# Stress-relaxing composite ligature wires: Formulations and characteristics

Ross P. McKamey, BS; Robert P. Kusy, PhD

**Abstract:** A stress-relaxing composite ligature was developed that has both mechanical and esthetic characteristics that make it attractive for use in orthodontics. The neutrally-colored polymer-polymer composite was created by encasing ultra-high molecular weight poly(ethylene) fibers in a poly(n-butyl methacrylate) polymer, which was formulated from a polysol and an optimal benzoin ethyl-ether concentration. The resulting composite ligature exhibited a tensile strength more than twice that of dead-soft stainless steel ligature, and a stress-relaxation decay significantly greater than stainless steel ligature. With these characteristics, the material could be used as an orthodontic ligature when tooth movement with negligible friction due to ligation is desired. A Maxwell-Weichert model predicted the load-decay profiles that ultimately resulted in the general loss of frictional forces with time.

**Key Words:** Composite, Ligature, Mechanical properties, Stress relaxation

A clinician's skill and experience can influence the magnitude, direction, and point of application associated with the force system used to move a tooth. When no binding occurs, the force system can be resolved into three components[1-3]: an applied force, a countervailing couple, and a frictional force, which results from the normal force of ligation (Figure 1a). The resolution of these forces around the center of resistance (Figure 1b) results in two additional couples: one due to the applied force, the other due to the frictional force (Figure 1c). Within the present context, these forces and couples must be delicately balanced in order to produce translational movement of a tooth.[1-3] The only means a clinician has to achieve this delicate balance is through the use of available appliances and acquired expertise. Initially, expansion arches were soldered to molar bands to transfer force.[1-3] Later, brass and stainless steel ligating components were used to transfer force.[1-3] With these components, a clinician's skill could have a significant impact on the amount of force applied by the proverbial "four turns of a ligating wire," for example. The frictional force encountered is proportional to the normal force of ligation via the coefficient of friction.

Currently, elastomeric components (rubber bands, chain modules, etc.) provide some consistency and predictability in force application. However, elastomeric components assimilate odors and colors, and they experience load reductions over time.[1-4] While these characteristics are predominantly undesirable, the load reduction feature may be useful in certain applications. The primary research goal was to develop a practical, nonmetallic alternative for potential use as a ligating device.

A unidirectional, fiber-reinforced composite* is one option for a ligating device. Such a composite ligature would be composed of a high-strength, flexible polymeric fiber encased in a chemically different polymeric matrix. To function as an orthodontic ligature, this composite ligature would need to be strong and flexible. Since a

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* Commonly, a composite is formed by combining two or more classes of material (ceramic, metal, polymer, or semi-conductor) to produce desirable physical and mechanical properties. In this context, we shall extend the definition to include man-made materials of different chemical structures that possess a physical interface.

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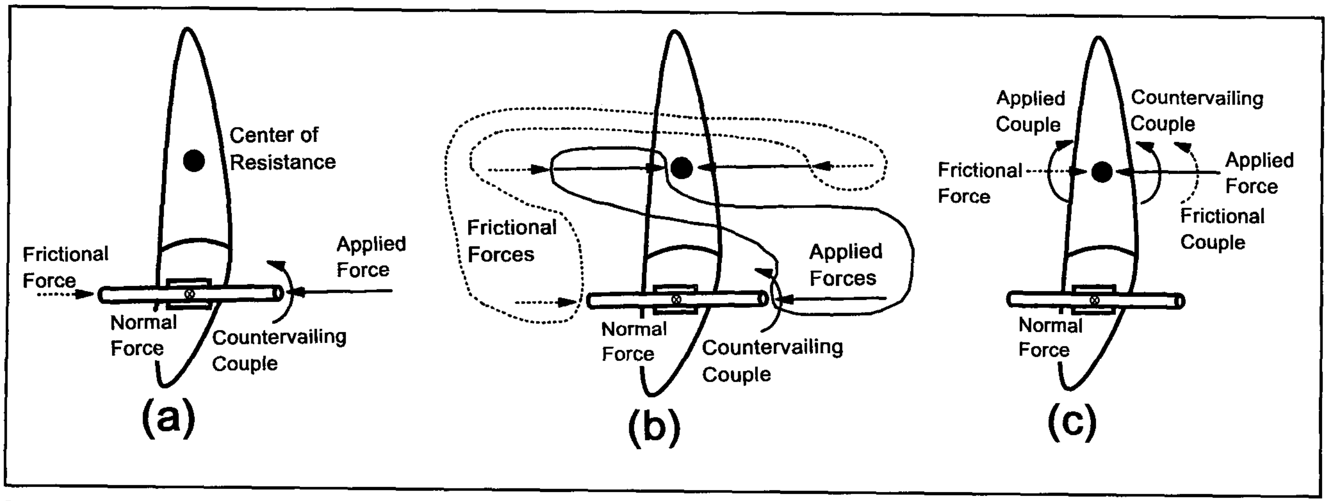

Figure 1
Basic tooth movement and mechanics when binding is absent: (a) force system at the bracket; (b) equivalent forces located at the center of resistance along with those designated that can form couples; and (c) resulting equivalent force system located at the center of resistance. Note that the normal force, which is perpendicular into the plane of the page, is shown because it is not only proportional to but also the cause of the frictional force. Figure does not represent a free-body diagram.

glassy copolymer matrix would not meet these requirements, a tough and rubbery matrix would be developed, having a glass transition temperature ($T_g$) below the ambient or working temperature range. The combination of a high-strength polymeric fiber encased in a rubbery matrix would produce a tough, flexible, strong composite.

