# Analytical Modeling of Stress Relaxation and Evaluation of the Activation Volume Variation: Effect of Temperature and Plasticizer Content for Poly(3-hydroxybutyrate-3-hydroxyvalerate)

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**ABSTRACT:** In this study, stress-relaxation tests that have been carried out at different temperatures (quite below the heat deflection temperature) on a poly(3-hydroxybutyrate-3hydroxyvalerate) (PHB-HV) matrix containing different amounts of the acetyl tributyl citrate plasticizer (added at 5 and 10 wt %) are investigated. The analytical modeling of the stress relaxation behavior by the coupling of Eyring's approach and the Guiu and Pratt model is successful. The activation volume results achieved are very interesting; in fact, not only the dependence of the activation volume from temperature is confirmed (and it resulted in dependence from the $\alpha'$ relaxation temperature) but also, for the first time, the dependence of the activation volume from the plasticizer content is shown. In particular, the presence of a linear relationship between the activation volume and the plasticizer volume content is observed.
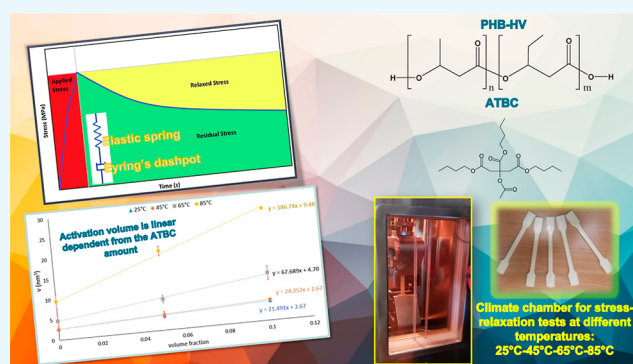
## 1. INTRODUCTION

Polymeric materials, being viscoelastic, exhibit time-dependent relaxations when they are subjected to stress or strain. The temperature also affects the deformation behavior on both microscopic and macroscopic scales due to the temperature dependence of the deformation mechanisms that operate in semicrystalline polymers.[1,2]

In particular, the relaxation phenomena can be detected during creep (applying a constant stress over the time) and stress relaxation tests (applying a constant deformation over the time). Both creep and stress relaxation tests are important from an engineering point of view because depending on the application, a polymeric material can be put in service under a fixed stress or strain for long periods.[3] The rate of creep and/or stress relaxation depends mainly on the molecular mobility of the polymeric chains, the stress and/or strain level, and time. In particular, as far as the molecular mobility is concerned, the effect of temperature must be considered because with the increase of the temperature, an increment of the molecular mobility is registered.[4] However, the plasticizer addition also increases the molecular mobility occupying the intermolecular spaces among the polymeric chains, thus reducing the energy for the molecular motion and increasing the free volume and the molecular mobility.[5,6]

In order to correlate the creep or stress relaxation rate to the molecular motion, Eyring and co-workers[7,8] assumed that the polymer deformation rate is a thermally activated process that involves the motion of polymeric chain segments over potential barriers. Eyring's approach provides a common basis to describe the nonlinear viscoelastic behavior of a polymer, correlating it to useful parameters that include an activation energy and activation volume that can give an indication of the molecular mechanism. The Eyring approach was applied successfully to describe the strain rate dependence of the yield stress in polymers,[1,9−12] creep,[13−16] and stress relaxation.[17−19]

In this work, the attention is focused on the stress relaxation phenomenon and its correlation to the activation volume through the Eyring equation. For the first time, not only the temperature effect was considered but also the effect on the activation volume of the plasticizer addition was considered. In fact, from the point of view of the molecular mobility, not only the temperature but also the plasticizer presence increases the polymeric chain mobility, probably affecting the Eyring activation volume.

Up to date, the literature works on the correlation of the stress relaxation to the Eyring activation volume are limited
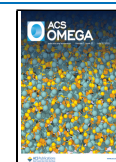
and concern mainly conventional fossil-based polymers (nylons, polyethylene, polyetheretherketone, etc...).[4,17,19,20] However, the limited disposal methods and the environmental impact of persistent plastic wastes have stimulated the research interest in biodegradable natural polymers.[21] In this context, investigations on the stress relaxation behavior and its analytical correlation through Eyring's model to the activation volume are very limited. Sweeny et al.[22] investigated the strain recovery of partially crystalline poly(lactic acid) (PLA) through stress relaxation experiments interpreted in terms of the Eyring process. The results obtained by Sweeny et al. demonstrated that Eyring's model is capable of useful prediction of the strain recovery for PLA.

Among biodegradable and biobased polymers, which in recent years are becoming more and more popular in correlation with environmental issues,[23] poly(3-hydroxybutyrate) (PHB) is the most common and characterized homopolymer which belongs to the polyhydroxyalkanoate (PHA) family.[24] The PHA family is very interesting to investigate due to the complete biodegradability in compost, soil, and marine water with noteworthy properties for single-use packaging and agriculture applications.[25] In particular, the elastic modulus and the tensile strength of PHB are comparable to those of polypropylene[26] with the exception of elongation at break, which is much lower, and it makes PHB an intrinsic brittle material, thus restricting it applications.[27] Nevertheless, the addition of different hydroxyalkanoate monomeric co-units in the PHB chains through microbial synthesis has led to an improvement of the PHB mechanical properties, widening the PHB potential applications.[28,29] More specifically, the most common investigated and used random copolymers of PHB are poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHB-HV).[30] From a mechanical point of view, these copolymers exhibit higher elongation at break and tensile strength and lower brittleness if compared to pure PHB,[31] and for this reason, they are largely investigated and commercialized on the market.

