Original Article

In Vitro Kinetic and Thermodynamic Staining Study of Three Energy Drinks on the Restorative Charisma Composite

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Abstract

Aim: The research utilized charisma composite resin, a dental restorative material known for its esthetic properties, with the chemical formula 2,2-bis[p(2-hydroxy-3-methacryloxy propoxyphenyl)] propane. The primary objective of the study was to examine the overall color change (ΔE^*ab) of the charisma resin after it was subjected to three distinct energy drink solutions: Monster Energy Ultra-Sunrise, Wild Tiger, and Red Bull. Further we examined the effects of temperature and time on the staining interaction and overall color difference ΔE^*ab on the surface of charisma restorative resin generated by three energy drink. **Materials and Methods:** A microfilled Charisma Classic composite resin was used in presented comparative study selected. The prepared 144 composite disk samples (subdivided n=48) with random allocation method were used for the three energy drinks to determine the effect of temperature and time over the course of 90 days. A metallic circulator mold was prepared. Every set of 48 specimens in the energy drink was heated in a water bath for 1, 7, 30, 60, and 90 days at four different temperatures This investigation spanned various time intervals, ranging from 1 to 90 days, and encompassed four temperature levels between 283 and 310 K. One-way ANOVA was used to evaluate the mean data for color change between the energy drinks, and Tukey's *post hoc* test was used for multiple comparisons, with a significance level of $P < 0.05$. **Results:** The study revealed that the rate of staining was most pronounced in the case of Wild Tiger, while it was comparatively lower for Monster Energy Ultra-Sunrise. These findings were established through an examination of the kinetic and thermodynamic behavior of surface color changes in micro-hybrid composites treated with the three energy drink solutions. **Conclusions:** The observed patterns aligned with the pseudo second-order model. It was observed that the Red Bull drink displayed a negative activation energy, resulting in a slower color change rate with increase in temperature. In contrast, endothermic, spontaneous, and regular staining activity was demonstrated throughout time by Monster Energy Ultra-Sunrise and Wild Tiger.

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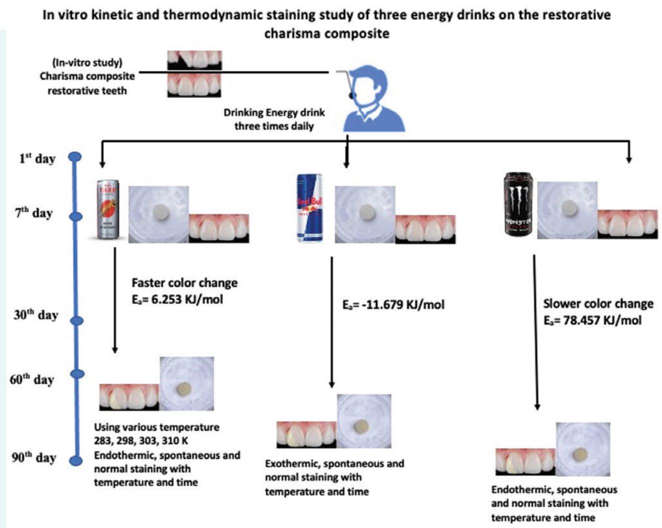

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Introduction

Over the past 10 years, dental restorative materials have undergone significant expansion to fulfill the esthetic needs of dental practices; fundamental component attributes are essential for many aspects of these materials. Dental restorations in the oral cavity are prone to a variety of circumstances that cause mechanical and physical changes such as wear and discoloration. Consequently, the quality of the repair deteriorates over time and requires replacement.[1]

The known factors influencing the discoloration of restorative materials are filler particle size, concentration, and resin formulation.[2] The modern era of esthetic dental composites ushered that the charisma composite resin that contains monomers with bisphenol A-glycidyl methacrylate (Bis-GMA) structure in their molecules has a unique hybrid monomer, the low polymerization contraction resins with the excellent setting behavior of acrylic monomers[3,4] and with a heterogeneous microstructure involving one or more interphases.[5] There are times when different dental materials or improper operating methods cause discolorations; these dentist-related discolorations are typically avoidable. Teeth discoloration can also be caused by microleakage surrounding composite restorations.[6] Chemicals may be able to pass through the margins and discolor the dentin underneath the restoration. Furthermore, composites have the potential to discolor with time, changing the crown's hue.[7,8]

