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Frequency Dependence of Glass Transition Temperature of Thermoplastics in DMA Analysis

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The aim of this study is to investigate the effect of oscillatory loading frequency on the dynamic-mechanical properties of 3D printed thermoplastics, namely acrylonitrile-butadiene-styrene (ABS), glycol-modified polyethylene terephthalate (PETG), and polylactide, also known as polylactic acid (PLA). The investigated samples were manufactured using fused filament fabrication (FFF) technology and tested at different oscillation frequencies (1, 5, 10, 15 and 20 Hz). Dynamic mechanical analysis (DMA) demonstrated that an increase in the oscillation frequency causes an increase in the glass transition temperature (T_g) for all analyzed materials, while in the case of the used loading frequencies above 5 Hz, an almost linear dependence between the magnitude of the applied frequency and T_g was observed. The findings also show that with increasing frequency of mechanical loading, there are changes in the viscoelastic properties of the investigated polymers, specifically in the value of the storage modulus (E'), loss modulus (E'') and loss angle ($tan\ \delta$), which points to the complex behavior of the materials under dynamic conditions. The results of this study provide valuable insights for the use of 3D printed polymer materials in applications where they are exposed to dynamic stress - in the automotive or aerospace industries.

Keywords: Dynamic mechanical analysis (DMA), Fused filament fabrication (FFF), Glass transition temperature (T_g), Oscillation frequency, Thermoplastics

1 Introduction

Additive manufacturing most often uses materials such as acrylonitrile butadiene styrene (ABS), polyethylene terephthalate glycol (PETG), and polylactic acid (PLA), each of which has unique properties that affect how they are processed and the resulting mechanical behavior. ABS is characterized by significant mechanical resistance, increased thermal stability and the ability to absorb shock without losing structural integrity, which makes it ideal for the production of functional parts and technical components. PETG combines strength and flexibility, while being less brittle than PLA and more resistant to chemicals [1]. Due to its low shrinkage, it is easy to print and is suitable for applications requiring good mechanical stability. PLA is a biodegradable material that is characterized by low heat resistance but high tensile strength and easy processing, making it ideal for prototyping [2,3]. Due to their different mechanical and temperature properties, these materials behave differently when subjected dynamic mechanical analysis (DMA), especially when the load oscillation frequency changes. DMA analysis is one of the frequently used methods for investigating the viscoelastic properties of polymer materials under various temperature and mechanical conditions. One of the main parameters evaluated by DMA is the effect of oscillation frequency on the glass transition temperature (T_g), whereas this factor is key when assessing the mechanical strength of thermoplastic materials created using 3D printing technologies. This issue is addressed by a number of authors who investigate the effect of oscillation frequency on the T_g and its importance in assessing the mechanical properties of additively produced thermoplastics. Their research points to a close connection between the dynamic mechanical properties of materials and their behavior under various loading conditions.

He and Khan investigated how 3D printing parameters affect the fatigue behavior of ABS material under dynamic thermo-mechanical loading. Their research confirmed that setting parameters during 3D printing has a significant impact on material behavior, with this most evident in the viscoelastic properties of the samples. The authors emphasized the role of frequency-dependent mechanical testing in understanding the long-term durability of printed ABS structures [4]. Similarly, Kaiahara et al. analyzed how the orientation of layers during 3D printing affects the mechanical behavior of polymer materials. Their results pointed to the anisotropic behavior of additively manufactured materials, which needs to be considered in applications requiring predictable mechanical performance [5].

