Challenging Glass Conference Proceedings – Volume 8 – 2022 – Belis, Bos & Louter (Eds.)
Challenging Glass Conference 8 – 23 & 24 June 2022 – Ghent University – Ghent – Belgium
Conference on Architectural and Structural Applications of Glass

Thermal Rheological Behavior of Composite Interlayer in Laminated Glass

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Abstract

Laminated glass is growing its application in structural entities. The thermoplastic polymeric interlayer plays an important role in transferring force and achieving the composite action in laminated glass, which reveals evident temperature-dependent behavior. In this study, a novel composite interlayer (SGE®) was devised to improve the resistance of laminated glass against environmental actions and to enhance the post-fracture performance. It is comprised of modified ethylene-vinyl-acetate (PVE®) and polycarbonate (PC). Through dynamic mechanical thermal analysis, the temperature-dependent characteristics of SGE, PVE, and PC materials were investigated in detail. The results show that the thermal rheological behavior of SGE is similar to that of PVE. The temperature ranges of glass transition and crystal melting of SGE material are -35°C ~ -25°C and 45°C ~ 75°C, respectively. The corresponding ranges are -35°C ~ -15°C and 35°C ~ 65°C for PVE material. And temperature ranges of the main transition are influenced by imposed frequency. Besides, the relationship between time and temperature for PVE, PC, and SGE material is extensively complicated and the complexity depends on the investigated mechanical property, temperature range, and time range. And the simple thermal rheological behavior emerges in the storage modulus of polymers, but loss modulus and loss factor conform to the complex thermal rheological behavior at the temperature range of -50°C ~ 120°C under the frequency range of 0.1 Hz ~ 10 Hz.

Keywords

Composite interlayer, Thermal rheological behavior, Glass transition, Ethylene-vinyl-acetate

Article Information

- Digital Object Identifier (DOI): 10.47982/cgc.8.408
- This article is part of the Challenging Glass Conference Proceedings, Volume 8, 2022, Belis, Bos & Louter (Eds.)
- Published by Challenging Glass, on behalf of the author(s), at Stichting OpenAccess Platforms

1. Introduction

The tendency that laminated glass is recognized as the structural component presents more obvious with time going. Laminated glass can be used as beams, columns, walls, and so on. And laminated glass presents a more excellent performance than the monolithic glass. The fragments in laminated glass can be maintained at the original position, which decreases the threat to people's lives. Meanwhile, other performances such as sound insulation and resistance against ultraviolet radiation are also improved. The key point of performance improvement is the addition of the polymeric interlayer. The representatives of the polymeric interlayer are polyvinyl butyral (PVB) (Hooper et al. 2012), ionomers (SentryGlas, SG) (Martín et al. 2020), and ethylene-vinyl acetate (EVA) (Schuster et al. 2018). But they belong to thermoplastic polymers, which are sensitive to temperature and suffer performance degradation under high-temperature action.

The thermoplastic polymers present an evident temperature-dependent property. As temperature increases, the falling of the modulus occurs. Therefore, it is of critical importance to investigate the thermal rheological behavior of polymers. Hooper et al. (2012) have investigated the gradual relaxation transform of PVB material with temperature. The result revealed that PVB underwent a gradual transition from glassy, transition, and rubbery states as temperature increased, and mechanical performance decreased dramatically in the transition region. SG material is less sensitive to temperature than PVB (Martín et al. 2020), but it behaves similarly to PVB whose mechanical parameters including initial modulus and yield stress become lower at a higher temperature. And the glass transition temperature of SG material is nearly 45°C ~ 65°C (Xu 2017), which means the softening of SG material will emerge at high temperatures. So the high temperature restrains the application of the laminated glass with SG interlayer. EVA material has a lower temperature of the glass transition that is -40°C ~ -15°C (Schuster et al. 2018). Besides, there is the crystal melting in the temperature range of 35°C ~ 70°C, which results in a second dramatic drop in modulus, which makes that Schuster et al. (2018) did not think EVA material follow the simple thermal rheological behavior.