The main objective of this study is to investigate the stress relaxation behavior of a commercial PHB-HV grade. Eyring's approach was adopted for the evaluation of the activation volume and its variation with temperature. Furthermore, with the activation volume correlated to the molecular mobility, the effect on the activation volume of the addition of a largely adopted biobased and biodegradable plasticizer [acetyl tributyl citrate (ATBC) added at 5 and 10 wt %] was also investigated.

## 2. THEORETICAL ANALYSIS

Eyring et al.[7] stated that the deformation of a polymer is a thermally activated process that involves the motion of polymeric chain segments over potential barriers. On the basis of this assumption, Eyring et al. modified the standard linear solid model[32,33] (that describes the behavior of polymers in their viscoelastic range), hypothesizing that the movement of the dashpot is governed by the activated process. The resulting model can describe the nonlinear viscoelastic behavior of a polymer, and it includes an activation energy and an activation volume that may provide an indication of the molecular mechanisms. Furthermore, the activated rate process can also provide a common basis for the interpretation of the polymer yielding, creep, and stress relaxation behavior.

Focusing on the stress relaxation behavior, Guiu and Pratt[18] show how a model consisting of an Eyring dashpot in series

with an elastic element (Figure 1) leads to a simple equation able to describe the stress relaxation curves in tension.
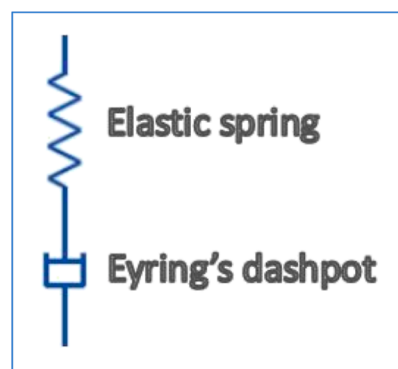


**Figure 1.** Guiu and Pratt model consisting of an elastic spring in series with an Eyring dashpot.

According to the model of Figure 1, the total strain of the system is the sum of the elastic component ($\varepsilon_E$) and the viscous (the Eyring dashpot) component ($\varepsilon_V$), as described by eq 1

$$\varepsilon = \varepsilon_E + \varepsilon_V \tag{1}$$

Differentiating eq 1 with respect to time gives eq 2

$$\dot{\varepsilon} = \dot{\varepsilon}_E + \dot{\varepsilon}_V \tag{2}$$

Now, replacing the viscous strain rate ($e_V$) with the conventional Eyring thermally activated process,[34] the plastic strain rate ($\dot{\varepsilon}_V$) corresponding to the stress $\sigma$ is given by

$$\dot{\varepsilon}_V = \dot{\varepsilon}_0 \exp\left(-\frac{\Delta H}{RT}\right)\exp\left(\frac{\sigma v^*}{RT}\right) = A\, \exp(B\sigma) \tag{3}$$

where the $A$ and $B$ constants have been introduced for brevity, $\dot{\varepsilon}_0$ is the plastic strain rate corresponding to zero stress, $\Delta H$ is the apparent activation enthalpy, $R$ is the universal gas constant, $T$ is the temperature (in Kelvin), and $v^*$ is the activation volume.

Assuming a linear relation for the elastic component (having the modulus equal to $E$), eq 3 can be rewritten in a manner that only stresses appear on the right-hand side (eq 4)

$$\dot{\varepsilon} = \frac{\dot{\sigma}}{E} + A\, \exp(B\sigma) \tag{4}$$

Under the conditions of stress relaxation, the total strain rate is equal to 0, so the stress decays in the following manner (eq 5)

$$0 = \frac{\dot{\sigma}}{E} + A\, \exp(B\sigma) \tag{5}$$

Solving eq 5 by separation of variables, the Guiu and Pratt expression can be obtained, which describes the trend of the stress as function of time (eq 6)

$$\sigma(t) = \sigma_0 - \frac{1}{B}\ln\left(1 + \frac{t}{c}\right) = \sigma_0 - \frac{RT}{V^*}\ln\left(1 + \frac{t}{c}\right) \tag{6}$$

where $\sigma_0$ is the stress at time $t = 0$ and $c$ is a constant.

In the literature,[35,36] the Guiu and Pratt expression (eq 6) has been found to be remarkably effective in representing stress relaxation curves for polymers.

# 3. MATERIALS AND METHODS

**3.1. Materials.** Commercial poly(3-hydroxybutyrate-3-hydroxyvalerate) (PHB-HV), trade name PHI002, purchased from Naturplast (Caen, France) was used as the polymeric matrix. The material was supplied in pellets, and according to the supplier data sheet, it contains 5 wt % of valerate [density:1.24 g/cm³, MFI (190 °C, 2.16 kg): 15−30 g/10 min].

ATBC, purchased from Tecnosintesi S.p.A (Bergamo, Italy), a biobased and biodegradable plasticizer, was used to plasticize the PHB-HV matrix. The plasticizer appears as a colorless and odorless liquid having a density of 1.05 g/cm³ and a molecular weight of 402.5 g/mol.

**3.2. Blend and Sample Preparation.** Pure PHB-HV and its blends containing two different ATBC concentrations (blend names and compositions are reported in Table 1) were

**Table 1. Blend Names and Compositions**

| blend name | PHB-HV (wt %) | ATBC (wt %) |
|---|---|---|
| PHB | 100 | |
| PHB_5 | 95 | 5 |
| PHB_10 | 90 | 10 |

processed in a Comac EBC 25HT (L/D = 44) (Comac, Cerro Maggiore, Italy) semi-industrial twin screw extruder to obtain pellets necessary for the subsequent injection molding process.