DMA of 3D printed PETG was performed by Subbarao et al., who analyzed the viscoelastic response of printed samples as a function of frequency. They found an increase in storage modulus (E') with increasing frequency, indicating that PETG exhibits time-dependent stiffness changes under oscillatory loading. The research also showed the impact of printing process parameters on the thermomechanical behavior of the manufactured components [6]. Bhandari et al. focused on improving the interlayer bond strength of 3D printed composites made of PETG and PLA, demonstrating that heat treatment can significantly improve mechanical performance. Their findings confirmed the potential of thermal post-processing to alleviate the limitations of additive manufacturing in the fused deposition modeling (FDM) process [7]. Hsueh et al. investigated the influence of printing parameters on the thermal and mechanical properties of PLA and PETG, using DMA to evaluate their frequency-dependent characteristics. Their study demonstrated that higher oscillation frequencies lead to increased T_g values, indicating that printed thermoplastics undergo mechanical stiffening under dynamic loading [8]. Lee et al. provided fundamental insights into frequency-dependent modulus variations in polymeric materials, which is crucial for interpreting DMA results in the context of 3D printed structures [9].

Valvez et al. demonstrated that adjusting the processing conditions leads to improved structural performance of printed PETG components, while Lopes et al. analyzed the influence of microstructural patterns and filling rates on the behavior of PETG materials under thermomechanical loading. Their findings show that the final mechanical properties of parts manufactured using additive technology are influenced not only by the material composition, but also by the parameters of the manufacturing process itself [10,11].

In this study, DMA analysis was used to study the viscoelastic behavior of ABS, PETG and PLA samples produced by FFF technology. The aim was to investigate the effect of oscillation frequency on the change in glass transition temperature (T_g) and the change in E', E'' and *tan δ*, as well as to determine the frequency dependence between the magnitude of the applied frequency and T_g for each investigated polymer material.

2 Materials and methods

The DMA Q800 instrument, a dynamic-mechanical analyzer from the manufacturer TA Instruments, was used to perform experimental measurements. The measured data were evaluated using the TA Universal Analysis software version 4.5A, which is integrated in the analyzer system. The results of the dynamic mechanical DMA analysis represent the temperature dependence of E', E'' and *tan δ*. These data were used to determine and compare the transition temperatures of the individual analyzed materials. The experiment compares samples of three types of plastics produced by additive FFF technology, which were measured at five different frequencies of oscillatory loading. ABS, PETG and PLA were used as materials. Each material was tested on five samples at different oscillation loading frequencies, namely 1, 5, 10, 15 and 20 Hz. DMA measurements were performed at temperatures ranging from 60 °C to 110 °C for ABS and PETG materials, while for PLA the range was 50 °C to 90 °C. The analysis was performed with a heating rate of 3°C.min^{-1}, at frequencies of 1 to 20 Hz and a set amplitude of 15 μm.

The analysis provided output curves for E', E'' and *tan δ* values along with measured T_g temperatures, which were subsequently evaluated and compared between the individual materials investigated. For each group of samples, average characteristic curves of the dependences E', E'' and *tan δ* were processed, while the data processing was carried out in the OriginPro software version 9.1.0. The results were obtained based on five measurements for each sample. The transition temperatures derived from E'' and tanδ were determined based on the maximum values of the respective peaks. The transition temperatures from E' were determined by extrapolating the OnSet value from the slope of the curve [12]. The procedure for determining the transition temperatures is based on the ASTM D4065 standard [13]. The experiment resulted in a comparison of data obtained from measurements at different load frequency values.

The Bambu Lab X1 Carbon 3D printer was used to produce the test samples. The materials used were ABS (Bambu Lab ABS Basic), PETG (Bambu Lab PETG Basic) and PLA (Bambu Lab PLA Basic) filaments designed for 3D printing with a diameter of 1.75 mm. The filaments passed through print nozzle with a hole diameter of 0.4 mm, which was heated to 270 °C for ABS, 260 °C for PETG and 220 °C for PLA. The material was deposited on the printing surface in layers with a thickness of 0.2mm during the 3D printing process. All samples were printed with the same infill geometry with a 70% infill density. Sample bodies were manufactured with dimensions of 60 × 12.8 × 3.2 mm, according to the Dual Cantiliver geometry used in DMA analysis (Figure 1). The printed samples were conditioned at room temperature for 8 hours before measurement.

