,9].

Previous studies provided proof of concept data on the feasibility and efficacy of thio-urethanes as oligomeric additives. In this study, the aim was to characterize the properties of composite resins formulated by six thio-urethane oligomers, with systematically varied backbone structures. The hypotheses of this study are that the addition of oligomers will (1) increase final degree of conversion and decrease maximum rate of polymerization, (2) improve mechanical properties, and (3) reduce polymerization shrinkage and stress. These changes will be dependent on the molecular structure of the final polymer, given by variations in the starting materials.

2. Materials and methods

2.1 Materials

The composites formulated for the study were composed of Bisphenol A diglycidyl methacrylate (Bis-GMA; Esstech, Essington, PA, USA) and tri-ethylene glycol dimethacrylate (TEGDMA; Esstech) in a 70:30 mass ratio. Photoinitiators were added to the matrix as follows: 0.6 wt% of a tertiary amine (EDMAB - ethyl 4-dimethylaminobenzoate; Avocado, Heysham, England), 0.2 wt% of dl-camphoroquinone (Polysciences Inc., Warrington, PA, USA), and 0.5 wt% inhibitor (BHT - 2,6-di-tert-butyl-4-methylphenol; SigmaAldrich, St. Louis, MO, USA).

Six oligomers were synthesized in solution in the presence of catalytic amounts of trimethylamine. Multi-functional thiols - pentaerythritol tetra-3-mercaptopropionate (PETMP) or trimethylol-tris-3-mercaptopropionate (TMP) – were combined with di-functional isocyanates - 1,6-Hexanediol-diisocyanate (HDDI) (aliphatic, AL) or 1,3-bis(1-isocyanato-1-methylethyl)benzene (BDI) (aromatic, AR) or Dicyclohexylmethane 4,4'-Diisocyanate (HMDI) (cyclic, CC) (Fig. 1). The isocyanate:thiol ratio was defined at 1:2 according to the Flory-Stockmeyer theory to avoid gelation [10], keeping pendant thiols. Oligomers were purified by precipitation in hexanes and rotaevaporation, and then characterized by $^1\text{H-NMR}$ and mid-IR spectroscopy [11]. The evidence of completion of isocyanate reaction and thio-urethane bond formation were confirmed by the disappearance of the isocyanate peak at 2270 cm^{-1} and the appearance of resonance signals at 3.70 ppm, respectively [12]. The thiol group (SH) concentration for each oligomer was determined using a titration method with Ellman's reagent as previous established [13]. Thio-urethane oligomers were added to the methacrylate organic matrix in proportion of 20 wt% [8]. A composite with the organic matrix formulated only by BisGMA/UDMA/TEGDMA (without oligomer) served as control.

Filler was introduced at 70 wt% (7% OX-50 - $0.04\text{ }\mu\text{m}$; 93% silica $0.7\text{ }\mu\text{m}$, density 3.0 g/ml , refractive index 1.553 - V117 4107, Esstech), with the aid of a mechanical mixer (DAC 150 Speed mixer, Flacktek, Landrum, SC, USA) with 5 min mixing time at 2400 rpm. All procedures were carried out under safe yellow light.

2.2 Photopolymerization reaction kinetics and degree of conversion

The degree of conversion (DC) was obtained using near-infrared (NIR) spectroscopy in specimens of 10 mm in diameter and 0.8 mm thick laminated between two glass slides. The methacrylate =CH₂ absorption at 6165 cm⁻¹ [14] was recorded before and after 60 s of irradiation at 700 mW/cm² (Bluephase, Ivoclar vivadent, Lichtenstein) with the light source in direct contact with the glass slide mold. Real-time monitoring of the polymerization kinetics was carried out in specimens of the same size at 2 scans per spectrum with 4 cm⁻¹ resolution, which provides a greater than 2 Hz data acquisition rate. Kinetic data was collected continuously for 5 min. Samples (*n*=5) were irradiated for 60 s at an incident irradiance of 550 mW/cm². The light attenuation in this case was due to a distance of 2 cm separating the tip of the light guide and the surface of the specimen.

2.3 Volumetric Shrinkage

The bonded disk method was used to evaluate volumetric shrinkage [15]. Composites were placed into a brass ring of approximately 16 mm in diameter and 1.5 mm in height bonded to a glass slide. The composite (*n*=5) was placed so that it did not come in contact with the brass ring, and then the assembly was covered with a microscope cover slip (approximately 0.1 mm thick). A linear variable differential transducer (LVDT) probe was placed in contact with the center of the cover slip. The composite was photoactivated for 60 s at an incidence of 700 mW/cm². As the composite cures and shrinks, it pulls the cover slip down and its deflection is monitored by the LVDT probe. Displacement data was obtained from the signal output of the transducer (in mV). The volumetric shrinkage (% VS) value was calculated as follows:

$$\%VS = \frac{(V_f - V_i) \times f}{h} \times 100$$

Where: V_f is the final displacement value given after polymerization and, V_i is the initial value given by the LVDT probe, in mV, f is the multiplier from the calibration curve and h , is the composite specimen thickness after the polymerization, in μm .