The restorative composite may get discolored at the interface of the filler and polymer or as a result of a color shift in the resin material itself. These factors can vary depending on factors such as surface roughness, nutritional habits, smoking habits, beverage consumption, and oral hygiene conditions, whereas inadequate polymerization may result in an unreacted methacrylate group or oxidation/alteration of the amine catalyst polymeric structure, which causes chemical staining.[9,10]

The younger generations love acidic energy drinks, which have been consumed in substantial quantities over the past few years.[11] The type of coloring agent, acidic erosion, surface roughness, type of composite material, temperature, and length of exposure to coloring agents are the main factors causing the physical consequences of excessive energy drink consumption on the tooth and composite material.[12] According to certain *in vitro* research, the weakening and cracking of the resin matrix may occur due to the drinks' acidity.[13,14] It has been proposed that patients should be made aware that composites that have already been placed might need to be replaced or reduced. However, after successful bleaching, composite restorations that are located in esthetically important places would need to be replaced in order to improve color matching.[15]

From 2004 to 2023, only 10 studies on the restorative charisma classic composite were conducted, three of which focused on the color change;[16,17] however, Tanthanuch *et al.* 2022 conducted an *in vitro* study to investigate the effects of energy drinks and sports drinks on the hardness, roughness, and color of the surfaces of several dental restorative materials, such as glass

Table 1: Some chemical properties of the Red bull, Wild Tiger, and Monster Energy Ultra-Sunrise energy drinks

Energy drink	Components	Manufactures	pH	ORP (mV)	Energy (kJ)
Red Bull	Carbonated water, sucrose, and glucose Citric acid Taurine (0.4%) Sodium and magnesium bicarbonate Color (caramel; riboflavin) Caffeine (0.03%) Vitamins (niacin, pantothenic acid, B6, and B12)	London United Kingdom	3.45	388	195
Wild Tiger	Carbonated water and sugar Citric acid, trisodium citrate, and benzoic acid Taurine (0.37%) Glucuronolactone 0.24% Color (caramel and positive E150C) Caffeine (0.03%) Vitamins (niacin, pantothenic acid, B2, B6, and B12)	Amman Jordan	2.92	421	215
Monster energy ultra-sunrise	Carbonated water and sugar Citric acid (calcium and sodium citrate) Taurine (0.4%) Panax Ginseng root extract 0.08% Color (Carotins) Caffeine (0.04%) Vitamins (B3, B5, B6, and B12) Sodium chloride; D-glucuronolactone, Guarana seed extract (0.002%), inositol	Dublin, Ireland	3.56	380	156

ionomer, bulk-fill resin composite, and nanohybrid resin composite. These drinks' acidity and titratable acidity were also evaluated.[18]

Notably, no investigations were conducted regarding the impact of time and temperature on color changes specifically related to energy drinks on the charisma classic composite resin. The purpose of this study is to examine the effects of temperature and time on the staining interaction and overall color difference ΔE^{*ab} on the surface of charisma restorative resin generated by three distinct energy drink types: Monster Energy Ultra-Sunrise, Wild Tiger, and Red Bull.

Materials and Methods

Setting and design

The current research and comparison studies were conducted from June 2023 to January 2024 at the Rizgary Teaching Hospital in Erbil, Iraq, in the Kurdistan area. Three distinct energy drink brands (Wild Tiger, Red Bull, and Monster Energy Ultra-Sunrise) were submerged in 144 prepared Charisma Classic composite resin disk-shaped specimens for varying periods of time over the course of 90 days at varying temperatures.

Sampling criteria

The commonest microfilled Charisma Classic composite resin type uses in Erbil city for anterior and posterior esthetic restoration were selected. The prepared 144 composite disk samples are randomly subdivided into three groups ($n = 48$) random allocated for the three energy drinks to determine the effect of temperature and time. A potential confounding variable in studies of color change is that the energy drinks may not actually be taking or decreased especially those that are more acidic.