The featured composite could also exhibit a stress-relaxation phenomenon in which the applied load decayed in minutes to a small fraction of its initial value. This characteristic could be important to practitioners in general and to residents and novice orthodontists in particular, who potentially use excessive force to ligate an archwire into a bracket. Under these circumstances, the composite would relax and the applied force would diminish to a negligible amount, thus reducing the frictional force component. A stress-relaxing composite ligature could help some practitioners achieve bodily tooth movement when tipping might otherwise occur with the use of an improperly adjusted stainless steel ligature. This stress-relaxation phenomenon can be characterized with

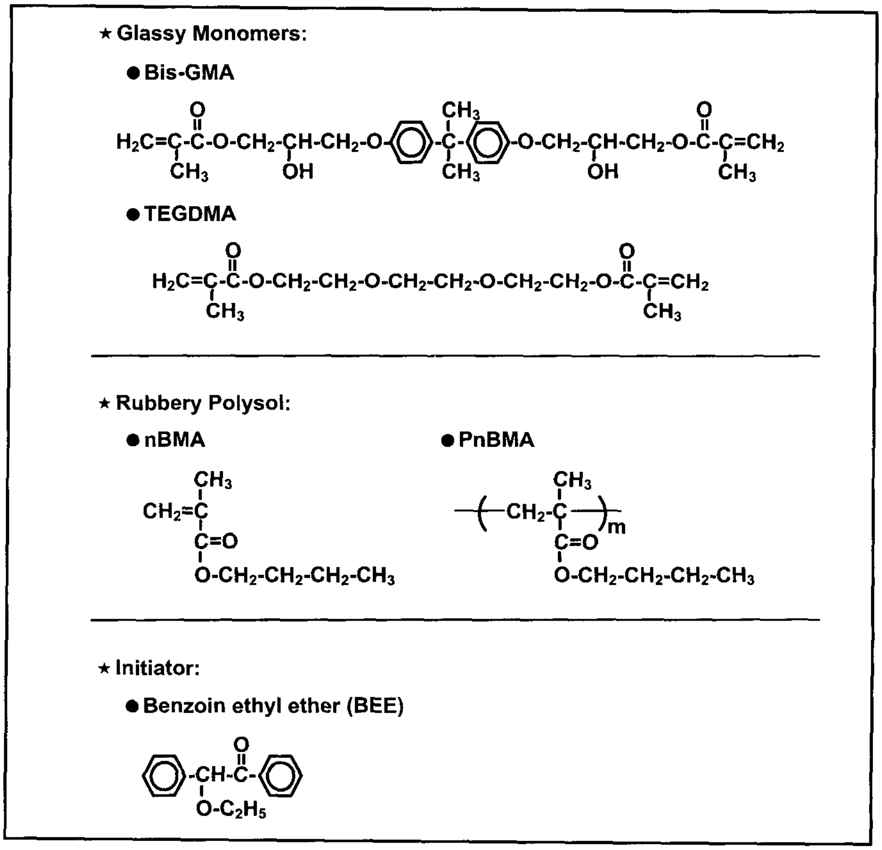

Figure 2
Chemical structures of glassy monomers, rubbery polysol, and initiator used to make the matrices of the composite ligatures. (See Tables 1 and 2 for compositions and concentrations.)

the Maxwell-Weichert model, such that the load-decay profile can be predicted as a function of time.

**Table 1**
**Materials investigated, their composition, and mean diameters**

| Material | Composition | Mean diameter (mm) |
|---|---|---|
| Bis-GMA-composite | 60.8 wt% Bis-GMA/ 38.8 wt% TEGDMA/ 0.4 wt% BEE matrix with SPECTRA® reinforcement | 0.230 ± 0.021 |
| PnBMA-composite | 30 wt% PnBMA/ 70 wt% nBMA/ 1.0 wt% BEE matrix with SPECTRA reinforcement | 0.210 ± 0.024 |
| Spiderwire™ | Three braided strands of SPECTRA | 0.333 ± 0.039 |
| Stainless steel | Single-stranded solid stainless steel ligature | 0.254 ± 0.028 |

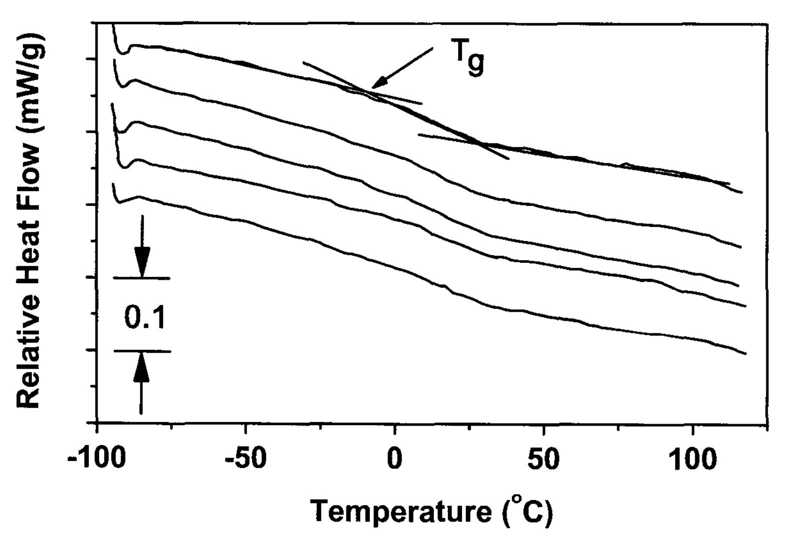

Figure 3
Typical glass transition ($T_g$) tracings for a neat 1.0 wt% BEE-initiated nBMA polysol. Also shown on the first of the five runs is the intersection of the initial baseline slope and its deviation to the heating baseline slope (which was used to calculate the $T_g$s) and the intersection of the heating baseline slope with its return to the final baseline slope. Note: mW/g = milliwatt/gram.