Before the extrusion, the polymeric matrix was dried for 12 h in a DP 604−615 dryer (Piovan S.p.A., Verona, Italy). PHB-HV pellets were introduced into the main extruder feeder, while ATBC was added using a peristaltic pump (Verderflex−Vantage3000) suitably calibrated to guarantee a constant flow rate and thus the fixed plasticizer concentration. The temperature profile adopted during the extrusion in the zones from 1 to 11 was 150/170/180/180/180/180/180/180/180/170/170 °C, with the die zone at 170 °C. The screw rate was 180 rpm, and the total mass flow rate was 15 kg/h. The extruded strands were cooled in a water bath at room temperature and reduced in pellets using an automatic knife cutter. Finally, all pellets were dried in the above-mentioned Piovan dryer at 60 °C for 12 h.

The extruded pellets were injection-molded in a Megatech H10/18 injection molding machine (TECNICA DUEBI s.r.l., Fabriano, Italy) to obtain ISO 527-1A dog-bone specimens (width: 10 mm, thickness: 4 mm, length: 80 mm) for mechanical characterizations (tensile tests and stress relaxation tests). The following main injection molding operative conditions were adopted: single screw extruder temperature 180 °C, mold temperature 40 °C, injection holding time 5 s, cooling time 10 s, injection pressure 60 bar, and post pressure 55 bar.

**3.3. Preliminary Characterization: Heat Deflection Temperature Measurements and Differential Scanning Calorimetry Analysis.** To find the range of temperatures to perform the mechanical test avoiding an excessive specimen deformation due to the temperature, heat deflection temperature (HDT) measurements were carried out. HDT tests were performed on an HVT302B (MP Strumenti, Italia) in accordance with ISO 75-1 (method A). The sample used for HDT was obtained from the ISO 527-1A injection molded specimens and suitably cut to obtain a parallelepiped having dimensions of 80 × 10 × 4 mm. The specimens were immersed in a silicone oil bath and subjected to a flexural stress

of 0.45 MPa at the midpoint of the flatwise position in a three-point bending (3PB) configuration. The test starts heating the bath with a heating rate of 120 °C/h. When the sample bar reaches a deflection of 0.34 mm, the corresponding bath temperature represents the HDT (Type A) value. At least five measurements for each composition were carried out, and the average value was reported.

Differential scanning calorimetry (DSC) analysis was also carried out to evaluate the final crystallinity of the injection-molded specimens in order to exclude eventual crystallinity differences among the various formulations that could influence the mechanical results. A Q200—TA DSC (TA Instruments, New Castle, UK) equipped with an RSC90 cooling system was used for DSC measurements. Indium was used as the standard for temperature and enthalpy calibration of the DSC, while nitrogen, set at 50 mL/min, was used as a purge gas. The sampling for DSC analysis has been carried out cutting few milligrams (about 10−15 mg) from the ISO 5271-A injection-molded specimens. Then the samples were sealed inside aluminum hermetic pans before measurements. The DSC program adopted consisted in heating the sample at 10 °C/min from room temperature up to 200 °C. The melting temperature of PHB-HV samples was recorded at the maximum of the melting peak, while the melting enthalpy ($\Delta H_m$) was determined from the corresponding thermogram peak area. The percentage of crystallinity ($X_c$) of PHB-HV formulations was calculated according to the following equation[37] (eq 7)

$$X_c = \frac{\Delta H_m}{\Delta H_m^\circ \times wt \%_{PHB-HV}} \times 100 \tag{7}$$

where $\Delta H_m^\circ$ is the theoretical melting heat of 100% crystalline polymer that for PHB-HV was set equal to 144 J/g.[38]

**3.4. Quasi-Static Uniaxial Tensile Tests and Stress Relaxation Tests.** Quasi-static uniaxial tensile and stress relaxation tests were carried out on ISO 527-1A dog-bone specimens using an MTS Criterion model 43 universal testing machine (MTS Systems Corporation, Eden Prairie, MN, USA) equipped with a 10 kN load cell and interfaced with computer running MTS Elite Software. Both uniaxial and stress relaxation tests were carried out after 3 days from the injection molding process, and during this period, the samples were stored in a dry keeper (SANPLATEC Corp., Osaka, Japan) in a controlled atmosphere (room temperature and 50% humidity). Tests were performed at different temperatures (25, 45, 65, and 85 °C) adopting an MTS climate chamber Eurotherm FEC 1200 that guarantees that the set temperature is kept constant during the tests. In Figure 2, the MTS configuration with the climate chamber is shown.

For standard uniaxial quasi-static tensile tests, at least five specimens for each material composition were tested at a constant crosshead speed of 10 mm/min.

For stress relaxation tests as well, five specimens for each blend were stretched at a constant rate of 10 mm/min until the elongation of 1.6 mm (corresponding to 2% of deformation) was achieved and then the strain was held constant for 2000 s while registering the stress decay.

**3.5. Dynamic Mechanical Thermal Analysis.** Dynamic mechanical thermal analysis (DMTA) was carried out using a Gabo Eplexor DMTA (Gabo Qualimeter, Ahiden, Germany) equipped with a 100N load cell in tensile configuration; liquid

**Figure 2.** MTS climate chamber configuration.

nitrogen was used to cool the chamber. DMTA was performed on the injection-molded ISO 527-1A specimens suitably cut in bars having dimensions of $50 \times 10 \times 4$ mm. At least three samples for each formulation were tested. The temperature range varied from $-30$ to $110$ °C with a heating rate of 2 °C/min and at a constant frequency of 1 Hz.