In this paper, a composite interlayer modified EVA/polycarbonate/EVA is come up with, whose abbreviation is SGE®. And modified EVA (PVE®) is through process improvement and chemical modification based on EVA material, which has good adhesion to glass and other polymers. Meanwhile, polycarbonate (PC) as a type of engineering plastic (Ying et al. 2020) with excellent performance is widely used in the fields of electronic appliances, medical supplies, auto parts (Dou et al. 2019), etc. It has a superior optical property and temperature resistance (Salazar-Martín et al. 2018). The glass transition temperature of PC is about 150°C (Mulliken et al. 2006), indicating that PC material can still maintain a high modulus elastic glass state in the normal service temperature range. So SGE material is constructed, aimed to improve the resistance against temperature for the laminated glass. And thermal rheological behavior of SGE and substrates are studied based on the dynamic mechanical thermal analysis (DMTA) test to investigate polymeric relaxation transition and the relationship between time and temperature.

2. Material and Procedure

2.1. Material

PVE, PC, and SGE material are provided by Shanghai Haiyouwei New Material Co., Ltd. Test samples are obtained by means of punching sheet products, preserved in a dark and sealed environment. And nominal thickness for the three polymeric materials are 1.52 mm, 0.25 mm, and 0.76 mm, respectively. The nominal thickness of every polymeric interlayer in the sandwich structure of SGE is 0.25 mm.

2.2. Procedure

DMTA tests utilized Q850 apparatus made by TA instruments (shown in Fig. 1) in America, and a two-point tension fixture (shown in Fig. 2) was used to provide uniform force at the position where the tension fixture keeps the sample fixed. Dynamic mechanical thermal analysis based on the dynamic response of polymers was used to investigate the temperature-related viscoelasticity and rheological behavior. Meanwhile, the frequency is also an important factor that affects polymeric performance. Different temperatures and frequencies were considered according to ISO 6721-1 (2019), and the detailed test design is shown in Table 1. The temperature range of PC material was increased to 130°C in the light of the results of the preliminary tests (Mulliken and Boyce 2006). Therefore, isothermal frequency sweep tests were carried out on the basis of the aforementioned parameters. And each test temperature was maintained for 5 minutes to avoid the thermal hysteresis effect of polymers.

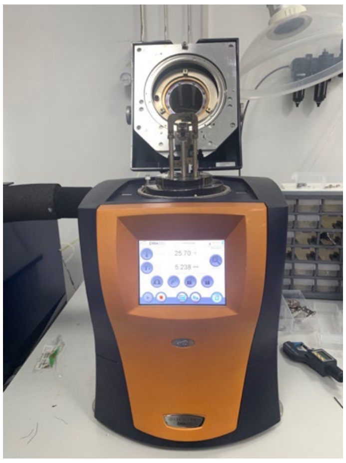


Fig.1: Q850 apparatus

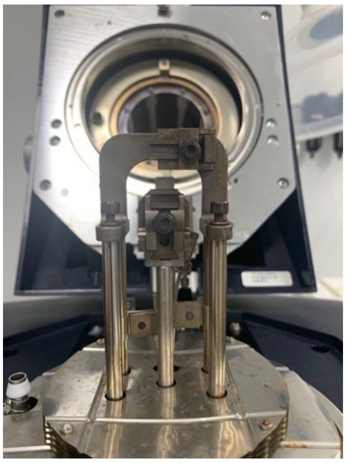


Fig. 2: Two-point tension fixture

Table 1: Design of DMTA tests

Polymer	Frequency [Hz]	Temperature [°C]
PVE PC SGE	0.1, 0.2, 0.4, 0.8, 1.0, 2.0, 4.0, 8.0, 10.0	-50 ~ 120 [Increment 5]