## Materials and methods

### Materials

***Glassy copolymer matrix.*** A copolymer of 60.8 wt% bisphenol-A diglycidyl methacrylate (Bis-GMA; Cook Composites and Polymers, Kansas City, Mo) and 38.8 wt% triethylene-glycol dimethacrylate (TEGDMA; Polysciences, Warrington, Pa)[5] was the first matrix composition investigated (Figure 2). This copolymer is commonly used in restorative dentistry, is easy to manipulate, and polymerizes to form a hard, tough polymer.[6] The ultraviolet initiator, benzoin ethylether (BEE; Aldrich Chemical, Milwaukee, Wis), was added at a concentration of 0.4 wt% (Figure 2). Park et al.[7] have shown BEE to be the best photoinitiator among the aromatic carbonyl compounds for polymerizing acrylic acid, methacrylic acid, and methyl methacrylate. A novel ultraviolet light-cured pultrusion process (Kusy & Kennedy, US Patent filed 1994) was used to mold and secure the reinforcing fibers in the glassy copolymer (Bis-GMA-composite ligature, diameter [dia.] = 0.230 mm [0.0091 in.]; Table 1). A single fiber strand (see *Reinforcement fibers*) having 60 filaments per bundle (fpb) provided the core around which the Bis-GMA-composite was formed and contained a volume percent of reinforcing fiber, $V_p = 46.7\%$.

***Rubbery polysol matrix.*** A polysol (polymer-solvent) mixture of 30 wt% poly(n-butyl methacrylate; PnBMA, Polysciences, Warrington, Pa) and 70 wt% n-butyl methacrylate (nBMA; Aldrich Chemical, Milwaukee, Wis) was blended (Figure 2). Prior to mixing, the inhibitor (methyl-hydroquinone) was removed from the nBMA monomer using a commercially available filtration column (Scientific Polymer Products, Ontario, NY). The BEE initiator was again used to polymerize the matrix.[7] Variations in the concentrations of BEE (0.1, 1.0, and 10.0 wt%) were investigated to establish their effect on the molecular weights and $T_g$s (Table 2).[8-11] The PnBMA-composite ligature was produced by encasing a single 60 fpb strand of reinforcing fibers ($V_p = 71.7\%$) in the 1.0 wt% BEE-initiated nBMA polysol. The PnBMA-composite (dia. = 0.210 mm [0.0083 in.]; Table 1) was photo-pultruded and exposed to an additional 15 minutes of ultraviolet radiation (BLAK-RAY Longwave Ultraviolet Lamp, Model B-100A, Ultra-Violet Products, Inc, San Gabriel, Calif).

***Reinforcement fibers.*** Ultra-high molecular weight poly(ethylene) fibers (SPECTRA© 1000, Allied Signal, Petersburg, Va), containing 60 fpb, were selected. This highly-oriented fiber of $-\!(\mathrm{CH}_2)\!-_{n>100{,}000}$ has mechanical properties comparable to polyaramid and carbon fibers on a weight-for-weight basis[14] and is used for personal and vehicle armor, sporting goods, cordage and netting, and cut-protection applications. While the stress-relaxation characteristics of this material have not been fully investigated, it served as a primary component in both the composite ligature wires.

***Other products.*** In addition to the Bis-GMA- and PnBMA-composite ligatures that were formed, two other products were evaluated as control samples (Table 1). A commercially available fishing line (30 lb. test Spiderwire™, dia. = 0.333 mm [0.013 in.]; Safariland, Mankato, Minn), composed solely of three braided yarns of 100% SPECTRA, was chosen as a control for the SPECTRA reinforcing fibers. As a clinically relevant control, a dead-soft, single-stranded stainless steel ligature wire (dia. = 0.254 mm [0.010 in.]; Item PL1010 ligature wire, GAC International, Commack, NY) was chosen.

## Polymer characterization

***Glass transition.*** Differential scanning calorimetry (DSC; model 990130, TA Instruments, Wilmington, Del) was used to monitor the $T_g$s of the neat polymeric matrices. The DSC thermocouple and temperature scale were calibrated using the melting points of indium and gallium.[11] Once the machine was calibrated, each test sample (15 mg) was sealed in an aluminum pan, heated at a rate of 10°C/min to a final temperature of 120°C, and quenched to -100°C. This heating and quenching process was repeated five more times for each sample. From these last five runs, each $T_g$ was determined from the intersection of the original baseline and its first deviation from the heating baseline slope[15] (Figure 3) and then averaged.

***Molecular weight.*** Using high-performance liquid chromatography (HPLC; Waters 590; Milford, Mass) and both a Shodex® KF-802 column (Showa Denko KK, Tokyo) and a Waters ultrastyragel linear column for low and high molecular weights, respectively, each formulation was evaluated under the following conditions: flow rate, 1.0 ml/min; injection volume, 100 µl; maximum sample concentration, 2.5 mg/ml; solvent, tetrahydrofuran. Initially a calibration curve was derived from 10 polystyrene Shodex standards ranging in weight average molecular weights from 1.32x$10^3$ to 3.03x$10^6$. Each number average molecular weight ($M_n$), weight average molecular weight ($M_w$), and polydispersity index (PDI) represented the average of three sample runs.[16]

**Table 2**

**Initiator concentration and the associated glass transition temperature ($T_g$), weight average molecular weight ($M_w$), number average molecular weight ($M_n$), and polydispersity index (PDI) of the PnBMA matrix. All materials analyzed over the time period from 12-17 minutes.**

| Initiator | $T_g$ (°C) | $M_w$ | $M_n$ | PDI |
|---|---|---|---|---|
| 0 wt% BEE (pure PnBMA*) | 24.0 ± 9.0 | 175,000 | 62,500 | 2.8 |
| 0.1 wt% BEE | 33.4 ± 2.7 | 139,000 | 17,900 | 7.7 |
| 1.0 wt% BEE | -2.3 ± 4.5 | 103,000 | 8,700 | 11.8 |
| 10.0 wt% BEE | -32.5 ± 2.5 | 58,100 | 4,700 | 12.2 |

* Only this formulation is received as 100% PnBMA or "pure" PnBMA; all others are polymerized from a polysol of 30 wt% PnBMA and 70 wt% nBMA