# 4. RESULTS AND DISCUSSION

**4.1. Preliminary Characterization Results.** The HDT and DSC results, reported in Table 2, show that all

**Table 2. HDT and DSC Results**

| blend name | HDT (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $X_c$ (%) |
|---|---|---|---|---|
| PHB | $137.9 \pm 1.7$ | 176.0 | 101.1 | 70 |
| PHB_5 | $136.2 \pm 0.5$ | 173.7 | 91.6 | 67 |
| PHB_10 | $108.4 \pm 0.6$ | 172.4 | 86.2 | 67 |

formulations are stable from the thermo-mechanical point of view until 100 °C. For PHB_10, 108 °C is the HDT value that was registered. In any case, in the temperature range chosen for the mechanical tests (25, 45, 65, and 85 °C), no significant deformation ascribable to temperature can be observed for all formulations. The plasticizer addition leads to a decrement of HDT values, coherently to what was observed in the literature.[39] The effect is marked when the plasticizer content reaches 10 wt %. The increased molecular mobility due to the plasticizer addition and temperature increment leads to less resistance to distortion with temperature[40] that is reflected in a decrement of the HDT values with the increase of the ATBC amount.

The DSC results (Table 2) show a decrease of $T_m$ and melting enthalpy with the increase of the ATBC content; the same trend was found in the literature for a PHB-ATBC system,[41,42] and it was ascribed to the polar and low-molecular weight ATBC that goes to insert between the polymeric chains and enlarges the polymeric distances among crystals (acting like a diluent[43]), leading to a reduction in melting enthalpy. A slight decrease of crystallinity is observed due to the presence of the plasticizer molecules that go to restrict the formation of packed structures.[44,45] However, the decrement of the PHB-HV crystallinity is not so marked, and it can be considered approximately the same (about 70%); consequently, the quantity of crystalline and amorphous fractions is not influenced by the presence of the plasticizer and remains almost unchanged not determining the mechanical results.[24,46] Moreover, the great crystallinity amount reflects the high HDT values registered with the plasticized matrix as well.

The stress−strain curves at different temperatures for the various formulations are reported in Figure 3.

As expected,[39,47] with the increase of the temperature, a decrement of the material stiffness (reflected in a slope reduction of the linear elastic part of the stress−strain curve) and elongation at break was observed. At the same temperature, the addition of the plasticizer leads to a greater ductility of the material, which decreases its stress at break, but it increases the elongation at break.

From the mechanical point of view, both the plasticizer and temperature promote a decrease in tensile strength and elastic modulus with regard to neat PHB-HV at room temperature.

**4.2. Stress Relaxation Results.** Loading and stress relaxation data for all the formulations at 25, 45, 65, and 85 °C are reported in Figure 4.

As can be expected, the initial stress, $\sigma_0$, registered when the deformation is applied, reflects the quasi-static uniaxial tests; $\sigma_0$ decreases with the increase of temperature and the plasticizer amount. The stress relaxation curves are fundamental to estimate the Eyring activation volume through the application of the Guiu and Pratt model (eq 6). The estimation of the Guiu and Pratt parameters, reported in Table 3, was performed by an iterative numerical method (using Excel Data Solver Function) and taking into account that the entire relaxation curve is fitted with time $t_0$ taken as the start of the stress relaxation process (in which a value of $t_0 = 0$ is assigned). The fitting of the Guiu and Pratt model is in excellent agreement with the experimental data as can be observed from Figure 4 (dashed lines). The good fitting obtained confirms that the long-term behavior of the stress-relaxation experiments can be successfully modeled using an Eyring process applied to the Guiu and Pratt model.

The results obtained in terms of activation volume are in the order of a few $nm^3$ and increase strongly with temperature (Figure 5), in accordance to what has been observed experimentally in other similar studies.[19,48−50]

In particular, the dependence of the activation volume from temperature becomes more marked, with an exponential growth, when the temperature exceeds 45 °C; below this temperature, the activation volume is almost constant. This behavior can be explained observing the DMTA results, reported in Figure 6, where the storage modulus ($E'$) and the loss or damping factor (tan δ) as a function of temperature are illustrated.