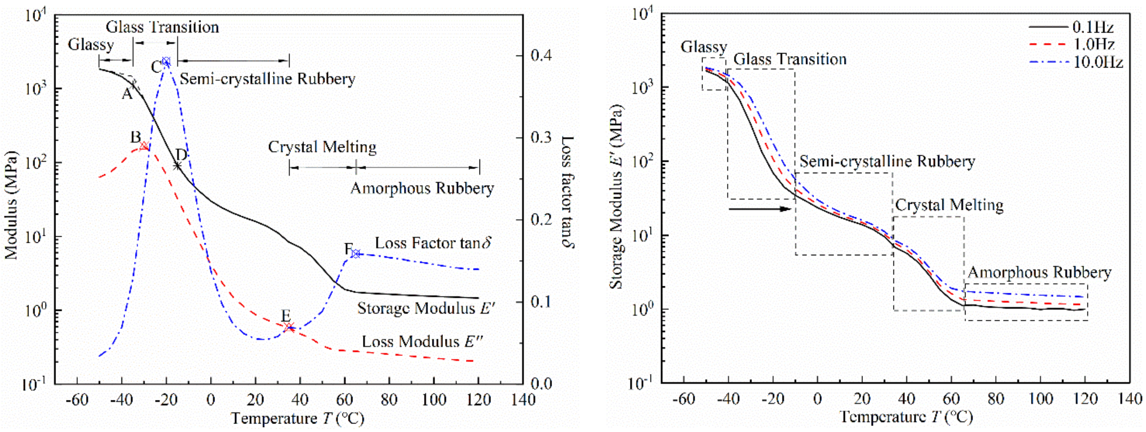
3. Result

3.1. Relaxation transition

Polymeric relaxation transition can be seen in Fig. 3 (a), Fig. 4 (a), and Fig. 5 (a). It is obvious that PVE and SGE material present two types of the main transition, while PC material presents the one main transition. The main transitions for PVE and SGE material are glass transition and crystal melting. They divide the whole into three states, which are glassy, semi-crystalline rubbery, and amorphous rubbery. For defining different phases of the relaxation transition, feature points have been marked in the figures. Point A is on the curve of the storage modulus corresponding to the interaction of tangents of curves in the glassy and glass transition. Point B, C, and F are the peak of the loss modulus and loss factor curves. Point D is on the curve of the storage modulus where the storage modulus declines fastest. Point E is on the curve of the loss modulus where the loss modulus increases slowest. In ISO standard, the temperature at point B is recognized as the glass transition temperature. But the more general definition that the glass transition temperature is recognized as the temperature range between A and D is considered in this paper. Therefore, Point A, D, E, and F are defined as the dividing points of five states.

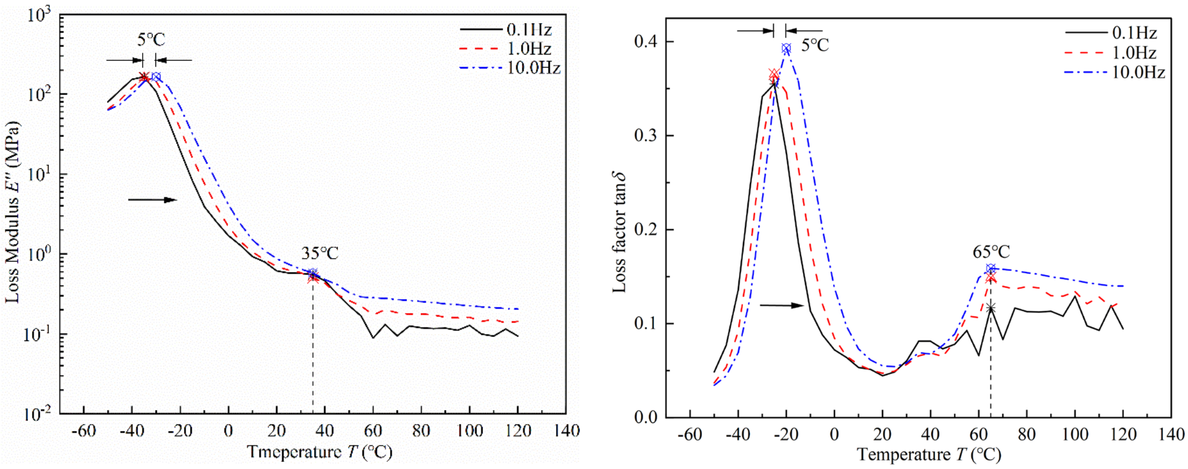
The temperatures of the characteristic points for PVE, PC, and SGE material are shown in Table 2. Therefore, the temperature ranges of different states can be derived according to the characteristic points. The main transitions for PVE material are glass transition and crystal melting, which occurs -35°C ~ -15°C and 35°C ~ 65°C, respectively. The relaxation transition of SGE material is similar to that of PVE material, where the corresponding temperature ranges are -35°C ~ -25°C and 45°C ~ 75°C. But PC material presents the only main transition, whose glassy state maintains until 120°C. When the temperature is beyond 120°C, the storage modulus of PC material starts decreasing dramatically.