**Table 3**

**Comparison of Young's modulus (E) and ultimate tensile strength (UTS) with respect to volume percent of reinforcing fiber ($V_p$) for SPECTRA-based materials**

| Material | $V_p$ (%) | E (GPa) | Relative E (%) | UTS (MPa) | Relative UTS (%) |
|---|---|---|---|---|---|
| SPECTRA | 100.0 | 172* | 100.0 | 3,000* | 100.0 |
| Bis-GMA-composite** | 46.7 | 65.0 ± 4.4*** | 80.7 | 1,260 ± 80 | 89.5 |
| PnBMA-composite** | 71.7 | 54.2 ± 5.3 | 43.9 | 1,940 ± 190 | 90.1 |
| Spiderwire** | 100.0 | 26.9 ± 1.1 | 15.6 | 1,540 ± 60 | 51.5 |
| Stainless steel ** | 0 | 199 ± 13 | N/A | 729 ± 36 | N/A |

* See ref. 14
** See Table 1
*** All means plus or minus one standard deviation were determined for five samples

## Other characterizations

***Dimensions.*** To determine average diameter, the Bis-GMA-composite ligature, PnBMA-composite ligature, and Spiderwire were measured optically, after calibrating a Zeiss microscope (Zeiss Corporation, Oberkuchen, West Germany, Table 1). Because stainless steel is rigid, a µ-Mate digital micrometer (Sony Magnescale of America, Inc, Orange, Calif) was used for the samples.

***Mechanical testing.*** Both composite ligatures, the Spiderwire, and the stainless steel ligatures were tested in tension using an Instron model TTCM (Instron Corp, Canton, Mass). Capstan grips at 80 psig air pressure secured each sample at an initial gage length of 152.4 mm (6 in.). Young's modulus (E) was determined using either an Instron 10% or 50% extensometer (0.5 in. span) at a displacement rate of 2 mm/min and a full-scale force of 2,000 g. The ultimate tensile

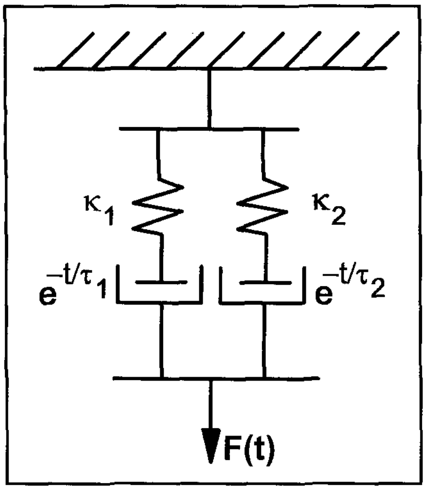

Figure 4
Geometry of springs and dashpots having pre-exponential elastic ($\kappa_1$, $\kappa_2$) and exponential time ($\tau_1$, $\tau_2$) constants, respectively, for the two element Maxwell-Weichert model (see equation).

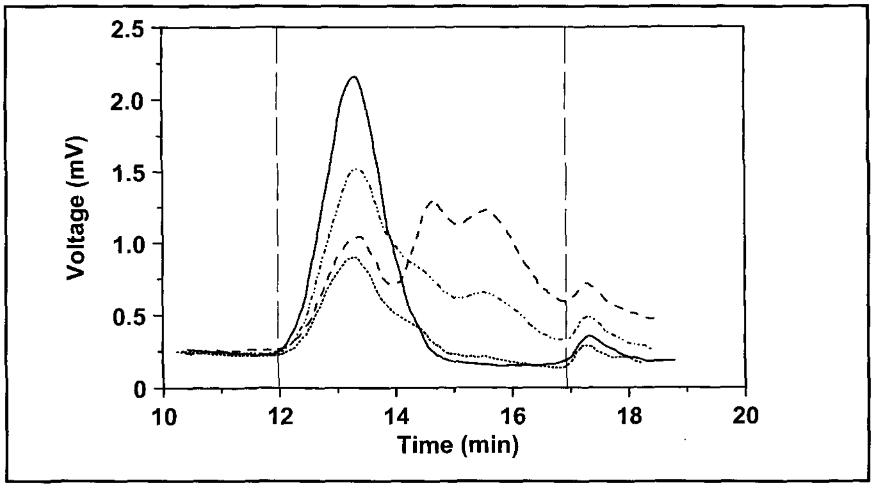

Figure 5
HPLC elution time tracings for the neat polymers: pure PnBMA (—), 0.1 wt% BEE-initiated nBMA polysol (···), 1.0 wt% BEE-initiated nBMA polysol (-··), and 10.0 wt% BEE-initiated nBMA polysol (---). See Table 2.

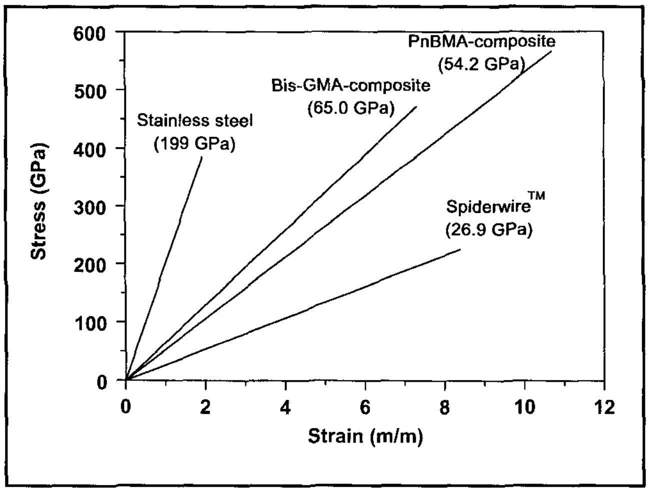

Figure 6
Comparison among the Young's moduli (E) of stainless steel ligatures, Bis-GMA-composite ligatures, PnBMA-composite ligatures, and Spiderwire.