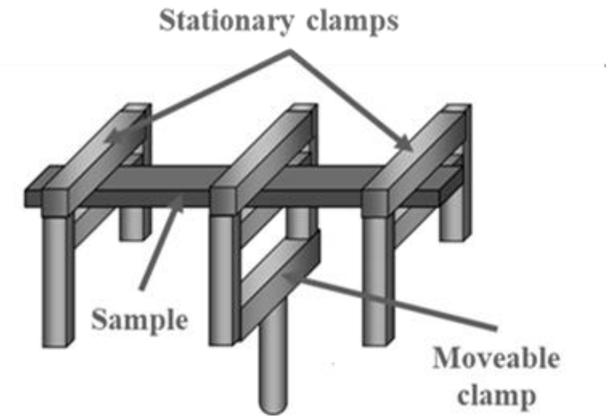

Fig. 1 *Dual Cantiliver geometry used in DMA analysis [14]*

3 Results and discussion

The analysis of the storage modulus (E') for ABS samples tested at different frequencies in the temperature range from 60 °C to 110 °C (Fig. 2) shows a clear trend – with increasing frequency of oscillating loading, there is an increase in E' values. This phenomenon indicates that the material behaves stiffer at higher frequencies and exhibits greater resistance to deformation. A closer look at the glass transition temperatures (T_g), which were determined from the E' curves, shows that the lowest T_g was measured at a frequency of 1 Hz (73.54°C), while the highest T_g value was recorded at a frequency of 20 Hz (75.50°C). This increase in T_g with increasing frequency is documented in Fig. 5. Such behavior indicates the dependence of the thermomechanical properties of ABS on dynamic loading conditions.

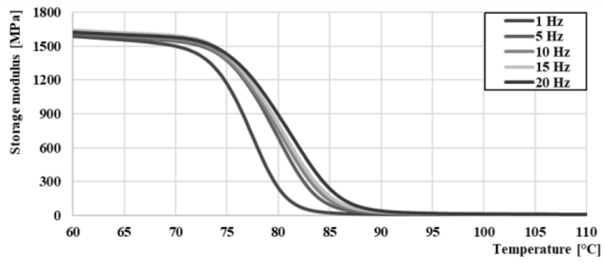

Fig. 2 *Storage modulus curves of ABS samples at different frequencies*

Analysis of the loss modulus (E'') curves for ABS samples measured in the temperature range of 60-110 °C (Fig. 3) shows that the frequency of the oscillating load significantly affects the course of the glass transition. At a frequency of 1 Hz, the transition is pronounced, steep and clearly defined, which indicates a rapid change in the viscoelastic properties of the material. On the contrary, at a frequency of 20 Hz, the transition curve is flatter and less noticeable, which indicates a more gradual transition process. The peak of the E'' curve, which signals the region of the greatest energy dissipation, is also more pronounced at lower frequencies. From the local maxima of the loss modulus, it follows that the temperature T_g at 1 Hz is the lowest (77.92 °C), while at 20 Hz it reaches the highest value (82.25 °C), as documented in Figure 5. This phenomenon reflects the typical frequency dependence of T_g in polymeric materials.

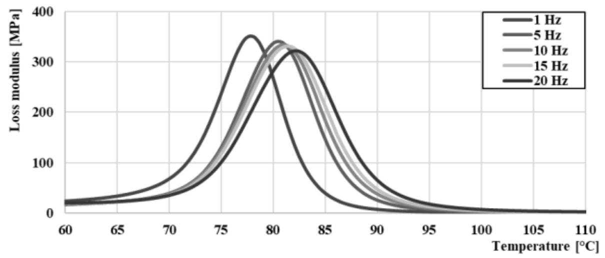

Fig. 3 *Loss modulus curves for ABS material at different loading frequencies*

Comparison of *tan δ* curves for ABS samples measured at different frequencies (Fig. 4) shows a similar character of the glass transition as in the case of the loss modulus (E''). With increasing frequency of the oscillatory loading, the course of this characteristic changes. At a frequency of 1 Hz, the transition is more pronounced, and the profile of the curve is sharper, while at a frequency of 20 Hz, this transition is less pronounced, and its course is smoother. From the comparison of T_g values, derived from the local maximum of the *tan δ* curves, it follows that the lowest T_g value was recorded at a frequency of 1 Hz (83.46 °C), while the highest value occurred at 20 Hz (89.50 °C), as shown in Fig. 5. This increase in T_g with frequency confirms the frequency-dependent viscoelastic behavior of the ABS material.