The variations of the storage modulus, loss modulus, and loss factor with temperature are the macroscopic reflection that the types of motional elements change with temperature microscopically. The molecular chain segments are frozen in the glassy state when the motional elements are mainly chain links, side groups, and other elements that are smaller than chain segments. Thereafter, molecular chain segments begin to move along with temperature increasing in the glass transition. Therefore, the molecular conformation will be changed more easily, which causes the polymeric stiffness decreasing. Besides, it can be seen from Fig. 3 (a) and Fig. 5 (a) that the loss factor peaks in the glass transition that is related to the conversion of the status of the molecular chain segments. The frozen molecular chain segments are equivalent to rigid springs in comparison to the free molecular chain segments that can be recognized as soft springs. Accordingly, the conversion that rigid springs turn to soft springs occurs in the glass transition. And rigid springs can store more energy than soft springs under the same deformation, which means that residual energy will dissipate during the conversion. So the viscous characteristic emerges obviously in the glass transition. After the glass transition, the performance of the material maintains relatively stable, which is called as semi-crystalline rubbery state for PVE and SGE material. The semi-crystalline rubbery state is the combination of amorphous and crystal status. And the motional elements cannot change with temperature, which are the chain segments. But when the temperature is up to the melting temperature of the material, the molecules break through the lattice energy limit from the crystalline phase to the liquid phase, and the long-range diffusion movement of molecular chain segments start to carry out. So the conversion from rigid chain segments to soft chain segments emerges again in the crystal melting, when the loss factor peaks again. After polymers go through the crystal melting, the performance keeps stable again, which is called as the amorphous rubbery state. For the linear polymers, there is the performance decreasing when the threshold that is the viscous flow temperature is reached. But PVE material belongs to crosslinked polymers that maintain amorphous rubbery state because of the structure of crosslinked molecules inside polymers. Because PC material maintains glassy state below 120°C, the characteristic of SGE material is lean to that of PVE material in the temperature range of tests.



a) Storage modulus, loss modulus, and loss factor with temperature

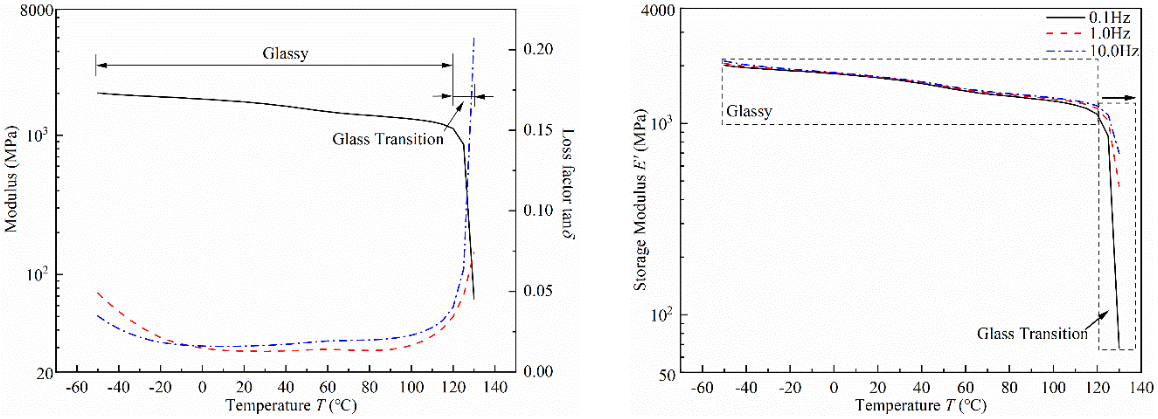
b) Storage modulus with temperature under different frequencies