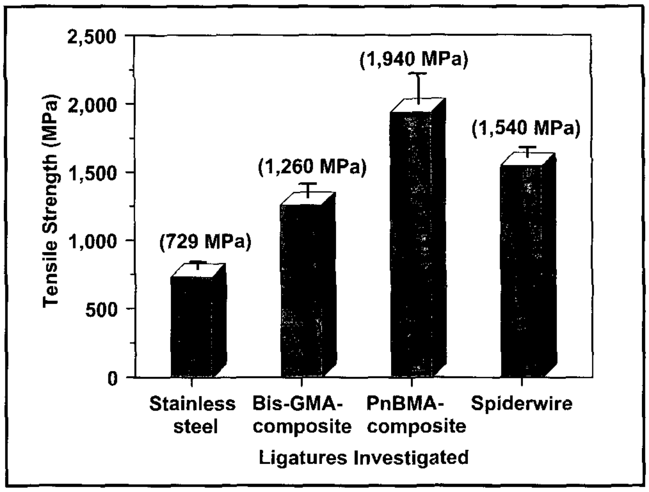

Figure 7
Comparison among the ultimate tensile strengths (UTS) of stainless steel ligatures, Bis-GMA-composite ligatures, PnBMA-composite ligatures, and Spiderwire.

strength (UTS) was determined by testing to failure a minimum of six samples at a rate of 20 mm/min.

Using the same instrument, stress-relaxation measurements were also made. The stainless steel, Bis-GMA-composite, and PnBMA-composite ligature samples were elongated 13, 9, and 25 mm, respectively, producing forces that ranged from 500 to 1,000 g. The load-decay profiles were then recorded. Assuming the cross-sectional area (A) remains constant, the change in force ($\Delta F$) was a direct indicator that a change in stress ($\Delta\sigma$) had occurred, since $\Delta\sigma = \Delta F / A$.

***Computer modeling.*** From the stress-relaxation studies of the Bis-GMA-composite ligature, PnBMA-composite ligature, and stainless steel ligature, a computer model was developed that simulated the decay rate and pattern of each material. A Maxwell-Weichert model,[17,18] consisting of a pair of spring-dashpot elements in parallel (Figure 4), was used to calculate the pre-exponential elastic constants ($\kappa_1$ and $\kappa_2$) and the exponential time constants ($\tau_1$ and $\tau_2$), given a particular fixed elongation (x) and a particular force (F) at time (t), hence the equation:

$$F(t) = x(\kappa_1 e^{-t/\tau_1} + \kappa_2 e^{-t/\tau_2})$$

Here, the pre-exponential spring constants ($\kappa_1$, $\kappa_2$) indicate the elastic response, whereas the exponential constants ($\tau_1$, $\tau_2$) indicate the viscous response. A least squares approach was used to evaluate the accuracy of the model. This approach calculated a best-fit curve by minimizing the so-called error, which was defined as the sum of the squares of the differences between the 10 calculated points and their corresponding experimental data. To reduce the error and avoid any local minima, each of the four parameters was serially adjusted.

## Results

The $T_g$ for the Bis-GMA-composite was above room temperature (RT = 20°C) as the specimen cracked and changed from transparent to translucent when the sample was bent. Since the goal was to produce a rubbery polymeric matrix with a $T_g$ < RT, further formulations of this copolymer were abandoned. Instead, the characteristics of the neat polymer produced by the nBMA polysol were investigated and found to be desirable and dependent on the amount of initiator used (Table 2). An initiator concentration of 0.1 wt% BEE produced a $T_g = 33.4 \pm 2.7$°C, and an initiator concentration of 1.0 wt% BEE produced a $T_g = -2.3 \pm 4.5$°C (Table 2). Further increases in the concentration to 10.0 wt% BEE reduced the $T_g$ to $-32.5 \pm 2.5$°C (Table 2). An initiator choice of 1.0 wt% BEE was made, since it acceptably fulfilled the criterion of producing a rubbery matrix.

Since the relationship between $T_g$ and molecular weight has already been determined for several systems,[8-11,19] changes in initiator concentration were expected to affect the molecular weight characteristics of the PnBMA matrices. The HPLC study indicated that varying BEE concentrations still produced polymers with high molecular weights (Table 2). Higher molecular weights improve the polymer's resistance to degradation, leaching, discoloration, and odor assumption. Pure PnBMA had a $M_w \approx 175 \times 10^3$, $M_n \approx 62.5 \times 10^3$, PDI = 2.8, and a resulting $T_g \approx 24$°C (cf. $T_g \approx 21$°C, ref. 20). These values provide a baseline reference for comparing the molecular weight distributions of the PnBMA matrices produced in the initiator study (Figure 5). When evaluated, each BEE concentration had a systematic effect on the $M_w$, $M_n$, PDI, and thus $T_g$ of the PnBMA matrix. Generally, as the

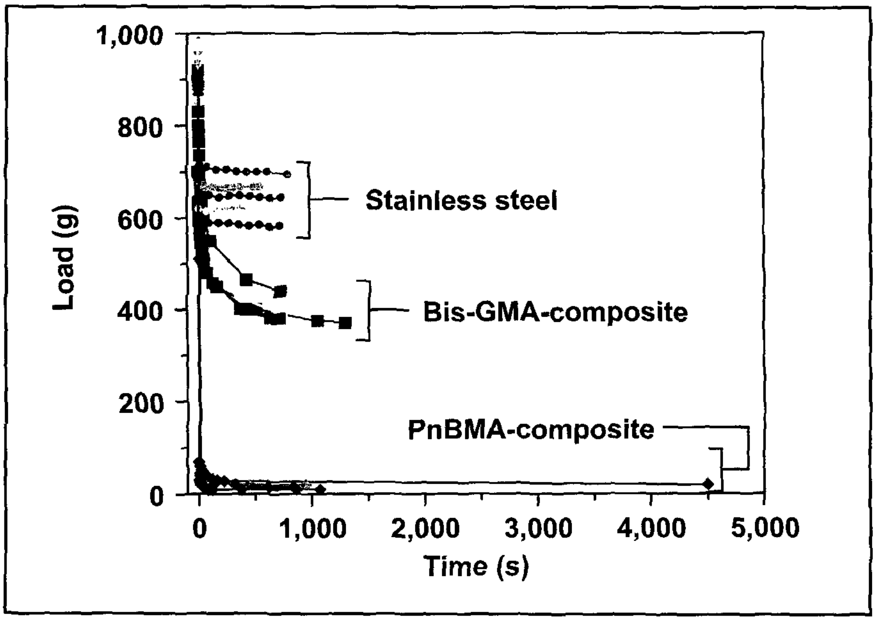

Figure 8
Load-decay profiles as a function of time for stainless steel ligatures, Bis-GMA-composite ligatures, and PnBMA-composite ligatures.