2.4 Polymerization stress

The Bioman apparatus [16] was used to assess the polymerization stress in real time. This system consists of a cantilever load cell whose extremity contains a 5-mm diameter, 0.5-mm tall steel rod. The surface of the rod was treated with a thin layer of Metal primer (Z-prime plus, Bisco, Schaumburg, IL, USA). The opposite surface was a rigid fused silica glass plate of 3 mm thickness, treated with a thin layer of silane ceramic primer (3M ESPE, St. Paul, MN, USA). The composite (*n*=5) was then inserted into the 0.5-mm gap between the upper rod and the lower glass slide and shaped into a cylinder, providing a C-factor of 4. The specimens were photoactivated through the glass during 60 s at an incident irradiance of 700 mW/cm² (Bluephase 2) and the stress followed for 600 s. The load signal from the cantilever cell was amplified and acquired by a computer.

2.5 Glass transition temperature and network heterogeneity

Glass transition temperature and tan delta curves were obtained with dynamic mechanical analysis, in tension mode (DMA Q800, TA Instruments, New Castle, USA). The temperature sweep was fixed at a range of $-50\text{ }^{\circ}\text{C}$ to $250\text{ }^{\circ}\text{C}$ with a ramping rate of $3\text{ }^{\circ}\text{C}$ per min [17]. Samples ($n = 3$, $15\text{ mm} \times 3\text{ mm} \times 1\text{ mm}$) were photoactivated at 700 mW/cm^2 during 60 s (Bluephase 2), stored for one week in dark containers at room temperature, then treated in an oven at $170\text{ }^{\circ}\text{C}$ for 15 h. This protocol was used to ensure the maximum achievable degree of conversion and prevent any further polymerization from occurring during the heating cycle required for the dynamic mechanical testing. The peak value of tan delta curve was used to define the glass transition temperature (T_g) [18]. The heterogeneity of the polymer network was defined by the width at half-height of the tan delta curve (the larger the width at half-height of tan delta peak, the more heterogeneous the polymer) [19,20].

2.6 Fracture toughness

The method utilized to determine fracture toughness (K_{IC}) was based on the evaluation of pre-cracked specimens under fatigue in linear-elastic, plane-strain conditions [21]. Single-edge notch beam (SENB) specimens were fabricated according to ASTM Standard E399- 90 [21] in a $5\text{ mm} \times 2\text{ mm} \times 25\text{ mm}$ split steel mold with a razor blade providing a 2.5 mm notch in the middle of the specimens. The composite was photoactivated during 60 s at an incidence of 700 mW/cm^2 . The bending fracture test was performed using a universal test machine (Q-test) at a cross-head speed of 0.5 mm min^{-1} and K_{IC} was calculated according the following equation:

$$K_{IC} = \frac{3PL}{2BW^{3/2}} \left\{ 1.93 \left(\frac{a}{W} \right)^{1/2} - 3.07 \left(\frac{a}{W} \right)^{3/2} + 14.53 \left(\frac{a}{W} \right)^{5/2} - 25.11 \left(\frac{a}{W} \right)^{7/2} + 25.8 \left(\frac{a}{W} \right)^{9/2} \right\}$$

where P is load at fracture (N), L the length, W the width, B the thickness, and a is the notch length (all in mm) [22].

2.7 Flexural strength, elastic modulus and toughness

The 3-point bending method was used to access the flexural strength. Tests were carried out with a universal test machine (Q-test, MTS, Eden Prairie, WI) at a cross-head speed of 0.5 mm min^{-1} . The bar specimens were prepared in dimensions of $2\text{ mm} \times 2\text{ mm} \times 25\text{ mm}$ according to ISO 4049 [23]. The specimens ($n=10$) were fabricated with the composites sandwiched between glass slides and photopolymerized with 60 s exposures (30 s at each side) at 700 mW/cm^2 . The light activation was performed in two steps considering the mold length of 25 mm, to ensure correct coverage of the light-curing tip on the specimen. Specimens were stored dry for one week in dark containers at room temperature. The flexural strength (FS) in MPa was then calculated as:

$$FS(\sigma) = \frac{3Fl}{2bh^2}$$

where F stands for load at fracture (N), l is the span length (20 mm), and b and h are the width and thickness of the specimens in mm, respectively.