c) Loss modulus with temperature under different frequencies

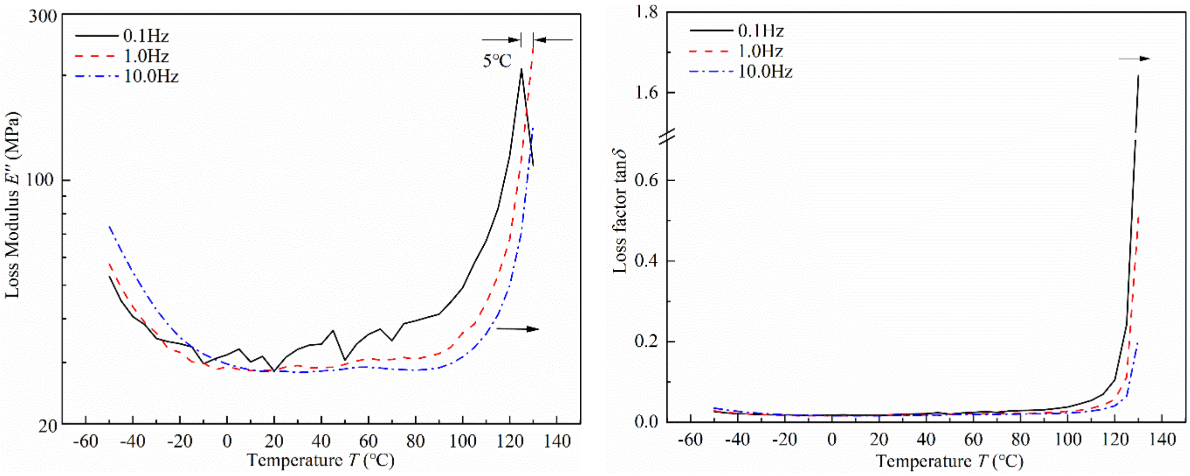
d) Loss factor with temperature under different frequencies

Fig. 3: Dynamic mechanical properties related to temperature and frequency for PVE material



a) Storage modulus, loss modulus, and loss factor with temperature

b) Storage modulus with temperature under different frequencies



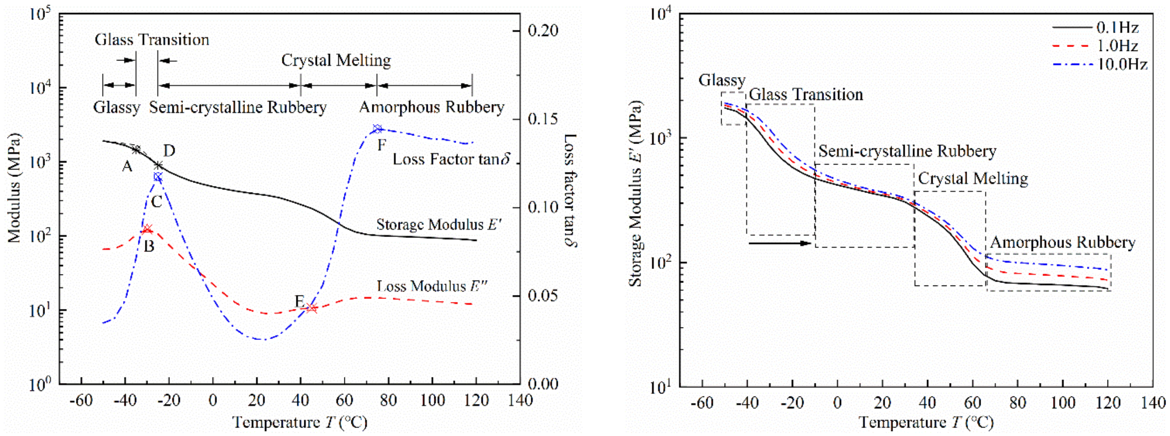
c) Loss modulus with temperature under different frequencies

d) Loss factor with temperature under different frequencies

Fig. 4: Dynamic mechanical properties related to temperature and frequency for PC material