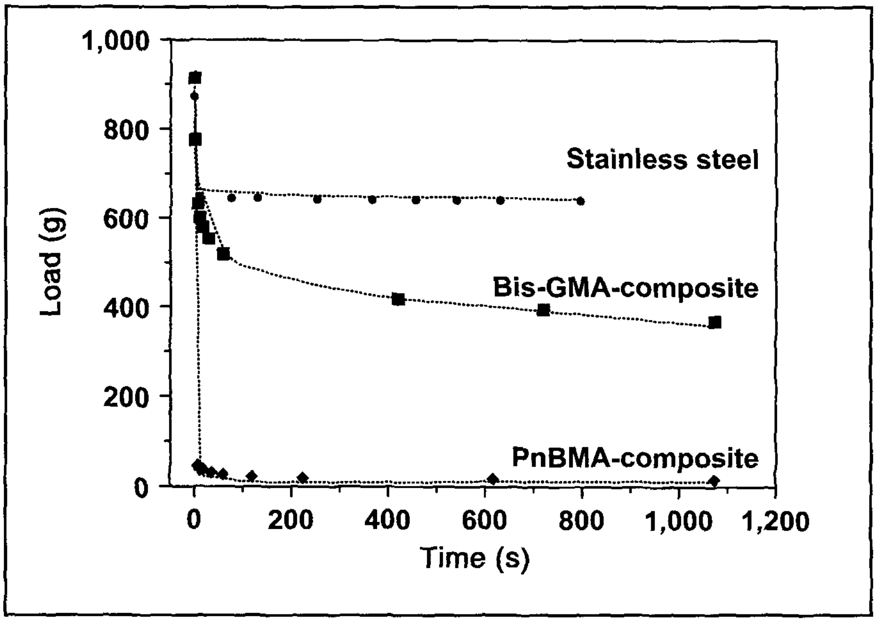

Figure 9
Comparison of computer-generated models (L) with the actual relaxation data of a stainless steel ligature, a Bis-GMA-composite ligature, and a PnBMA-composite ligature.

weight percent of BEE increased, the $M_n$ of the polymer decreased more rapidly than the $M_w$, which consequently increased the PDI (Figure 5 and Table 2). Although the polymers had a PDI as high as 12.2, polymer systems can have PDIs as high as 30.[10]

Mechanical testing of the four materials provided comparative data of Young's moduli, ultimate tensile strengths, and stress-relaxation characteristics.

Young's modulus (E) measurements proved that the stainless steel ligature was substantially stiffer, E = 199 GPa* (28.9 Msi), than any of the polymeric materials tested (Figure 6). The glassy Bis-GMA-composite at E = 65.0 GPa (9.43 Msi) proved stiffer than the rubbery PnBMA-composite at E = 54.2 GPa (7.87 Msi). Both were stiffer than the Spiderwire at E = 26.9 GPa (3.91 Msi). The E of pure SPECTRA from the literature is E = 172 GPa (25 Msi)[14] (Table 3).

Ultimate tensile strength (UTS) measurements indicated that the stainless steel commonly used in orthodontics was the weakest of the samples (Figure 7), having a UTS = 729 MPa (106 ksi). Due to its ductility, the stainless steel dissipated energy by plastic deformation (via dislocations) and consequent reduction of its cross-sectional area (via necking). All SPECTRA-based fibers experienced brittle failure, with no noticeable reduction in cross-sectional area. The Bis-GMA-composite ligature failed at UTS = 1,260 MPa (182 ksi), which is slightly less than the failure stress of the Spiderwire, at UTS = 1,540 MPa (224 ksi). The best material was the PnBMA-composite ligature, which failed at UTS = 1,940 MPa (281 ksi). The UTS of pure SPECTRA is UTS = 3,000 MPa (435 ksi)[10] (Table 3).

**Table 4**
**Maxwell-Weichert model parameters for the Bis-GMA-composite, PnBMA-composite, and stainless steel ligatures**

| Material | Test # | $\kappa_1$ (g/cm) | $\tau_1$ (s) | $\kappa_2$ (g/cm) | $\tau_2$ (s) | Error* ($g^2$) |
|---|---|---|---|---|---|---|
| Bis-GMA-composite | 1 | 1,060 | 10.0 | 1,180 | 5,300 | 4,580 |
| | 2 | 1,160 | 10.0 | 1,280 | 2,700 | 2,370 |
| | 3 | 1,030 | 7.6 | 1,240 | 2,400 | 2,720 |
| | 4 | 1,000 | 8.4 | 1,240 | 2,700 | 3,220 |
| | 5 | 687 | 5.5 | 1,610 | 2,000 | 2,850 |
| | 6 | 733 | 5.6 | 1,310 | 2,200 | 1,610 |
| | Mean ± sd | 945±190 | 7.9±2.0 | 1,310±150 | 2,900±1,200 | 2,890±990 |
| PnBMA-composite | 1 | 339 | 8.0 | 12.2 | 10,700 | 10 |
| | 2 | 336 | 10.0 | 10.6 | 1,100 | 144 |
| | 3 | 387 | 6.5 | 4.6 | 20,000 | 11 |
| | 4 | 374 | 5.8 | 10.9 | 3,100 | 37 |
| | 5 | 353 | 10.0 | 5.0 | 20,000 | 52 |
| | Mean ± sd | 358±22 | 8.1±1.9 | 8.7±3.6 | 11,000±9,000 | 51±55 |
| Stainless steel | 1 | 211 | 0.5 | 537 | 100,000 | 121 |
| | 2 | 184 | 0.4 | 496 | 100,000 | 36 |
| | 3 | 135 | 0.3 | 473 | 48,500 | 45 |
| | 4 | 161 | 0.3 | 568 | 35,600 | 48 |
| | 5 | 200 | 0.4 | 520 | 100,000 | 26 |
| | Mean ± sd | 178±31 | 0.4±0.1 | 519±37 | 76,800±32,100 | 55±38 |

*The error (in "grams squared" or $g^2$) is an indicator of the accuracy of the model and equals the sum of the squares of the differences between the ten calculated points and their corresponding experimental data.