Ethical approval and informed consents

On August 16, 2023, the Health Science College Research Ethics Committee of Hawler Medical University granted approval for this study under the number Sc.E.C. 11C. Despite the fact that this article/study type may not require informed consent because of the materials used, it is claimed that the information provided is accurate to the best of its knowledge and belief.

Methodology

A metallic circulator mold was used to produce 144 specimens with a diameter of 12 mm and a thickness of 2.0 mm. The specimens were then positioned on top of a glass slide and filled with the charisma traditional micro-hybrid composite resin material. This material had the characteristics of an A2 shade with a Bis-GMA matrix and barium aluminum fluoride glass, with a filler loading of 61/78 (vol%/wt%) and a filler type of 0.005–10 mm. Germany's Heraeus Kulzer GmbH manufactured the specimens. To apply pressure on the excess composite material, an LED device and an additional glass slide were positioned on top of the mold. The composite specimens' polymerization was cured using a (LEDition polymerization unit, Ivoclar Vivadent AG, Liechtenstein). The objects' surfaces were polished, beginning with rough and ending with ultrafine (coarse–medium–fine–ultrafine) subsequently.

Every set of 48 specimens in the energy drink was heated in a water bath for 1, 7, 30, 60, and 90 days at four different temperatures (283, 298, 303, and 310 K). The oxidation reduction potential (ORP), energy, pH, and components of the three energy drinks utilized in this study, Red Bull, Monster Energy ultra-Sunrise and Wild Tiger, are listed in Table 1.

The specimens for the experimental groups were submerged in their corresponding energy drinks for 5 min, three times a day, in order to replicate the average frequency of energy drink use. In contrast, the control specimens for the composite were maintained in distilled water. An adequate amount of energy drink (25 mL) was present in each group's Petri plate during the immersion time. The energy drinks in each group were switched out everyday until the immersion program was over. The test subjects' samples were soaked in distilled water at room temperature in between immersions, and they were then exposed to the equivalent energy drink. Using distilled water, the specimens were cleaned, and any leftover residue from the surface was removed from the energy drinks. The tested composite disks (color stability) were cleaned, and they were dried using absorbent paper.

Observational parameters

The VITA Easyshade Advance 4.0 (Model Deasysu, VITA Zahufabrik, Bad Sackingen, Germany) was used to record baseline color values for each temperature of 283, 298, 303, and 310 K after all prepared samples were submerged in 20 mL of distilled water in separate containers. The following formulas were used to derive the colorimetric values L^*, a^*, b^*; the differences in parameters ΔL^*, Δa^*, Δb^*; and the total color difference ΔE^{*ab}.[19,20]:

$$\Delta L^* = L^* - L_0^* \quad (1)$$

$$\Delta a^* = a^* - a_0^* \quad (2)$$

$$\Delta b^* = b^* - b_0^* \quad (3)$$

$$\Delta E_{ab}^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (4)$$

where the a* and b* coordinates indicate the color chromaticity and range from green to red and blue to yellow, respectively, and L* represents the color brightness, which ranges from white to black.

Kinetic and thermodynamic analysis for staining of the composite

Kinetic models' applicability and the pace at which material property P changes at time t can be described by[21,22]:

$$\frac{dP}{dt} = \pm kP^n \quad (5)$$

where the reaction order is denoted by n.

where k is the chemical reaction's rate constant and P is the composite's color change value (ΔE^{*ab} values) with time t in the energy drink.