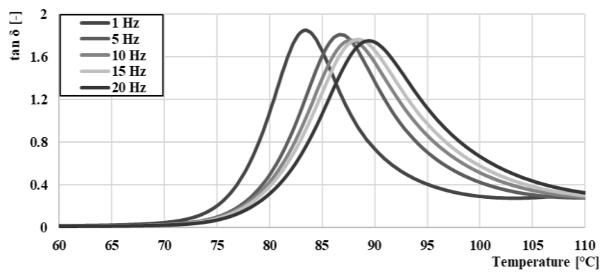

Fig. 4 *Tan δ curves of ABS samples at different frequencies*

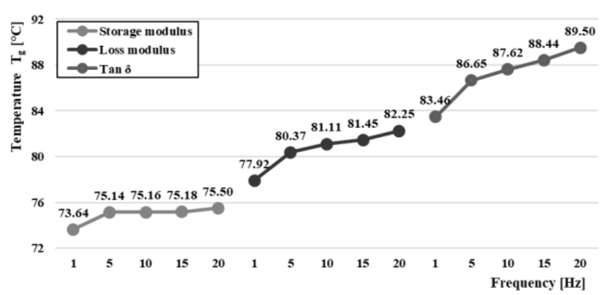

Fig. 5 *Measured T_g values of ABS samples at different frequencies*

When comparing the storage modulus (E') curves for PETG samples measured at different frequencies (Fig. 6), a clear trend can be observed – with increasing frequency of oscillating loading, E' values increase. This phenomenon indicates that the material exhibits greater stiffness and resistance to deformation at higher frequencies. Analysis of T_g, determined from the E' curves, shows that at a frequency of 1 Hz the lowest T_g value (72.33 °C) was recorded, while the highest T_g (76.70 °C) was measured at 20 Hz. These differences are shown in Fig. 9 and again confirm that the mechanical behavior of PETG depends on the frequency of dynamic loading.

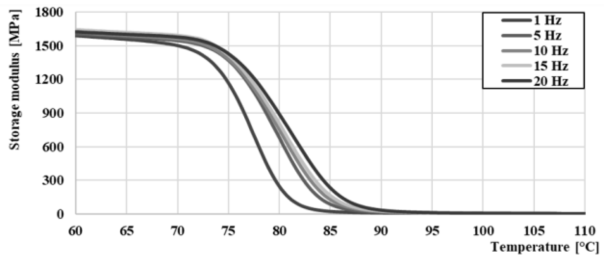

Fig. 6 *Storage modulus curves of PETG samples at different frequencies*

A comparison of the loss modulus (E'') curves for PETG samples shows that the frequency of the oscillating load has a significant effect on the nature of the glass transition. At a lower frequency, namely 1 Hz, the transition appears sharper and more pronounced, while at a higher frequency of 20 Hz the transition is more gradual and less pronounced. This difference is also evident in the shape of the curve, where the characteristic peak for the T_g region shows a higher intensity at a lower frequency, indicating a more pronounced energy dissipation. From a comparison of the local maxima of the E'' curves, it can be determined that the T_g at a frequency of 1 Hz reaches the lowest value (76.65 °C), while at 20 Hz it is the highest (84.55 °C), as shown in Figure 9. This trend again confirms the frequency dependence of the viscoelastic behavior of the PETG material.