The addition of the plasticizer leads to a decrement of the storage modulus ($E'$) with temperature and with the plasticizer
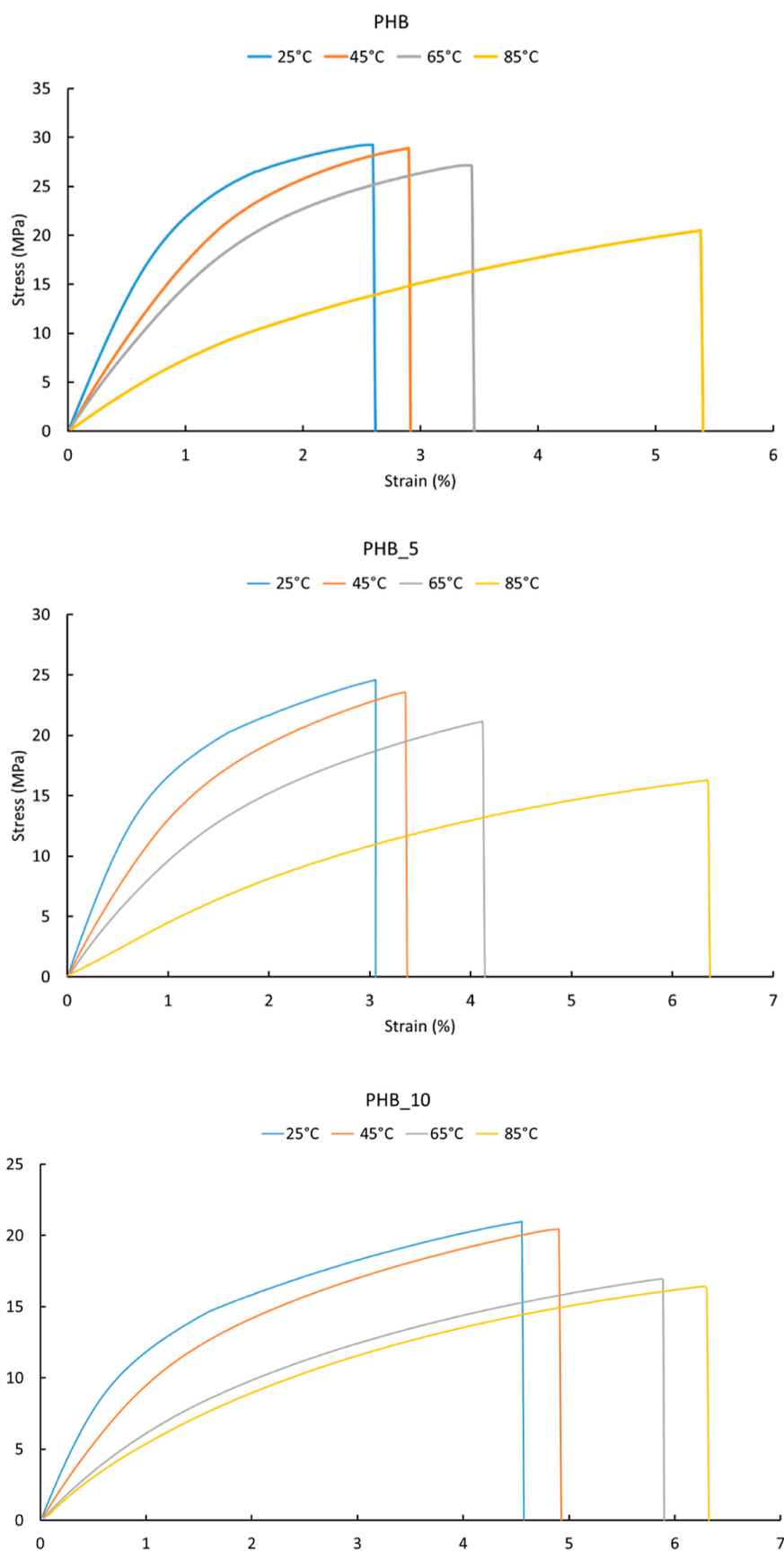
**Figure 3.** Stress−Strain curves for PHB, PHB_5, and PHB_10 at different temperatures.

content, confirming the trend observed from the stress−strain curves. Considering the glass-transition temperature $(T_g)$,

evaluated as the maximum peak of the damping factor, a shift toward a lower temperature with the increase of ATBC content
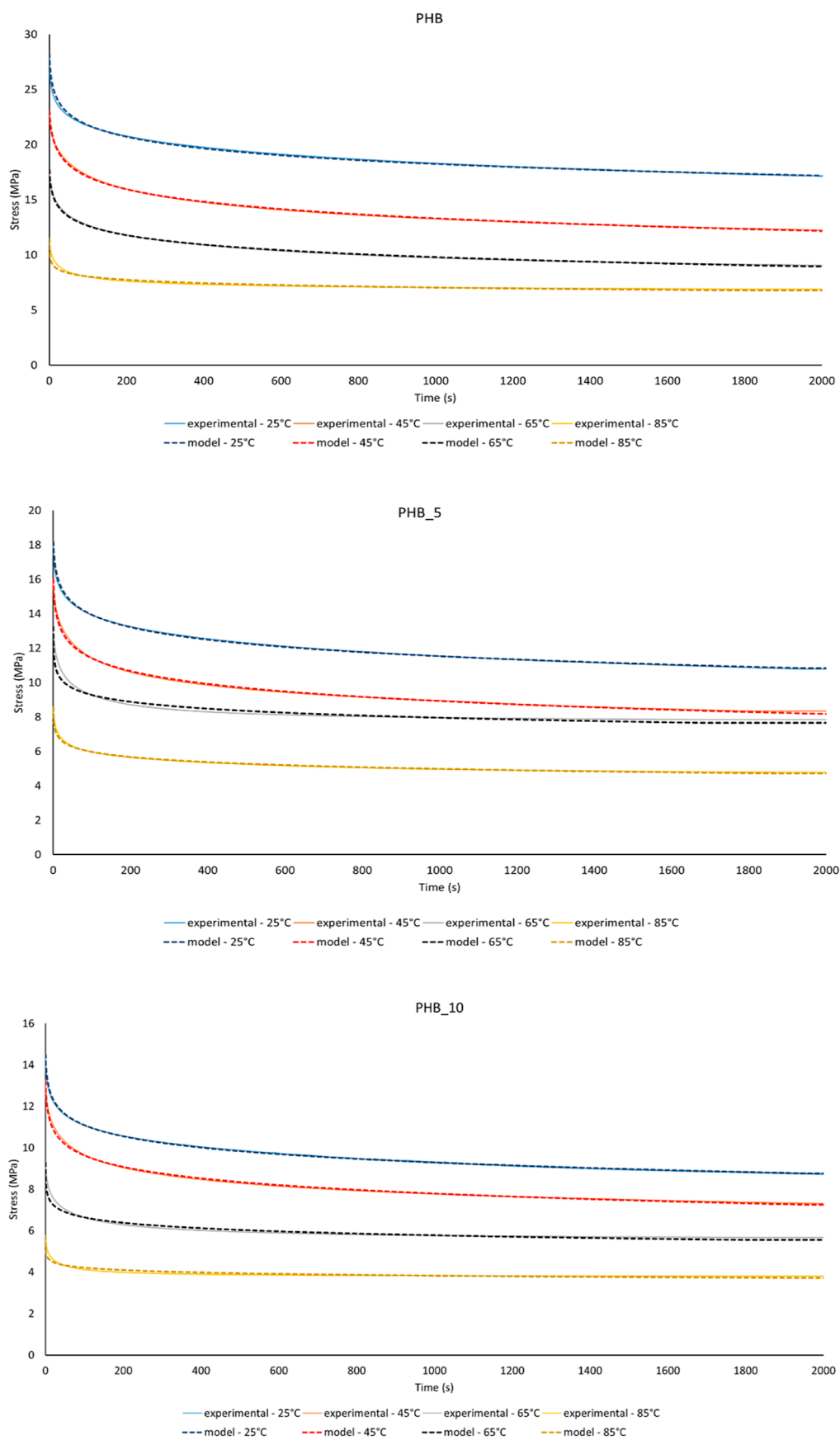
**Figure 4.** Experimental stress relaxation curves fitted with the Guiu and Pratt equation.