The elastic modulus was determined from the slope of the initial linear part of force x displacement curve.

$$E = \frac{Fl^3}{4bh^3d}$$

F = the load at some point on the linear region of the stress-strain curve

d = the deflection at load F

l , b , and h are as defined above

Toughness was calculated in MPa from the integration of the stress x strain curve using software (Origin 9.1, OriginLab Corporation, Northampton, MA, USA).

2.8 Statistical analysis

Statistical analysis was carried out using one-way ANOVA. Multiple comparisons were done using Tukey's test. All tests were carried out at a global level of significance of 95%.

3. Results

3.1 Degree of conversion and maximum rate of polymerization

The degree of conversion (DC, Table 1) of all thio-urethane groups was similar to the control. Among the experimental groups, TMP_AL (68.4±0.7%) has shown significantly higher DC than TMP_AR (61.5±2.7%) and TMP_CC (62.4±1.4%).

The maximum rate of polymerization ($R_{p_{max}}$, Table 1, and Fig. 2) had a statistically significant reduction in all composites formulated with the oligomers. $R_{p_{max}}$ decreased from 4.9 %. s^{-1} in the control group to a range of 1.3–2.0 %. s^{-1} in thio-urethane groups, with a reduction of up to 73.3%.

3.2 Volumetric shrinkage and polymerization stress

Volumetric shrinkage (VS, Table 1) has shown lower values for all composites formulated by thio-urethanes but only PETMP_CC (2.07%) was statistically different from the control (2.54%).

Polymerization stress (PS, Table 1 and Fig. 3) has shown a significant reduction in all composites containing thio-urethane oligomers in regards to the control. The lowest value, representing a 56.8% reduction in relation to the control (15.5± 1.4 MPa) was presented by PETMP_CC and TMP_AR (6.7±1.3 MPa) also significantly lower than PETMP_AL (11.9±1.0 MPa).

3.3 Glass transition temperature and heterogeneity of network

Glass transition temperature (T_g , Table 1) had a statistically significant reduction in all thio-urethane-based composites in comparison to the control. The type of oligomer was not shown to significantly influence the T_g .

The heterogeneity of network, represented by the half-width of tan-delta peak (HWTDP, Table 1) has shown lower values for all composites formulated by thio-urethane oligomers, but only TMP_AL (40.5 ± 2.5 °C) was statistically lower in comparison to the control (49.3 ± 3.0 °C).

3.4 Fracture toughness, elastic modulus, toughness and flexural strength

All composites containing thio-urethanes had a significant increase in fracture toughness (K_{IC} – Table 2) in comparison to the control. PETMP_AR has shown the overall highest values, also statistically higher than PETMP_AL, TMP_AR and TMP_CC. K_{IC} increased by up to 60%, from 1.21 ± 0.1 MPa.m^{1/2} for the control group to 1.94 ± 0.1 MPa.m^{1/2} for the PETMP_AR oligomer.

A statistically significant increase in elastic modulus (E , Table 2) was observed for composites containing thio-urethanes (except for PETMP_CC). The type of oligomer did not significantly affect the elastic modulus.

Composites containing thio-urethanes presented a significant increase in toughness (T , table 2) in regards to the control. T increased up to 115% from 0.91 ± 0.26 MPa (control) to 1.95 ± 0.37 MPa (PETMP_CC). The different oligomer groups were all statistically similar to each other.

Flexural strength of composites has shown to be similar for all groups (FS, Table 2). FS values ranged from 111.3 ± 11.2 MPa (TMP_AL) to 117.0 ± 6.5 MPa (TMP_AR).

4. Discussion

This study used six types of thio-urethane oligomers to formulate restorative composite resins for evaluation of several properties, including polymerization kinetics, mechanical behavior and volumetric shrinkage, and the resulting polymerization stress. The presence of oligomers provided a significant reduction in the maximum rate of polymerization (up to 73.3%, from 4.9 %. s^{-1} in the control group to a range of 1.3 – 2.0 %. s^{-1} in thio-urethane groups), which is result of chain-transfer reactions of the thiol functionalities pending from the thio-urethanes to the secondary methacrylate matrix. This is a chain breaking mechanism, which results in delayed vitrification of the network [24]. In practical terms, that means that the conversion can theoretically progress to higher levels through this radical-assisted step-growth mechanism before diffusion limitations preclude further polymerization [24]. The effect of the chain-transfer reactions can be easily assessed in the conversion vs. rate curves, where a significantly delayed and slower deceleration is observed, as was the case in this study (Fig. 2). This is expected to lead to significantly lower stress development [8], as well as improvement in mechanical properties [25], as will be discussed later. Increases in conversion with the use of thio-urethanes have indeed been reported previously