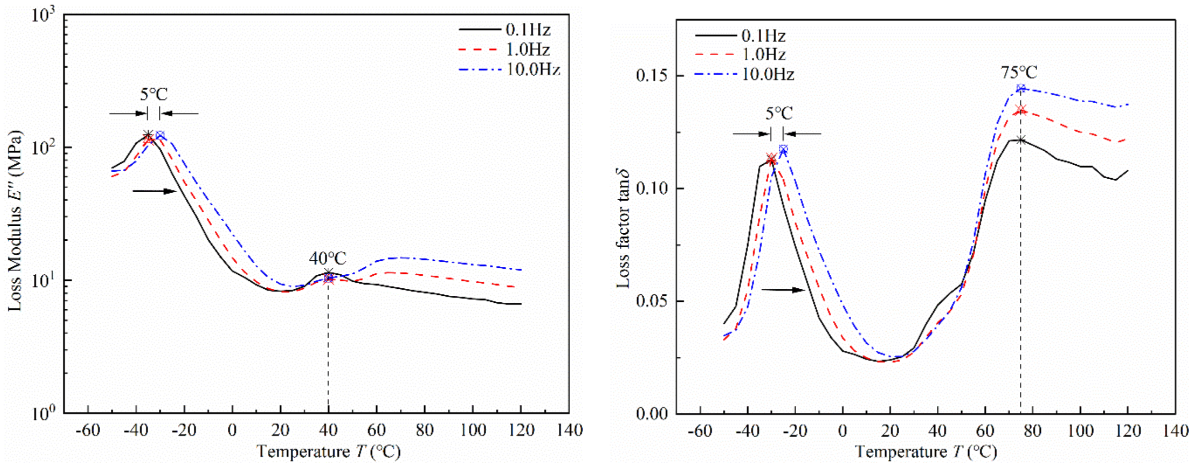
Besides, the influence of the temperature on the relaxation transition, the frequency presents a significant impact on materials. As shown in Fig. 3 (b) ~ (d), Fig. 4 (b) ~ (d), and Fig. 5 (b) ~ (d), the offset curves can be observed evidently under different frequencies. As PVE material for example, point B and C shift towards right by 5°C when the frequency is increased from 0.1 Hz to 10 Hz, which means the temperature range of the glass transition shifts to the right by 5°C. What the interesting thing is that point E and F are located at the same temperature. Therefore, the crystal melting is insensitive to the frequency. Moreover, it can be seen from Fig. 3 (b) that the glass transition and amorphous rubbery state are more susceptive to the frequency than the other three states. The raising frequency has different levels of positive influence for increasing the storage modulus at different states, especially more obvious in the glass transition and amorphous rubbery state. And the frequency has a semblable influence on the relaxation transition for SGE material compared to the substrate PVE material.

Although the thermal rheologic behavior of SGE material is lean to PVE material, the addition of PC material makes the tension stiffness higher than PVE material. The storage modulus declines by two orders of magnitude when PVE material goes through the glass transition, followed by one order of magnitude decreasing in the crystal melting as shown in Fig. 3 (a). However, the storage modulus of SGE material presents the phenomenon that the tendency of decreasing is less dramatic, in which the sum of decreasing of the two main transitions is nearly of one order of magnitude. Therefore, the thermal sensitivity of SGE material declines obviously compared to PVE material.