**Table 3. Guiu and Pratt (eq 6) Fitting Parameters**

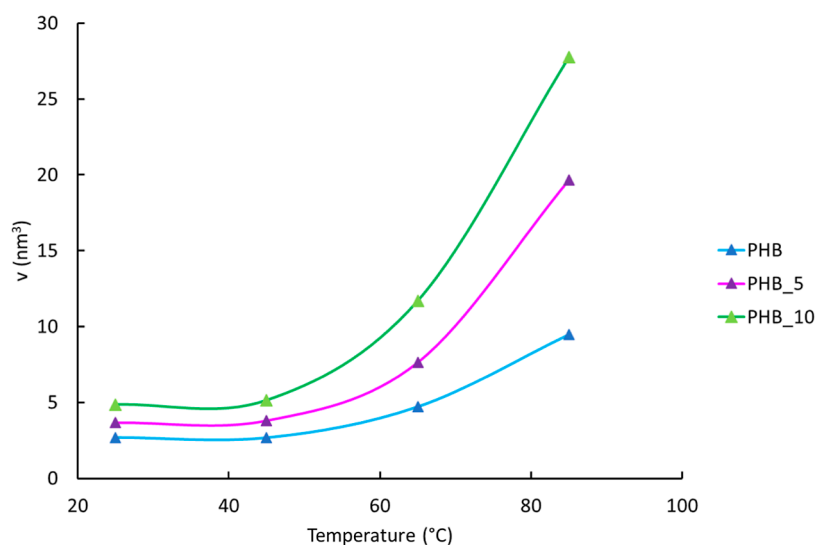| Blend name | Temperature (°C) | $v$ (nm³) | $c$ (s) | R-Square of fitting curves |
|---|---|---|---|---|
| PHB | 25 | 2.67 | 1.39 | 0.997 |
| | 45 | 2.67 | 2.73 | 0.998 |
| | 65 | 4.71 | 1.66 | 0.997 |
| | 85 | 9.49 | 0.35 | 0.946 |
| PHB_5 | 25 | 3.68 | 1.78 | 0.998 |
| | 45 | 3.81 | 2.94 | 0.998 |
| | 65 | 7.64 | 0.10 | 0.932 |
| | 85 | 19.64 | 0.24 | 0.991 |
| PHB_10 | 25 | 4.85 | 1.38 | 0.999 |
| | 45 | 5.13 | 1.11 | 0.996 |
| | 65 | 11.69 | 0.10 | 0.945 |
| | 85 | 27.75 | 0.10 | 0.927 |



**Figure 5.** Trend of the volume activation versus temperature for PHB, PHB_5, and PHB_10.

can be observed, in accordance with the literature.[5] This phenomenon is correlated to the increment of the polymer chain mobility caused by the addition of the low-molecular weight plasticizer.[51] Corresponding to the tan $\delta$ peak, the drop of the storage modulus ($E'$) is observed. Noteworthily, the second $E'$ drop (reflected in an increment of tan $\delta$) that occurs at a temperature range from 45 to 110 °C is correlated to the $\alpha'$ relaxation of the amorphous–crystalline interphase.[43,52,53] Therefore, comparing the DMTA data with those of Figure 5, it is evident that $\alpha'$ relaxation is also responsible for the sudden increment of the activation volume registered above 45 °C.

The $\alpha'$ relaxation is also responsible of the deflection recorded during the HDT tests and reported in Figure 7. It can be noticed that although the critical deflection (equal to 0.34 mm) occurs at high temperatures (around 110–140 °C according to the HDT results reported in Table 2), for all formulations, the specimens begin their deflection around 45 °C, corresponding to the $\alpha'$ relaxation that therefore also influences the flexural strength of the material.

Noteworthily, how the plasticizer content affects the activation volume needs to be observed. In fact, it is well

known that the addition of a plasticizer, having a low molecular size with respect to the polymeric matrix, can occupy the intermolecular spaces among the polymeric chains, leading to a reduction of the molecular motion and to an increase of the free volume. All these concepts lead to a growth of the molecular mobility and to a decrement of the glass-transition temperature.[5,6] However, up to date, no studies about the variation of the activation volume with the plasticizer content, adopting the Guiu and Pratt model, have been performed. The results obtained show that there is a linear correlation between the activation volume and the plasticizer volume fraction. The activation volume follows the following equation (eq 8)