Generally speaking, the Arrhenius equation can be used to explain a chemical reaction[23]:

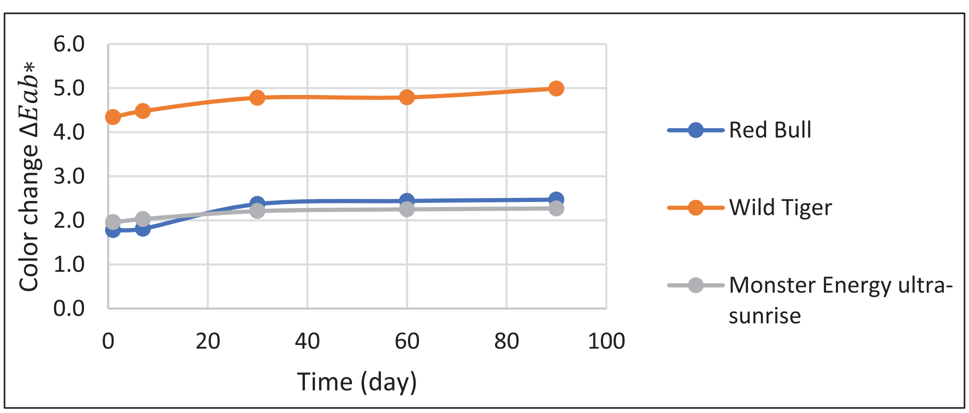

Figure 1: The effect of time from 1 to 90 days for the energy drinks Red Bull, Wild Tiger, and Monster Energy Ultra-Sunrise on the charisma composite at 298 K

Table 2: Compression of the rate constants and coefficient of determination among several kinetic models to changes in the color values during the temperature treatment 283–310 K

Energy drinks	Temperature (K)	Zero-order		First-order		Second-order	
		k (mole/L.day)	R^2	k (1/day)	R^2	k (L/mole. day)	R^2
Red bull	283	0.0082	0.82	0.0118	0.99	0.0072	0.99
	298	0.0082	0.76	0.0104	0.97	0.0051	0.98
	303	0.0088	0.78	0.0106	0.98	0.0051	0.98
	310	0.01	0.85	0.0101	0.98	0.0047	0.99
Wild tiger	283	0.0034	0.91	0.0035	0.99	0.0018	0.99
	298	0.0034	0.79	0.004	0.97	0.0019	0.98
	303	0.0043	0.81	0.0045	0.89	0.0021	0.98
	310	0.0033	0.64	0.0032	0.88	0.0024	0.99
Monster Energy Ultra-Sunrise	283	0.0037	0.87	0.0016	0.99	0.0004	0.99
	298	0.0065	0.87	0.0029	0.97	0.0007	0.97
	303	0.006	0.88	0.0032	0.98	0.0006	0.98
	310	0.0077	0.93	0.0029	0.97	0.0006	0.97

Table 3: Thermodynamic parameters for the staining color on the charisma composite due to energy drink at temperature range 283 to 310K

Energy drinks	Temperature (K)	E_a (KJ/mol)	$\triangle H^{\#}$ (KJ/mol)	$\triangle S^{\#}$ (KJ/mol K)	$\triangle G^{\#}$ (KJ/mol)
Red Bull	283	− 11.679	− 14.032	0.975	− 289.894
	298		− 14.157	0.974	− 304.512
	303		− 14.198	0.974	− 309.384
	310		− 14.256	0.974	− 316.203
Wild Tiger	283	7.253	4.900	1.084	− 302.002
	298		4.776	1.084	− 318.266
	303		4.734	1.083	− 323.686
	310		4.676	1.083	− 331.272
Monster energy Ultra-Sunrise	283	78.427	76.075	1.253	− 278.618
	298		75.950	1.253	− 297.415
	303		75.908	1.253	− 303.679
	310		75.850	1.253	− 312.448

$$\ln k = \ln A - E_a / RT \quad (6)$$

where T is the reaction's absolute temperature, A is the frequency factor, E_a is the activation energy, and R is the gas constant (8.314 J/mol.K).

The following equations are used to get the entropy $\Delta S^{\#}$, Gibbs free energy of activation $\Delta G^{\#}$, and enthalpy of activation $\Delta H^{\#}$ from the results of the activation energy E_a.[24]:

$$\Delta H^{\#} = E_a - RT \quad (7)$$

$$A = \frac{ek_b T}{h} e^{\frac{\Delta S^{\#}}{R}} \quad (8)$$

$$\Delta S^{\#} = R\left(\ln A - \ln\left(\frac{ek_b T}{h} \right) \right) \quad (9)$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \quad (10)$$

where k_b Boltzmann constant is $1.3806 * 10^{-23}$ J/K, h and Planck's constant is $6.626 * 10^{-34}$ J s.