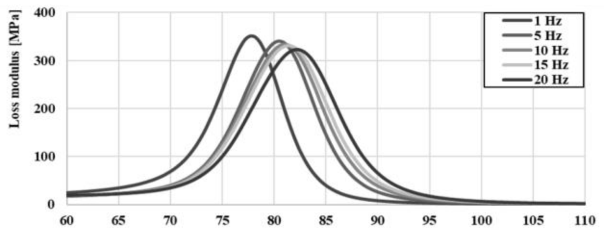

Fig. 7 *Loss modulus curves of PETG samples at different frequencies*

The analysis of *tan δ* for PETG samples measured at different frequencies (Fig. 8) shows a similar glass transition behavior as in the case of the loss modulus (E''). With increasing frequency of oscillating loading, the profile of the curve changes – at a frequency of 1 Hz the transition is pronounced and steep, indicating a sharp change in the viscoelastic response of the material. On the contrary, at a higher frequency of 20 Hz this transition is less pronounced, and its course is more gradual, indicating a damping of the dynamic response. Comparison of T_g values obtained from local maxima of *tan δ* confirms that at 1 Hz T_g reaches the lowest value (82.15 °C), while at 20 Hz it shifts to a higher value (91.05 °C), as documented in Fig. 9. This increase in T_g with frequency points to a typical frequency dependence of the thermomechanical behavior of PETG.

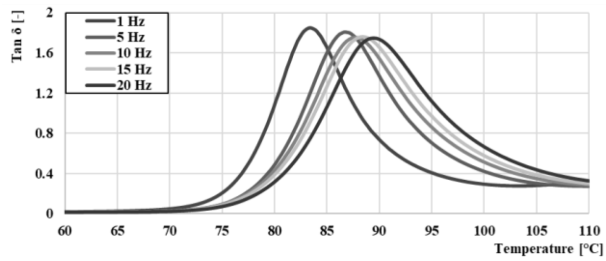

Fig. 8 *Tan δ curves of PETG samples at different frequencies*

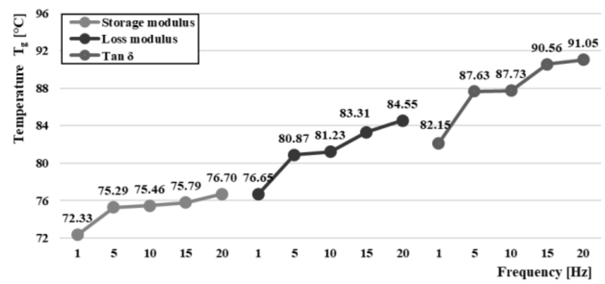

Fig. 9 *Measured T_g values of PETG samples at different frequencies*

The analysis of the storage modulus (E') of PLA samples (Fig. 10) confirmed an increasing trend of E' values with increasing frequency of oscillatory loading. Higher frequencies contribute to increased stiffness of the material, which is typical for viscoelastic polymers. Comparing the T_g values derived from the E' curves, it can be stated that at a frequency of 1 Hz the lowest glass transition temperature (57.78 °C) was recorded, while at 20 Hz the T_g reached the highest value (59.98 °C), as is evident from the results shown in Figure 13.

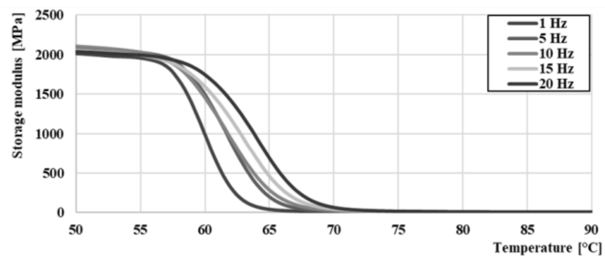

Fig. 10 *Storage modulus curves of PLA samples at different frequencies*

Analysis of the loss modulus (E'') of PLA samples (Fig. 11) revealed that the course of the glass transition is influenced by the loading frequency. At a frequency of 1 Hz, this transition is more pronounced and abrupt, while at 20 Hz it is less pronounced, and the transition zone is distributed over a wider temperature range. The prominence of the characteristic maximum, which represents the T_g transition, is higher at lower frequency, which indicates more intense energy dissipation. A comparison of the T_g temperatures, derived from the local maximum E'', shows that at a frequency of 1 Hz, T_g reaches a value of 60.44 °C, while at a frequency of 20 Hz it rises to 64.58 °C (Fig. 13). This shift documents the frequency-dependent behavior of PLA material in the region of viscoelastic transitions.