$$v = v_0 + m \times V_{pl} \tag{8}$$

where $v_0$ is the activation volume of the pure matrix (without the plasticizer) and $V_{pl}$ is the plasticizer volume fraction. In Figure 8, it can be observed that eq 8 fits quite well the experimental data, confirming the linear proportionality between the plasticizer amount and the activation volume found experimentally.
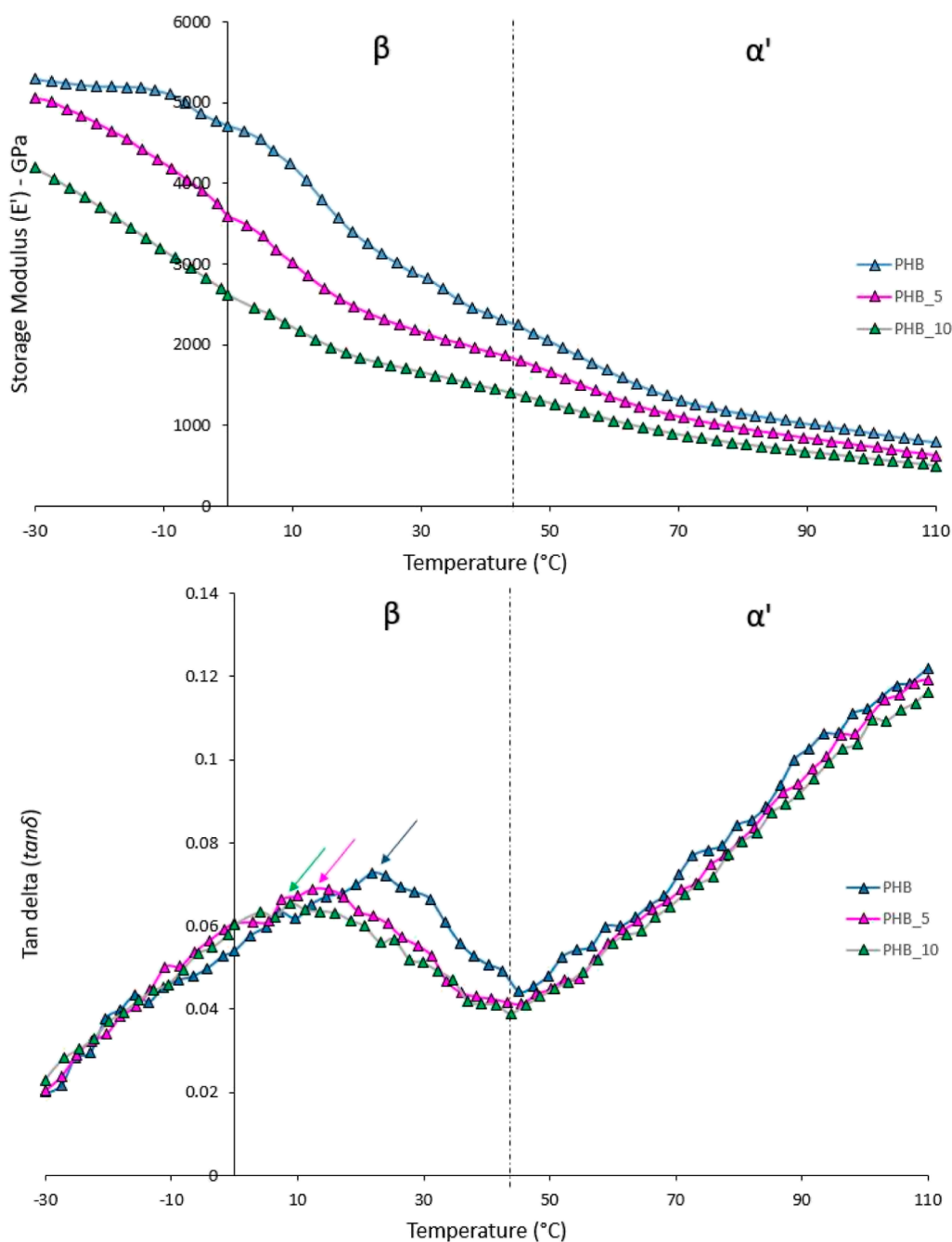
**Figure 6.** Storage modulus ($E'$) and tan $\delta$ as a function of temperature for PHB, PHB_5, and PHB_10.

Plotting the angular coefficients ($m$) obtained by linear regression (as illustrated in Figure 8) as a function of the inverse of temperature in Kelvin (Figure 9), it can be observed that below a certain temperature value, identifiable from the intercept in the graph, which corresponds to 320 K (47 °C), the activation volume is almost constant; above this temperature, an "Arrhenius" dependence is observed. The temperature is registered where the slope change occurs corresponding to $\alpha'$ PHB-HV relaxation observed from DMTA tests, and it is reflected in a similar manner for the plasticized systems. Consequently, the activation volume is strictly correlated to the molecular motion that occurs at the amorphous—crystalline interphase; when this motion is hindered, below a certain temperature, the dependence of the activation volume from temperature is negligible.