a) Storage modulus, loss modulus, and loss factor with temperature

b) Storage modulus with temperature under different frequencies



c) Loss modulus with temperature under different frequencies

d) Loss factor with temperature under different frequencies

Fig. 5: Dynamic mechanical properties related to the temperature and frequency for SGE material

Table 2: Temperatures of the characteristic points for PVE, PC, and SGE material

Temperature [°C]	A	D	E	F
PVE	-35	-15	35	65
PC	120	-	-	-
SGE	-35	-25	45	75

3.2. Relation of time and temperature

The data in the isothermal frequency sweep tests can be utilized to judge whether the material conforms to the simple or complex thermal rheologic behavior. Different curves under different temperatures need to be shifted in both horizontal and vertical directions. In this paper, 20°C is chosen as the reference temperature, which is closer to the indoor temperature. So the curves for storage modulus, loss modulus, and loss factor at 20°C keep the original position. The curves beyond 20°C are shifted towards left. Besides, the higher the temperature the farther the curves are shifted towards left. Similarly, the curves below 20°C are shifted towards right. However, the process of manual shifting can be subjectively empirical. Adjacent curves can be overlapped to different degrees that all maintain a good consistency of slope. Therefore, different resultants will yield based on different shift factors. But the relationship of temperature and time in polymers has been ruled by the specific motional laws which are the Arrhenius and WLF functions. Accordingly, shift factors need to obey the two functions to restrain the shifting magnitude of curves under different temperatures. Meanwhile, it should be noted that the loss factor is the ratio of storage modulus to loss modulus, which means the influence on the modification of the density can be offset. So only the horizontal shift factor is needed to obtain the master curve of the loss factor.

The detailed procedure of the construction of the master curves is elaborated as following. First of all, the horizontal shift factors are determined according to the loss factor. Starting from the reference temperature of 20°C, the curves of loss factor at other temperatures are shifted horizontally, and shift magnitude needs to meet the Arrhenius and WLF functions. Meanwhile, the relative smoothness of the master curve is another criterion needed to be considered during the shifting process. Then, the curves of storage modulus and loss modulus are shifted based on the same horizontal shift factors that are derived from the first step. At last, the vertical shift factors can be derived on the basis of the storage modulus or loss modulus. The curves at the reference temperature are the benchmark, others are shifted vertically to achieve successive overlap. So the master curves of storage modulus and loss modulus can be obtained.

The master curves of storage modulus, loss modulus, and loss factor for three types of polymers are shown in Fig. 6, Fig. 7, and Fig. 8. The horizontal shift factors are shown in Fig. 9, Fig. 10, and Fig. 11, and the parameters of Arrhenius and WLF functions are listed in Table 3. It can be seen that adjacent curves for storage modulus present relatively smooth connection, which means the storage modulus of polymers follows the simple thermal rheologic behavior. However, many discontinuities emerge in the master curves of the loss modulus and loss factor, especially for PVE and SGE material. The loss factor curves for PVE and SGE material at about 20°C ~ 70°C are almost parallel to each other and they are at different heights, so they cannot be shifted to overlap each other for deriving a smooth master curve. Besides, the loss factor curves at above 75°C almost overlap completely, which reveals that temperature has little influence on the mechanical properties of PVE and SGE material when the temperature is above 75°C. The loss factor curves at below 15°C raise sightly relative to adjacent curves at one end. It can be guessed that the master curve of the loss factor can be smooth if the sub-curves at below 15°C are constructed in a certain frequency range. And the “ending raising” phenomenon also exists in the loss factor curves of PC material. Therefore, the relationship between time and temperature for PVE, PC, and SGE material is complex and depends on the special mechanical property, temperature range, and time range. According to the results of tests, the storage modulus of polymers follows simple thermal rheological behavior, but the loss modulus and loss factor conform to complex thermal rheological behavior at temperature range of -50°C ~ 120°C under frequency range of 0.1 Hz ~ 10 Hz.

