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HYBRID POLYMER BASED COMPOSITE MATERIALS' KINETIC PARAMETERS RETRIEVAL FROM DMA DATA

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Abstract: *The herein paper aims to present an applied modeling concept directed towards kinetic parameters' estimation during glass transition as retrieved from dynamic mechanical measurements for hybrid particle-fiber polymer based composites. This dynamic process will be described by the aid of Arrhenius law applied to experimental data thus enabling the conversion degree at glass transition retrieval. The concept will be used to model and debate on the temperature-dependent overall complex moduli for the particle-fiber type hybrid polymer composite under the focus.*
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1. INTRODUCTION

Thermo-mechanical properties of hybrid polymer based composite materials can be ranked as one of the latest interests of both designers and developers since temperature-dependent properties are often misunderstood or ignored. It has been proven that dynamic mechanical analysis (DMA) is one of the effective methods used to study the relaxation phenomena in polymer materials and thereby the behavior of polymer based materials under various loading and temperature conditions.
In terms of theoretical prediction, literature reports few models used to describe the above relation processes. Next, predicted and retrieved data were used to develop or modify existing empirical or statistical models proposed in literature. Thus, the most referred theoretical model is the one proposed by Mahieux et al. [1]. Their models compromises of Weibull-type functions that were used to describe the complex modulus change over the full range of transition temperatures in case of a polymer material or polymer based composite.
Furthermore, the well-known Arrhenius law was used to predict the kinetic parameters during the transition changes in few polymer based composite materials or solely polymer materials. Experimental data used were retrieved from DSC curves (DSC – Differential Scanning Calorimetry), proven the accuracy of the method. Modified versions of this were the subject of many reference works. Nonetheless, the model can be used in conjunction with thermo-mechanical measurements as can be retrieved from DMA or any other temperature-dependent setups [2].
Overall material properties in case of hybrid polymer composites are rather tricky to be predicted by the aid of theoretical models. The herein author was co-authored several papers regarding the previous issue by approaching the subject of predicting the overall properties, including dynamic ones by the aid of micro-mechanics formalism [3]-[5]. A multi-step procedure was employed and few theoretical models used to predict the overall mechanical properties of particle-fiber or fiber-fiber type reinforced polymer composite tailored architectures. Mathematical formalism associated with these models is difficult to manage due to the employment of complex modulus that requires skills and computer programs to collect the factors.
Besides of above, there were reported the influences of few external loading conditions and changes of theirs upon the kinetic parameters of fiber-reinforced polymer composites, including the water absorbed by this while immersed for a certain time interval [6].
Next, interest on dynamic properties of natural fiber-reinforced composites can be referred to be a recently topic approached by several researchers [7]-[8]. To the best knowledge of the herein author, there are no theoretical models developed to hold in case of these architectures neither in use modified ones.

The herein paper aims to present a framework for kinetic parameters' assessment using experimentally retrieved data retrieved from dynamic mechanical testing. Few influencing factors can be identified to be responsible for values obtained proven the identified sensibilities due to the testing configuration.

2. MATHEMATICAL FORMALISM

Due to experimental related restrictions in DMA data available for the herein hybrid polymer composite architecture (i.e. one heating rate) a modified Coats-Redfern formalism will be deployed to estimate the kinetic parameters during the glass transition (see [1]). Simple mathematical manipulation in the method's expression leads directly to the following:

$$ln\left(-ln\left(1-\alpha_g\right)/T^2\right)=ln\left(A_g R/\quad E_{A,g}\right)\cdot\left(1-2RT/E_{A,g}\right)-\left(E_{A,g}/RT\right) \tag{1}$$

where α_g is the conversion degree of the glass transition, T is the temperature, R is the universal gas constant (8.31J/mol K), A_g is the corresponding pre-exponential factor from Arrhenius law, β is the constant heating rate (set to 1 in this work) and $E_{A,g}$ is the activation energy.

Furthermore, the dynamic mechanical properties (e.g. complex modulus, either storage or loss modulus) can be expressed in function of the conversion degree such as:

$$E_{exp}=E_g\left(1-\alpha_g\right)+E_r\alpha_g\left(1-\alpha_d\right) \tag{2}$$

where E_{exp} is the experimentally retrieved dynamic property and α_d is the conversion degree during decomposition. Since decomposition was not recorded for the herein hybrid polymer based composite material the parameter will be neglected. Thus, expression (2) allows the conversion degree at glass transition estimation proven the E_g and E_r will be taken from the glassy and rubbery plateau in storage/complex modulus variation with temperature.

3. EXPERIMENTAL DATA.DISCUSIONS

3.1 Materials manufacturing and characterization

An open molding method based on wet lay-up technology was used to manufacture the hybrid polymer based composite plates. The particle-fiber type hybrid composite was obtained by intimately mixing alumina particles (10% out of the total reinforcement's volume content) and random E-glass fibers as five layers architecture. The matrix material was selected to be an unsaturated polyester resin, commercially available and employed due to its attractive price that is balancing the overall manufacturing associated costs.

The dynamic mechanical properties were retrieved in accordance with ASTM D5023-07 using a DMA 242 C analyzer from Netzsch GmbH (D) running into a 3-point bending mode at an oscillating frequency of 1 Hz. The temperature range was imposed between - 30°C up to 200°C and applied upon the samples at a scan rate of 3 °C/min under a controlled atmosphere.

3.2 Results and discussions

In Figure 1 were plotted the storage modulus and damping factor variation within the temperature range for the hybrid polymer composite under the focus. As it can be seen, the glass transition occurs mainly between 75° and 150° C. From the experimental data one has to retrieve the dynamic property associated to the glassy and rubbery plateau, respectively. Herein, the storage modulus values were employed and thus retrieved for 25° C and 150° C even mean values of their may be also used.