A comparison of the typical force-decay profiles for stainless steel, Bis-GMA-composite, and PnBMA-composite ligatures shows marked differences (Figure 8). While all experienced a sharp decline after initial loading, the magnitude of loss is the most interesting feature. The stainless steel and the Bis-GMA-composite dropped to 71% and 44% of their initial loading, respectively; whereas, the PnBMA-composite ligature dropped to only 2% of the initial load.

The computer model predicted the force-decay profiles of the stainless steel and PnBMA-composite ligatures when tested against a representative set of experimental data (Figure 9). The $\kappa$ and $\tau$ parameters are indicative of each material's mechanical performance (equation and Table 4). For example, for the PnBMA-composite ligature, the mean values obtained to model decay include the pre-exponential elastic constants ($\kappa_1$ = 358 g/cm, $\kappa_2$ = 8.7 g/cm) and the exponential time constants ($\tau_1$ = 8.1 s, $\tau_2$ = 11,000 s). This equates in the physical world to a fast-acting, stiff spring ($\tau_1$, $\kappa_1$) being paired with a long-acting, weak spring ($\tau_2$, $\kappa_2$, Figure 4).

## Discussion

### Clinical importance

Bodily tooth movement via a countervailing couple is one means of sliding teeth and generally correcting malocclusion. But to achieve bodily movement, even transiently, a delicate balance must be achieved between the applied force and the countervailing couple (Figure 1). The bodily movement is also influenced, in part, by the ligation force applied to the bracket via the archwire. This is a result of the encountered frictional force being proportional to the normal force of ligation. If the amount of frictional force is not accurately

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* In this text: $10^9$ Pa ≡ GPa, $10^6$ Pa ≡ MPa, $10^6$ psi ≡ Msi, $10^3$ psi ≡ ksi

compensated for, the tooth experiences controlled tipping that is due, in part, to the resulting frictional couple. By using a stress-relaxing ligature, the normal force due to ligation decays rapidly with time, thereby reducing the frictional force and consequently the frictional couple. As the present PnBMA-composite ligature relaxes to a negligible amount, the PnBMA-composite ligature facilitates planned treatment goals. Thereby, this stress-relaxing, composite ligature exerts a "tight" ligating normal force for a short time and then quickly relaxes to a minimal (2%) ligating force (Figure 8). In effect then, the ligature is passively active—that is, the PnBMA-composite ligature acts as a passive restraint until it is activated by forces applied to the archwire-bracket combination.

### Various properties

The $T_g$ of the resulting composite material is of critical importance to the mechanical properties. The PnBMA-composite ligature embodies a $T_g < RT$. This feature enables the composite to stress-relax or dissipate load by permitting movement between polymeric chains. In a glassy copolymeric matrix, such as that found in the Bis-GMA-composite, the chemical crosslinks prevent the chains from sliding past each other. The stress relaxation of the PnBMA-composite ligature is crucial to its potential use in orthodontics. By blending the monomer with the polymer, the number of small chains is substantially increased, thereby decreasing the $M_n$ and increasing the PDI (Table 2). Thus, the number and effectiveness of initiator sites increase.

Although various methods can define the $T_g$ of a material,[15,21,22] the DSC method was chosen to indicate the actual physical response of each polymeric matrix. Although at least three ways of defining the $T_g$ exist, the intersection of the original baseline and its first deviation from the heating baseline slope provided the best representation of the material's physical response (Figure 3). This definition produces the minimum $T_g$s for all sampled materials; and, like all conventions, the $T_g$s are consistent within each sampled material.

An interesting observation was noted with regard to the dimensions of the photo-pultruded composites. Although each composite contains the same 60 fpb reinforcing fiber and was pultruded through the same 0.254 mm (0.010 in.) die, the mean diameter varies from 0.230 mm for the Bis-GMA-composite to 0.210 mm for the PnBMA-composite (Table 1). This small difference in overall diameter has a substantial effect, when calculating the $V_p$ of the reinforcing fiber at 46.7% and 71.7%, respectively. This phenomenon is attributable to the characteristic differences (e.g., thermal expansion coefficients, die swell, and monomer shrinkage) that each monomer and its polymer exhibit.

In this work a tacit assumption was made that the mechanical properties of Spiderwire would be similar to the published reports of SPECTRA. However, the mechanical properties differed, when normalized with respect to the $V_p$ of SPECTRA in each of the materials (Table 3). The rule of mixtures presumes that a composite will possess the properties of the constituent materials in direct proportion to the volume percent that each constituent occupies.[23] Although Spiderwire is comprised entirely of SPECTRA, Spiderwire retains only 16% and 52% of the E and UTS of SPECTRA, respectively (Table 3). During the processing of Spiderwire, the characteristics of SPECTRA are somehow compromised. On the other hand, the Bis-GMA-composite ($V_p = 47\%$) retains nearly 81% and 90% of the E and UTS of SPECTRA, respectively. And although the PnBMA-composite ($V_p = 72\%$) performs equally as well as the Bis-GMA composite in tension, the PnBMA-composite retains only 44% of the E of SPECTRA. Upon gross physical examination, the glassy Bis-GMA/TEGDMA matrix apparently bonds better to the reinforcing fibers, thus transferring any applied load more effectively to the fibers.