in composite materials with relatively low filler content [8,11]. In this study, the degree of conversion of oligomer-containing groups did not differ from the control. One factor that may help explain this finding is the fact that the materials used here were heavily filled (70 wt% filler), so the overall thio-urethane concentration was only 6 wt% of the total mass of composite. This level might not have been enough to lead to appreciable increases in conversion. However, since the maximum rates of polymerization and the deceleration profiles for all thio-urethane-modified groups were almost three times lower than the control, there is clear evidence for the efficacy of the pendant thiol functionalities in delaying gelation/vitrification. Therefore, our first hypotheses was only partially accepted.

Dynamic mechanical analysis is a very powerful tool in providing insight on the network formed, as it allows for the calculation of glass transition temperature, network homogeneity and crosslinking density. The addition of thio-urethanes led to a significant decrease in glass transition temperature for the composites in comparison to the control. This reduction in T_g occurs due to the great flexibility provided by the thio-urethane and thiol-methacrylate networks when compared to methacrylate only, as previously described in thiol-ene [26] and thiourethane networks [11]. In fact, the T_g for these thiourethane additives has been evaluated in a previous study, showing values below room temperature, at around 16 °C [6]. It is important to note, however, that the final T_g values were all well above 130 °C, and therefore, well within clinically acceptable ranges. The benefits of the inclusion of thio-urethanes are evident by the decrease on the width at half-height for the tan delta peak. The decrease was not statistically significant for all groups, except for TMP_ which can be explained by the lesser potential for crosslinking density with the tri-functional thiol, allied with the highly flexible chains in both TMP and HDDI. This may have facilitated chain packing during polymerization and favored the formation of a more homogeneous network with this specific group.

Regardless of the structure, the addition of a low T_g oligomer to the highly glassy methacrylate network led to a significant increase on the elastic modulus, toughness and fracture toughness in comparison to the control group formulated from pure methacrylate, as expected [26]. Flexural strength was not affected, while E increased by up to 12% and was significantly higher than the control (except for PETMP_CC). Toughness increased by up to 115% with the PETMP_CC version of oligomer. Fracture toughness increased by up to 60% with PETMP_AR. It is interesting to note that the highest toughness/fracture toughness values were observed with the oligomers made with the tetra-functional thiol, which can be due both to a higher degree of crosslinking and also to a greater concentration of thiol functionalities, as demonstrated previously [6]. These properties have been considered of great interest in a previous study and correlated with the clinical success of restorations [3]. The fracture toughness is the ability of material to avoid crack propagation, which is important clinically because micro defects are relatively common in these restorative materials. The more homogenous network formed by thio-urethane oligomers is another factor responsible for increasing the mechanical properties [26]. As will be discussed in more detail later, the addition of thio-urethane oligomers also reduces polymerization stress, which leads to lower residual stress build up around inorganic filler particles and lower stress intensity when the crack tip reaches the filler, favorably increasing K_{IC} [25,27,28].

Thus, only for the fact that the flexural strength did not increase, our second hypothesis, that the presence of oligomer would increase mechanical properties, was partially accepted.

Based on the relatively low concentration of thio-urethane in highly filled composites (about 6 wt% as stated above), it is not surprising that the reductions in volumetric shrinkage observed here were only nominal, ranging from 8–18.5%. This is consistent with the amount of pre-polymerized organic matrix added, and is not statistically significant. There was one exception, where shrinkage was reduced by 18.5% in relation to the control – PETMP-CC, which can be explained by a potential lower density of said oligomer (which means the same weight of this oligomer would have occupied more volume in the overall mixture). We have not analyzed the free volume in these networks, however, and this is therefore merely speculative.

The polymerization stress for all thio-urethane modified groups, without exception, were statistically lower than the control. Reductions in stress ranged from 23–57%, which is impressive considering that the oligomer accounted for only 6 wt% of the total composite mass. The greatest stress reductions were observed with the PETMP-CC group (which also showed the only statistically significant reduction in shrinkage) and TMP-AR. The reductions in volumetric shrinkage, in general, were not enough to justify this much reduction in stress. Therefore, this outcome is consistent with delayed gelation provided by the chain-transfer reaction of oligomers to the methacrylate matrix [29]. It is also noteworthy that this reduction in stress did not come at the expense of mechanical properties, which, much on the contrary, actually increased (especially fracture toughness). Based on these results, the third hypothesis, that thio-urethanes would reduce volumetric shrinkage and polymerization stress, was accepted.