Statistical analysis

One-way ANOVA was used to evaluate the mean data for color change between the energy drinks, and Tukey's *post hoc* test was used for multiple comparisons, with a significance level of $P < 0.05$. Microsoft Excel 2024 was used for statistical analysis of the data.

Results

Figure 1 illustrates the time-dependent nature of the color change ΔE^*ab. During the first 30 days, the Wild Tiger energy drink and Red Bull both induced faster color changes than Monster Energy ultra-sunrise.

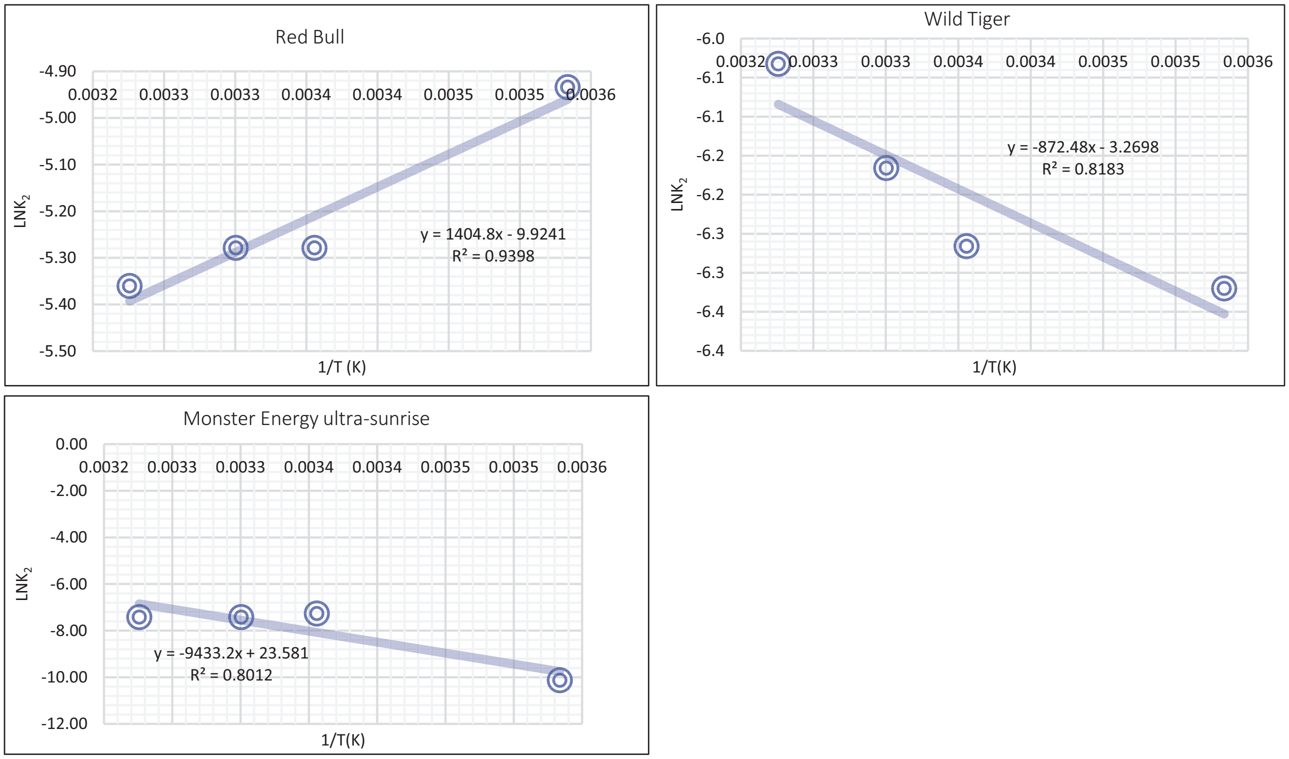

Figure 2: Arrhenius's plot of the staining effect of three energy drinks (Red Bull, Wild Tiger, and Monster Energy Ultra-Sunrise) on the charisma composite resin for the four temperatures 283, 298, 303, and 310 K

The development of the staining, or color change, over time is explained by the mathematical description in Table 2. Rate constant values demonstrate how quickly a reaction happens, and correlation coefficients (R^2) identify which experimental data fit the model. Table 2's tabulated data reveal that the pseudo-second-order model has the value that is closest to unity. This helps quantify how quickly staining happens owing to the interaction between the energy drink and the composite material's nature. It can be expected that the pseudo-second-order rate of reaction is proportional to the square of the concentration of two reactants.