Based on expression (1), a plot of $ln\left(-ln\left(1-\alpha_g\right)/T^2\right)$ against $1/T$ was provided in Figure 2. Simple linear regression applied to the selected data (correlation factor 0.97) followed by parameter identification from slope value provided enables glass transition associated energy of activation retrieval. The activation energy, $E_{A,g}$ was calculated to be 2.04 kJ/mol as provided in Table 1. Next, this value was substituted in expression (1) allowing the retrieval of pre-exponential factor A_g (see provided values).

With respect to the value predicted for energy of activation, one might debate on the relatively small value retrieved compared with other polymer materials. The latter can be assigned to the polymer used as matrix in this hybrid composite architecture that is an unsaturated polyester resin. Apart for being one of the less costly material often employed by manufacturers it's polymerization process strongly depend on several factors such as: storage environment, manufacturing conditions, content of relaxing agents, etc. The activation energy strongly depends upon the constitutive content within the composite and reveals the effectiveness in stress transfer between the particles, fibers and matrix. Further insights into the issue should be closely approached.

Furthermore, one may further use the kinetic parameters to predict the temperature-dependent complex/storage or loss modulus and deploy an error minimization scheme between theoretical predicted and experimentally retrieved values. Consequently, the above formalism can be applied to the loss modulus experimental values and may be used to model the temperature-dependent viscosity. Since the viscosity in the leathery and rubbery states appears to be different, the analysis should be individually carried out. It is beyond the purpose of the article to further debate on the issue.

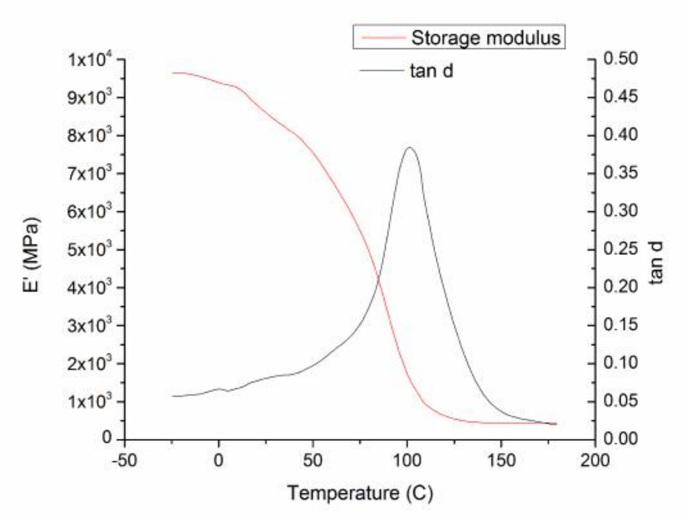

Figure 1: Storage modulus and damping factor variation within the temperature range

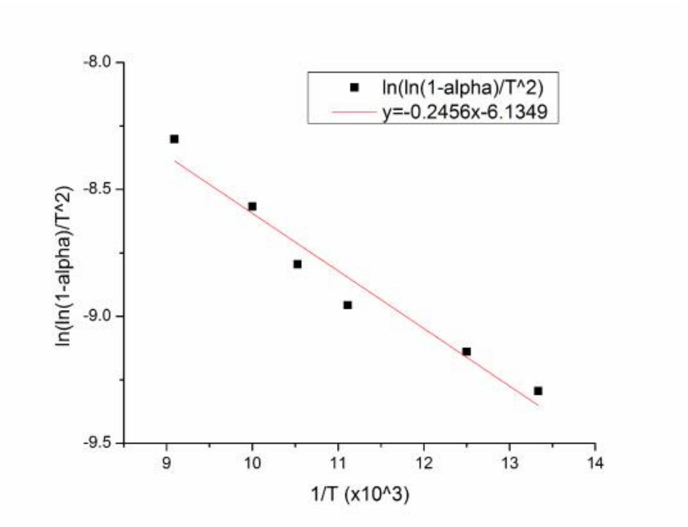

Figure 2: Experimental data related values to estimate $E_{A,g}$ during glass tansition

Table 1: Kinetic parameters associated to glass transition in hybrid particle-fiber composites

T (°C)	α_g (%)	A_g ($x10^{-7}$ min^{-1})	$E_{A,g}$ (kJ/mol)
75	40	37.07	2.04
80	50	40.57	
90	65	43.30	
95	75	48.21	
100	85	57.50	
110	95	68.12	

4. CONCLUSIONS

A mathematical formalism adopted by modifying the well-known Arrhenius law was used to estimate the kinetic parameters of a particular hybrid polymer based composite material architecture. Based on the estimates and their related plots, the following conclusions can be drawn:

- The hybrid composite state changes with temperature increase up to a certain value imposed by settings. Three different temperature-dependent material states can be indentified (glassy, leathery and rubbery) as well as their associated transitions (glass, leathery-to-rubbery).
- Kinetic parameters can be identified using the kinetic theory and Arrhenius equations by considering the experimental values retrieved for one of the dynamic properties (e.g. storage or loss modulus).
- The value of activation energy is relatively small in comparison with other types of polymers and an insight into the reasons relaying beneath this can be identified the relaxations' processes within unsaturated polyester resins.

Further approaches can be led with respect to the kinetic parameters in order to model the temperature-dependent viscosity of the herein hybrid composite architecture and next, directed towards other types of materials.

Other temperature-dependent material properties can be identified and subjected to modeling by using the conversion degree of glass transition. Based on author's experience, significant differences are being expected despite the idea of setting the same temperature programs for all composite specimens.

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