GLASS TRANSITION IN PLASTIC ARTWORK ARTEFACTS

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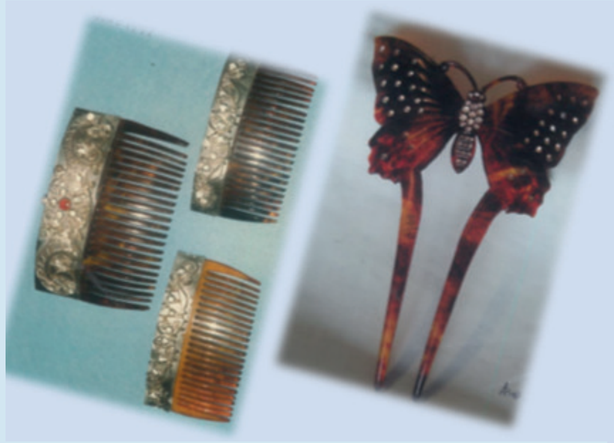
Introduction

The conservation of early plastics in heritage collections is a challenge, given the presence of degradation processes leading to changes in the artefacts properties [1].



The glass transition temperature, T_g, is sensitive to changes in the polymer structure, and is therefore a powerful source of information about the degree of degradation. Dynamic mechanical analysis (DMA) allows for the determination of the T_g with higher sensitivity in comparison to the traditional differential scanning calorimetry (DSC) analysis, especially when applied to semi-crystalline materials with a low amorphous content, such as that seen in cellulose nitrate (CN) based artefacts. However, different methods are suggested for defining T_g from DMA experimental data, resulting in distinct T_g values. This work evaluates DMA and DSC techniques for determining the T_g of artefacts based on cellulose nitrate, in order to develop structural relationships between T_g and the article's properties. Samples were analysed in a Tritec 2000 DMA and in a Shimadsu TA60 Heat-Flux DSC system.

Results and Discussion

Fig. 1 (a) shows the DSC thermograms for two distinct CN based materials, indicating the start of the thermal decomposition at nearly 170 °C. However, the derivative of the heat flow, Fig. 1 (b) did not allow for identification of the T_g.

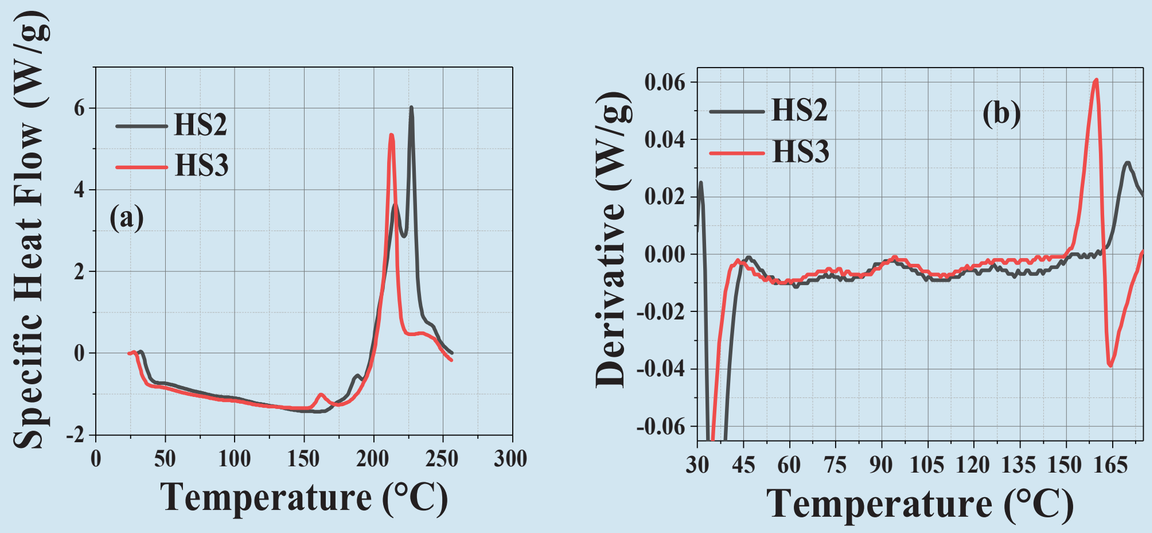


Fig. 1. DSC thermograms (a) and thermograms derivative (b) for the cellulose nitrate based samples HS2 and HS3 at the heating rate of 40 °C/min.

In contrast, the variation of the storage and loss moduli with the temperature allowed for a clear observation of the T_g, at nearly 100 °C, Fig. 2 (a-c). In addition, the increase of the loss modulus at nearly 75 °C, Fig. 2 (c), indicated the presence of a relaxation process, in agreement with the endothermic peak observed at lower temperature from the DSC thermograms, Table 1.