5. Conclusion

The results of the present study allow us to conclude that the addition of thio-urethane oligomers to highly filled resin composites significantly improved mechanical properties and reduced polymerization stress. More specifically elastic modulus, toughness and fracture toughness all increased. The use of this additive is a relatively simple approach that does not require any modifications on the initiator system, nor on the techniques clinicians use to polymerize composites.

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Highlights

The addition of TUs led to an increase in toughness, fracture toughness and Young's modulus;

Narrower tan-delta peaks suggest more homogeneous networks for the TU-modified materials;

Polymerization Stress showed a reduction of 23–57% for TU-modified groups.

Figure 1.

Structures of isocyanates (A: 1,3-Bis(1-Isocyanato-1-Methylethyl)Benzene, BDI – aromatic isocyanate; or Dicyclohexylmethane-4,4'-diisocyanate, HMDI - Desmodur, cyclic isocyanate; 1,6-Hexanediol diisocyanate, HDDI – aliphatic isocyanate) and thiols (B: Trimethylol tris-3-mercaptopropionate (TMP) or Pentaerythritol tetra-3-mercaptopropionate (PETMP)).

Figure 2.

Degree of conversion as a function of the rate of polymerization for the control and thio-urethane-based groups. Samples were irradiated for 60 s at an incident irradiance of 550 mW/cm². Kinetic data was collected continuously for 5 min.

Figure 3.

Polymerization stress as a function of time for thio-urethane groups in comparison with the control. Materials were photoactivated with 700 mW/cm^2 for 60 s, while polymerization stress development was followed in real time for 600 s.

Table 1

Mean and standard deviation for degree of conversion (DC), maximum rate of polymerization ($R_{p_{max}}$), volumetric shrinkage (VS), polymerization stress (PS), glass transition temperature (T_g) and half-width of tan-delta peak (HWTDP) for all composites. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	DC (%)	$R_{p_{max}}$ (% $\cdot s^{-1}$)	VS (%)	PS (MPa)	T_g (°C)	HWTDP (°C)
Control	63.6(1.7)ab	4.9(0.4)a	2.54(0.0)a	15.5(1.4)a	178.4(4.6)a	49.3(3.0)a
PETMP_AL	67.0(0.7)ab	1.3(0.1)b	2.22(0.2)ab	11.9(1.0)b	155.8(5.1)b	42.5(2.7)ab
PETMP_AR	65.1(1.8)ab	1.6(0.1)b	2.20(0.1)ab	8.2(1.5)c	136.2(3.3)b	41.7(4.1)ab
PETMP_CC	63.6(3.4)ab	1.3(0.1)b	2.07(0.1)b	6.7(1.3)c	138.7(7.8)b	42.8(1.5)ab
TMP_AL	68.4(0.7)a	1.4(0.1)b	2.33(0.1)ab	8.4(2.9)bc	145.5(4.4)b	40.5(2.5)b
TMP_AR	61.5(2.7)b	1.3(0.1)b	2.21(0.1)ab	6.7(1.4)c	146.1(4.9)b	43.1(2.1)ab
TMP_CC	62.4(1.4)b	2.0(0.1)b	2.28(0.0)ab	8.2(2.0)c	148.6(14.4)b	42.3(2.7)ab
<i>p-value</i>	0.011	0.001	0.038	0.001	0.001	0.039

Table 2

Mean and standard deviation for fracture toughness (K_{IC}), elastic modulus (E), toughness (T) and flexural strength (FS) for all composites. Values followed by the same superscript within the same test are statistically similar ($\alpha=5\%$).

	K_{IC} (MPa.m ^{1/2})	E (GPa)	T (MPa)	FS (MPa)
Control	1.21(0.0)d	3.9(0.1)b	0.91(0.2)b	111.5(9.5)a
PETMP_AL	1.69(0.1)bc	4.4(0.3)a	1.89(0.4)a	113.7(11.0)a
PETMP_AR	1.94(0.0)a	4.4(0.1)a	1.91(0.2)a	116.7(6.1)a
PETMP_CC	1.78(0.0)ab	4.1(0.1)ab	1.95(0.3)a	114.8(8.0)a
TMP_AL	1.79(0.0)ab	4.3(0.2)a	1.70(0.4)a	111.3(11.2)a
TMP_AR	1.6(0.0)c	4.4(0.2)a	1.87(0.2)a	117.0(6.5)a
TMP_CC	1.7(0.1)bc	4.3(0.1)a	1.82(0.5)a	111.9(15.2)a
<i>p-value</i>	<i>0.001</i>	<i>0.001</i>	<i>0.001</i>	<i>0.852</i>