### Maxwell-Weichert model

Using the equation, a mean value of each parameter was determined, providing a general equation for determining the stress-relaxation characteristics of each ligature material. Although the values for a particular parameter were assumed constant for each material, this assumption did not hold for the less attractive and consequently abandoned Bis-GMA-composite ligature. Instead, those $\kappa$ and $\tau$ values did not accurately predict the observed profile and generated relatively large error values (Table 4). This fact indicates that the decay process is more complex for the Bis-GMA-composite. This could be a result of the glassy matrix and its crosslinks restricting sliding within this composite, thereby complicating its decay profile.

The model was able to accurately predict the decay profiles of both the PnBMA-composite and the stainless steel ligatures (Table 4). For all but one of the PnBMA-composite and stainless steel profiles, errors were calculated to be much less than 100. Although their decay profiles may appear markedly different (Figures 8 and 9), both share the features of a fast-acting element paired with a long-lasting element. In the future, such a model will allow the contemporary clinician to predict the magnitude of the force and its associated time dependence, thereby facilitating more exact treatment outcomes.

## Conclusions

The ultra-high molecular weight poly(ethylene) fibers of the rubbery matrix composite relaxed substantially more than the same fibers in a glassy matrix composite.

The rubbery matrix composite was smaller in diameter, one quarter as stiff, and over twice as strong as the dead-soft stainless steel ligature wire.

A two-element Maxwell-Weichert model accurately predicted the stress-relaxation decay of the rubbery matrix composite and the stainless steel ligature wire.

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## References

1. Reitan K, Rygh P. Biomechanical principles and reactions. In: Graber TL, Vanarsdall RL, eds. Orthodontics: Current principles and techniques, 2nd ed. St. Louis: Mosby-Year Book, 1994: 96-192.
2. Burstone CJ. Application of bioengineering to clinical orthodontics. In: Graber TL, Vanarsdall RL Jr, eds. Orthodontics: Current principles and techniques, 2nd ed. St. Louis: Mosby-Year Book, 1994: 235-267.
3. Vaden JL, Dale JG, Klontz HA. The Tweed-Merrifield edgewise appliance: Philosophy, diagnosis, and treatment. In: Graber TL, Vanarsdall RL, eds. Orthodontics: Current principles and techniques, 2nd ed. St. Louis: Mosby-Year Book, 1994: 627-684.
4. Stevenson JS, Kusy RP. Force application and decay characteristics of untreated and treated polyurethane elastomeric chains. Angle Orthod 1994; 64: 455-467.
5. Kennedy KC, Chen T, Kusy RP. Mechanical properties of micron-sized pultruded composite profiles. In: Advanced composites X: Proceedings of the 10th Annual ASM/ESD Advanced Composites Conference, ASM International, Materials Park: Ohio, 1994: 191-200.
6. Kennedy KC, Kusy RP. UV-cured pultrusion processing of glass-reinforced polymer composites. J Vinyl & Additive Tech 1995; 1:182-186.
7. Park H-R, Chung Y-G, Ham H-S. Photoinitiated polymerization of acrylic acid derivatives in methanol. Bull Korean Chem Soc 1994; 15: 169-171.
8. Kusy RP, Greenberg AR. Influence of molecular weight on the dynamic mechanical properties of poly(methyl methacrylate). J Thermal Analysis 1980; 18:117-126.
9. Lu X, Jiang B. Glass transition temperature and molecular parameters of polymer. Polymer 1991; 32:471-478.
10. Painter PC, Coleman MM. Crystallization, melting, and the glass transition. In: Fundamentals of polymer science: An introductory text. Lancaster, Pa: Technomic, 1994:247-287.
11. Mark JE, Eisenberg A, Graessley WW, Mandelkern L, Koenig JL. The glassy state and the glass transition. In: Physical properties of polymers. Washington, DC: American Chemical Society, 1984: 55-95.
12. Greener EH, Harcourt JK, Lautenschlager EP. Polymers in dentistry. In: Materials science in dentistry. Baltimore: Williams & Wilkins, 1972: 299-351.
13. Craig RG, ed. Plastics (prosthetic applications). In: Restorative dental materials, 6th ed. St. Louis: Mosby, 1980: 345-393.
14. Jones FR, ed. Fibrous reinforcements for composite materials. In: Handbook of polymer-fibre composites. Essex, England: Longman Scientific & Technical, 1994: 54.
15. Bair HE. Glass transition measurements by DSC. In Seyler RJ, ed. Assignment of the glass transition. ASTM STP 1249. Philadelphia: American Society for Testing and Materials, 1994:50-74.
16. Simon MA, Kusy RP. The molecular, physical and mechanical properties of highly plasticized poly(vinyl chloride) membranes. Polymer 1993; 34:5106-5115.
17. Rosen SL. Linear viscoelasticity. In Fundamental principles of polymeric materials, New York: Wiley-Interscience, 1982: 236-277.
18. Aklonis JJ, MacKnight WJ, Shen M. Viscoelastic models. In Introduction to polymer viscoelasticity. New York: Wiley-Interscience, 1972: 143-191.
19. Dibenedetto AT, Dilandro L. Correlation of glass transition temperature and molecular weight: A model based on the principle of corresponding states. J Polymer Sci: Part B: Polymer Phy 1989; 27: 1405-1417.
20. Nielsen LE. Transitions in high polymers. In: Mechanical properties of polymers. New York: Reinhold, 1962: 11-46.
21. Todoki M. Thermal analysis of plastics and rubbers. Inter Polymer Sci Tech 1988; 15: T50-61.
22. Stoklasa K, Tomis F. Thermal analysis of polymeric materials. Inter Polymer Sci Tech 1990; 17: T31-34.
23. Callister WD. Composites. In: Materials science & engineering: An introduction, 3rd ed. New York: John Wiley & Sons, 1994: 513-545.