Plotting the natural logarithm of the second-order rate constant, lnk, against the inverse absolute temperature (1/T) in Kelvin allows one to use the Arrhenius equation [Figure 2] to understand temperature-dependent processes for each energy drink on the composition at a specific temperature and determine the energy activation of the color change of the reaction. The staining process's activation energy, or E_a, was calculated from the plot's slope ($-E_a/R$).

As computed and displayed in Table 3, the positive slope for the Red Bull energy drink color change on the charisma composite indicated a negative activation energy. The minimum of energy is needed for the restorative composite to be stained. In addition to the kinetic effect, that is, the change in composite resin and energy drink concentration over time, there is also a thermodynamic influence on the staining of the restorative components.

Thermodynamic parameters, such as temperature and Gibbs free energy of activation ($\Delta G^{\#}$), entropy ($\Delta S^{\#}$), and enthalpy of activation ($\Delta H^{\#}$), found in Table 3, characterize the energy change related to chemical reactions. In the case of an energy drink, it affects the staining color of a composite material at temperatures between 283, 298, 303, and 310 K, or roughly 10, 25, 30, and 37°C. Understanding whether a chemical reaction would happen spontaneously or not under specific conditions is made easier with the help of Gibbs free energy of activation $\Delta G^{\#}$. The staining reaction will tend to proceed toward the more staining product, as indicated by the non-spontaneous staining interaction indicated by the negative values for all energy drinks. The $\Delta G^{\#}$ values are in the order of Wild Tiger > Red Bull > Monster energy Ultra-Sunrise .

The positive shift in entropy $\Delta S^{\#}$, which indicates spontaneously influencing the distribution or absorption of colorants under various temperature settings, provides information about the randomness and disorder of the staining process.

Red Bull (14.0–14.2) and Wild Tiger (4.6–4.9) yielded the lowest enthalpy of activation ($\Delta H^{\#}$) values, while Monster Energy Ultra-Sunrise (75.6–76.2) yielded the highest enthalpy values. Lower values indicate a lower activation barrier, which speeds up the staining process.

Discussion

Kinetic staining study of the energy drinks on charisma classic matrix

For dentists, the gradual change in color of the resins used in restoration procedures as well as the teeth itself is crucial because even a small color shift can be quite noticeable and unfavorable. Both external and intrinsic factors might frequently be the cause of the polymer components of the restoratives' color change (staining). Intrinsic factors for discoloration are the type of the polymer of the resin and the aging of it or decomposition with time. Extrinsic factors for discoloration of the restoratives are the amount of their adsorption and absorption properties of the texture from the exogenous surface with the natural colors and artificial in food, tea, coffee, nicotine, beverages, and mouth rinses.[25]

Kinetic analysis was needed to predict the staining that happens with age, so this study aims to ascertain how long energy drinks have been consumed before affecting the color of the charisma chemical composite, which is made *in vitro* in the lab and consumed three times a day for each energy drink—Red Bull, Monster Energy Ultra-Sunrise, and Wild Tiger. Figure 1 illustrates how the charisma composite's color changes with time, which is consistent with the color changes of another composite that Tanthanuch *et al.* 2022 and Aldharrab 2013 were able to obtain.[18,26]

Table 2 calculates the kinetic equation models for the impact of the color shift, and the pseudo-second-order best fitted model was determined by calculating the correlation coefficients and rate constant values, clarifying that the type of energy drink and the composite's characteristics both contribute to the staining rate and that the concentration of the energy drink and the charisma composite texture contribute to the discoloration rate. Hence, the mechanism that leads to color change with time may be due to the intrinsic factors that the composite resins containing hydrophilic monomers have a greater capacity to absorb water. This allows hydrophilic colorants to be absorbed into the resin matrix. The greater filler particles typically cause greater flaws, which results in a rougher surface, so the substance is more likely to discolor the rougher surface, and from extrinsic factors due to the type of energy drinks because of the high polarity of these artificial dyes, sticky effect of sugars, and low pH, which will form surface degradation on the charisma composite.