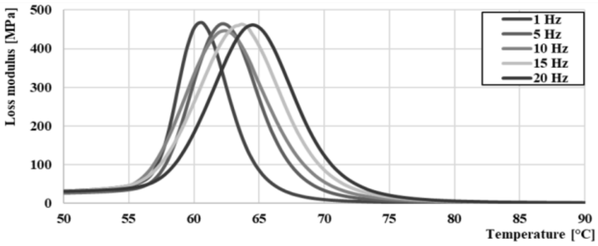

Fig. 11 *Loss modulus curves of PLA samples at different frequencies*

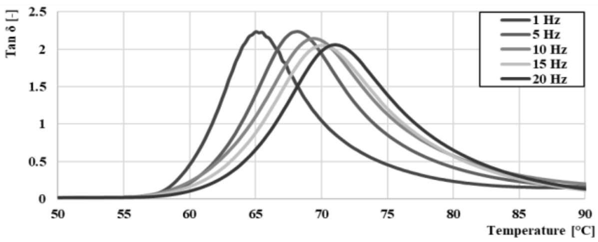

Fig. 12 *Tan δ curves of PLA samples at different frequencies*

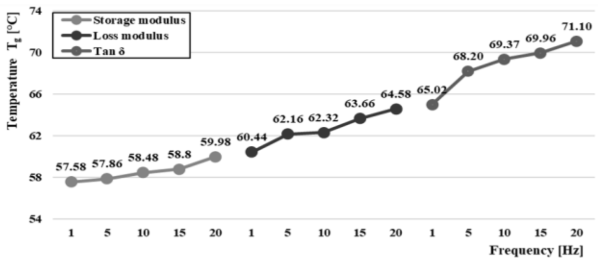

Fig. 13 *Measured T_g values of PLA samples at different frequencies*

By comparing the *tan δ* curves for PLA samples (Fig. 12), it can be observed that the glass transition shows the same frequency dependence as in the case of the E''. At a frequency of 1 Hz, the transition curve has a more pronounced and sharp character, while at 20 Hz it is clearly more muted and gradual. The prominence of the *tan δ* peak is higher at lower frequencies, which indicates a more intense viscoelastic response of the material. The T_g temperatures derived from the local *tan δ* maxima indicate that at 1 Hz the PLA sample reaches the lowest value (65.03 °C), while at 20 Hz the T_g is the highest (71.10 °C), as documented in Fig. 13. This shift in the glass transition temperature confirms the dependence of the thermomechanical behavior of PLA on the loading frequency.

DMA analysis of ABS, PETG and PLA samples confirmed that the T_g shows an increasing trend with increasing oscillating loading frequency. This conclusion follows from the comparison of E', E'' and *tan δ* curves, as well as from the evaluation of the measured T_g for the individual materials. It can be stated that the nature of the applied load on the sample during DMA analysis has a significant impact on the resulting value of T_g of the analyzed material.

Since the DMA analysis revealed a dependence between the used frequency and the temperature T_g, which was the subject of research by several authors [8,9,14], this fact was verified by a mathematical description of the dependence, which is shown in Figure 14 for ABS, in Figure 15 for PETG and in Figure 16 for PLA material.