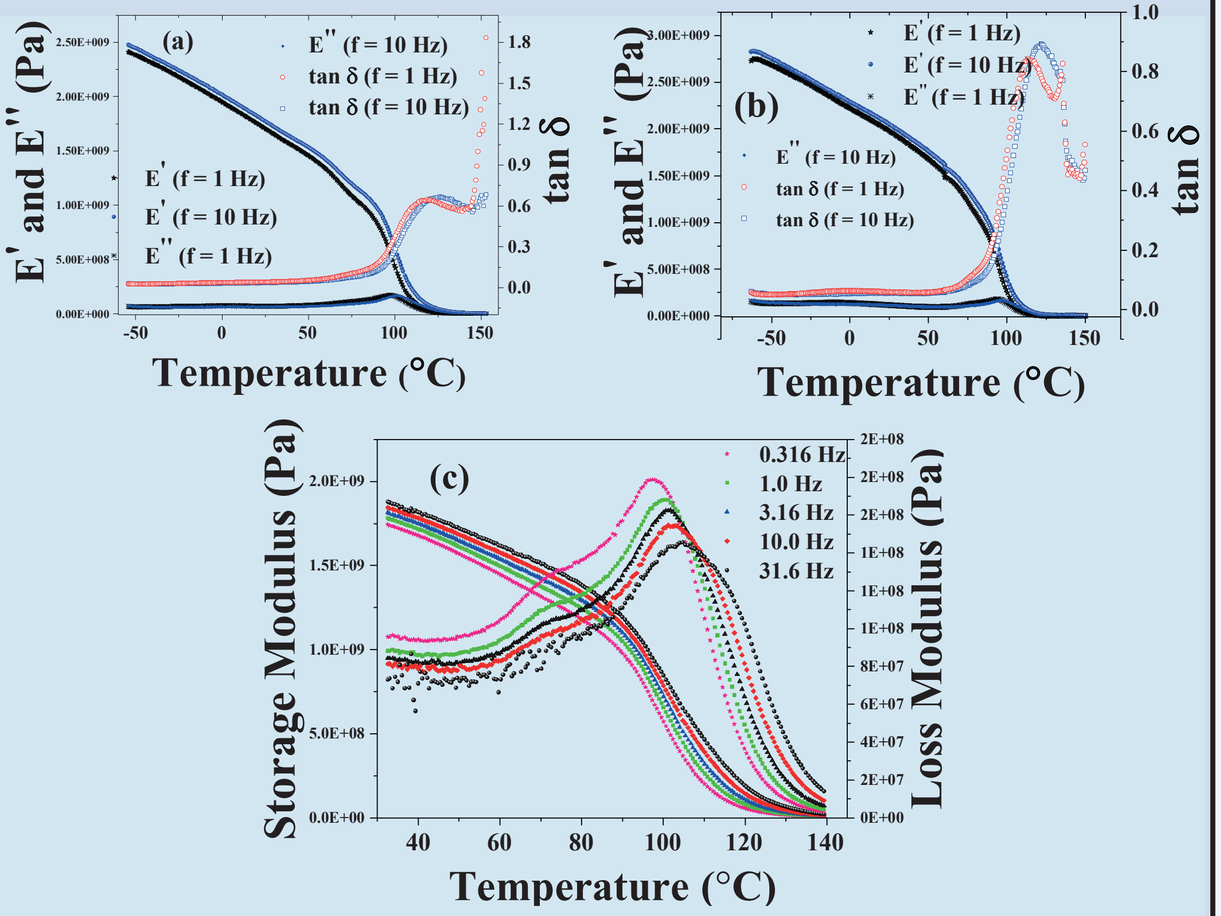


Fig. 2 – Variation with temperature of storage and loss modulus and tan δ signal for the CN samples HS2 (a and c) and HS3 (b) at different stress frequencies.

Table 1 summarises the T_g values obtained from the different DMA definitions of the glass transition [2], as well the temperature at the minima of the DSC derivative thermograms. The high glass transition temperatures observed could be associated with the degradation stage of the samples [3]. Further work is ongoing.

Table 1 – Values of T_g obtained from different definitions of the glass transition.

Sample	DSC	DMA frequency	DMA		
	T_g (°C)	(Hz)	T_g (°C)		
			E'	E''	tan δ
HS2	62.23	1	97.20	98.16	116.84
	80.18	10	99.99	101.29	125.22
	109.17				
HS3	57.27	1	94.49	93.95	114.11
	84.05	10	96.56	96.27	121.06
	110.83				

Conclusions

DSC measurements were demonstrated to be valuable in the characterisation of thermal behaviour of CN based artefacts. However, a better understanding of the glass transition process was obtained with multifrequency DMA measurements.

References

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[3] Curran et al., Classifying Degraded Modern Polymeric Museum Artefacts by Their Smell, Angewandte Chemie, 2018, DOI:10.1002/ange.201712278.

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