Thermodynamic staining study of the energy drink on charisma classic matrix

The Arrhenius equation can be used to describe a staining chemical reaction, as is known empirically. To explore the influence of temperature, plot lnk against 1/T for the designated temperatures at which these energy drinks may be stored or consumed.[23] Dos Santos *et al.*[27] found that the charisma composite resin significantly deteriorated when it was submerged in coffee at a high temperature. Table 3 lists the Arrhenius parameters, entropies, activated enthalpies, and Gibbs free energy derived from the shown graphs.

The minimum amount of energy needed for the reaction between the Red Bull energy drink with the restorative charisma resin has a negative value $E_a = -11.679$ kJ/mole, implying that with the increased temperature, the rate of color change decreases; this may be due to decreasing the effect of other chemicals that will decompose with increasing temperature. While the lower activation energy obtained for Wild Tiger $E_a = 7.253$ kJ/mole helps in more easily reacting with the composite than Red Bull after that Monster Energy Ultra-Sunrise $E_a = 78.427$ kJ/mole. Due to the high sugar content that reacts and decays the composite and the presence of substantial amount of other caffeine, acidic chemicals, and the positive values of ORP resulting from an oxidizing environment that can erode the surface of the restorative charisma composite, more color change is induced. Based on kinetic analysis, color changes caused by heat oxidation during aging can be predicted, according to the results.

From the thermodynamic parameters, activated enthalpy change $\Delta H^{\#}$ on the staining charisma composite by Red Bull is exothermic, while the Wild Tiger and Monster energy Ultra-Sunrise activated enthalpy change $\Delta H^{\#}$ are endothermic, the values of Gibbs free energy $\Delta G^{\#}$ and entropy change $\Delta S^{\#}$ that all the color change are spontaneous and undergo normal change with time.

Color is essential to achieving optimal esthetics. Greater esthetic demands from patients have prompted the development of restorative materials with excellent esthetic properties, which are now often utilized in dental offices. However, a notable disadvantage of resin composites is their tendency to discolor, which may have a substantial impact on the replacement of restorations. Therefore, restoration materials must be as similar to the original shade as possible in order to preserve the restored tooth's esthetic attractiveness over time.[28]

Conclusion

Dental professionals must be knowledgeable about the reasons behind tooth restorative staining in order to explain to patients the exact nature of the restorative resin. It is possible to conclude, within the parameters of this *in vitro* study, that each energy drink solution used in the study affected the color stability of the resin composite materials under evaluation as the aging durations and temperature varied. The impact of energy drink solutions on the stability of resin composites' color varies based on the kind of solution and the presence or absence of acids in the composition during the aging process. Further studies with longer aging periods are recommended by the study's findings.

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Conflict of interest

There are no conflicts of interest.

Authors contributions

Not applicable.

Ethical policy and institutional review board statement

Not applicable as *In-Vitro* Study.

Patient declaration of consent

The authors certify that they have obtained all appropriate patient consent forms. In the form the patient(s) has/have given his/her/their consent for his/her/their images and other clinical information to be reported in the journal. The patients understand that their names and initials will not be published and due efforts will be made to conceal their identity, but anonymity cannot be guaranteed.

Data availability statement

Not applicable.

Abbreviations

A Frequency factors
Bis-GMA Bisphenol A-glycidyl methacrylate
E_a Activation energy
h Planck's constant
J Joule
K Kelvin
k Rate constant
k_b Boltzmann constant
LED Light-emitting diode
ORP Oxidation reduction potential
P Material property
R Gas constant
sec Second
t Time
T Absolute temperature

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