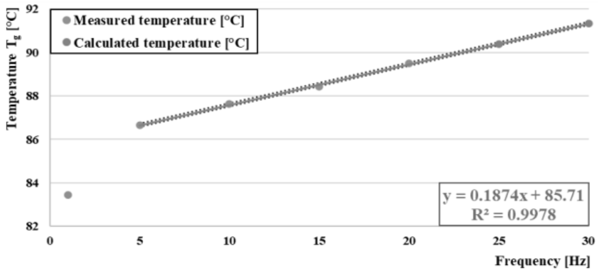

Fig. 14 *Temperature dependence of T_g on frequency calculated for ABS*

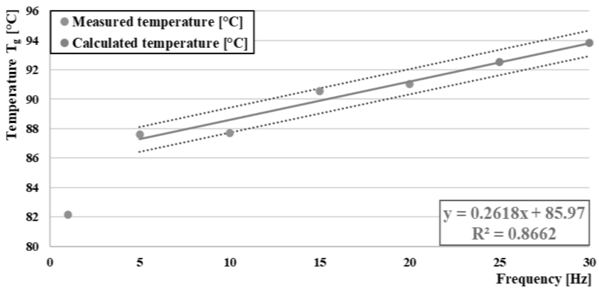

Fig. 15 *Temperature dependence of T_g on frequency calculated for PETG*

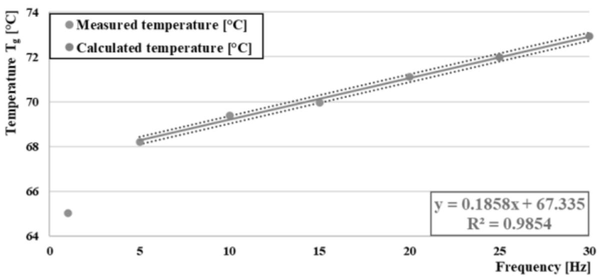

Fig. 16 *Temperature dependence of T_g on frequency calculated for PLA*

As can be seen in Figures 14, 15 and 16, the dependence of the T_g temperature on frequency shows a nonlinear character, and this dependence can be divided into two regions, with the cut-off frequency being 5 Hz. If the frequency region ≥ 5 Hz is analyzed, the behavior of the material changes and the dependence of T_g on frequency can be well approximated by a linear function. This assumption was verified by approximating the measured values in the range of 5 – 20 Hz and subsequently calculating the glass transition temperatures for frequencies of 25 Hz and 30 Hz. In order to validate the obtained results, additional experimental measurements were carried out for all three investigated materials (ABS, PETG and PLA), on the basis of which the maximum relative measurement error was determined. The analyzed results show that the highest relative error for ABS was 0.092%, while for PETG it reached 0.978%, which represents the largest deviation among all the materials studied. PLA showed a maximum relative error of 0.094%. These differences indicate slight variations in accuracy between the individual materials, with the most significant deviation being observed for PETG. These results indicate that in the higher frequency range, it is possible to predict T_g values with high accuracy based on linear interpolation or extrapolation, while the error remains within acceptable limits. This approach may be useful in material design for applications where accurate determination of the glass transition at different dynamic loading frequencies is important.

4 Conclusion

Based on the measurements and comparison of dynamic-mechanical properties (E', E'' and *tan* δ) together with the analysis of glass transition temperatures (T_g) of samples made of ABS, PETG and PLA materials, it can be concluded that with increasing frequency of oscillating load, there is a systematic increase in T_g. This effect confirms that dynamic conditions significantly affect the thermomechanical response of these polymers.

The results show that the nature of the mechanical load during DMA analysis significantly affects the measured T_g values, while from a frequency of 5 Hz and above this dependence can be expressed by a linear function. This assumption was confirmed by approximating the measured values in the interval 5 – 20 Hz, and subsequently calculating the T_g values for frequencies of 25 Hz and 30 Hz. The validation was performed by experimental measurements, with the maximum relative error being 0.092% for ABS, 0.978% for PETG and 0.094% for PLA. In all three cases, a linear relationship between T_g and frequency was confirmed, with the strongest linear relationship being observed for ABS, followed by PLA and finally PETG.

These findings may be important for applications where accurate determination of T_g under various dynamic loads is required, and at the same time provide a basis for further studies in the field of mechanical behavior of thermoplastics under different frequency regimes.

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