## 5. CONCLUSIONS

In this work, a PHB-HV polymeric matrix containing different amounts (5 and 10 wt %) of a plasticizer was investigated under stress-relaxation conditions. Analytical modeling of the stress-relaxation behavior at different operating temperatures (all above the HDT) was successfully performed applying the Guiu and Pratt multi-element constitutive model coupled with the Eyring model. The fitting was very good, and consequently, it was possible to obtain the activation volume. The activation volume results are in accordance with literature values; they are of the order of a few nm$^3$. The activation volume results are in accordance with other similar studies that can be found in the literature mainly for oil-derived polymers, and up to date, no data are available on a PHB-HV matrix. Furthermore, it was
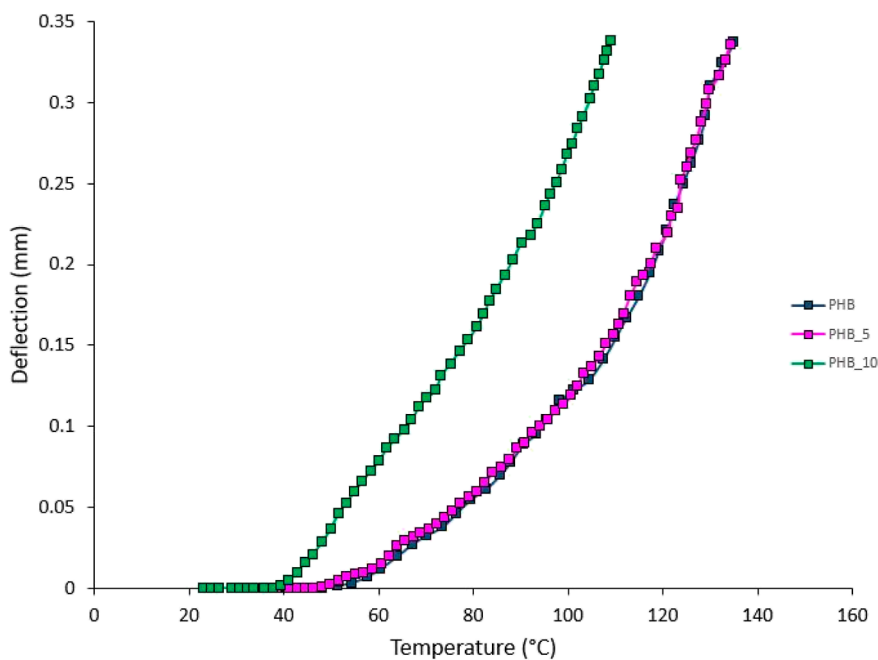
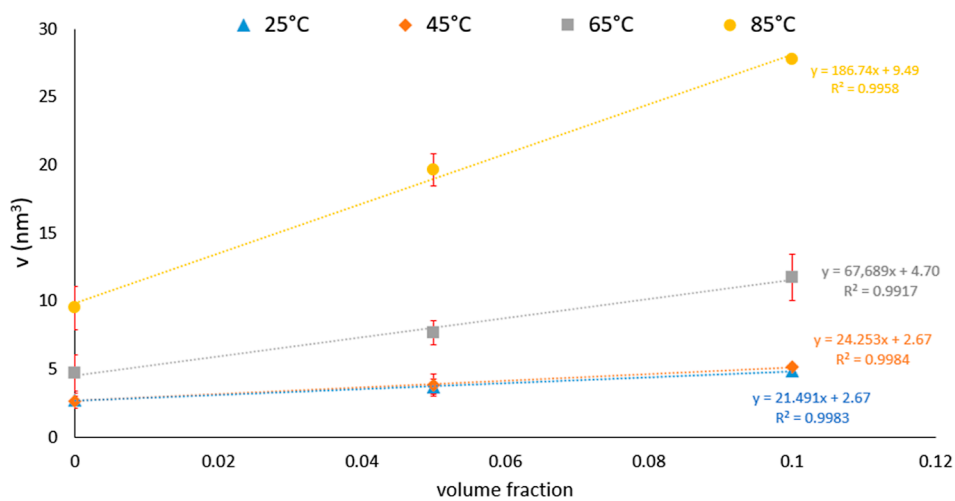**Figure 7.** Deflection trend recorded during HDT tests for PHB, PHB_5, and PHB_10.



**Figure 8.** Trend of the volume activation versus the plasticizer mass fraction at different temperatures.
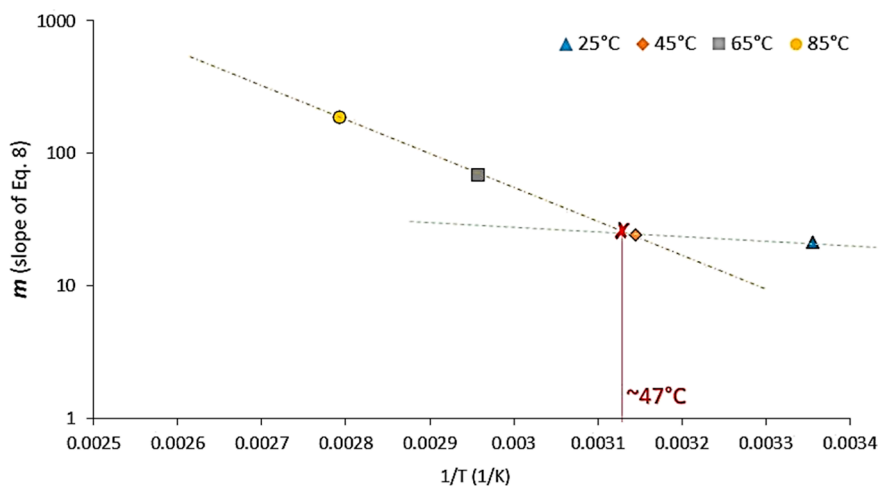


**Figure 9.** Trend of the slope of eq 8 against 1/T that highlights the different behaviors above and below the $\alpha'$ relaxation.

observed that the activation volume is strongly dependent from temperature increment. It was detected that below a certain temperature that was found to correspond to the $\alpha'$ PHB-HV relaxation, the activation volume is almost constant, and then, it increases exponentially.

Nevertheless, the main novelty of this study is correlated to the calculation of the activation volume for plasticized systems to evaluate the effect of the plasticizer addition. The results obtained are very interesting and lay the foundations for further investigations; in fact, it emerged that the activation volume is linearly dependent from the plasticizer volume fraction, thus increasing linearly with the plasticizer content.

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### Author Contributions

L.A.: Conceptualization, methodology, data curation, visualization, and writing original draft. V.G.: Conceptualization, methodology, data curation, visualization, and writing original draft. A.L.: Conceptualization, supervision, resources, and review and editing.

### Notes

The authors declare no competing financial interest.

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