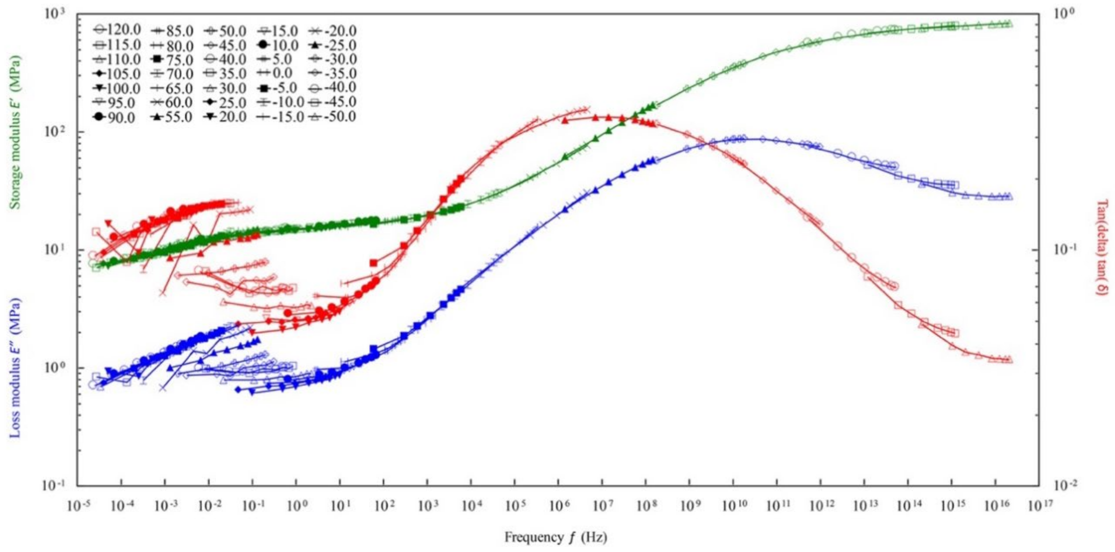


Fig. 6: Master curves for PVE material

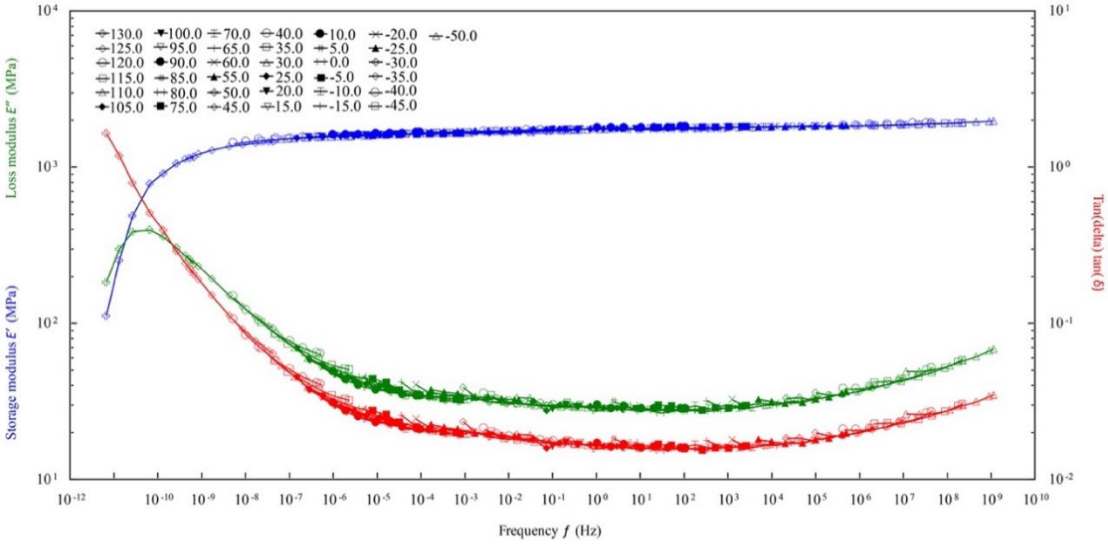


Fig. 7: Master curves for PC material

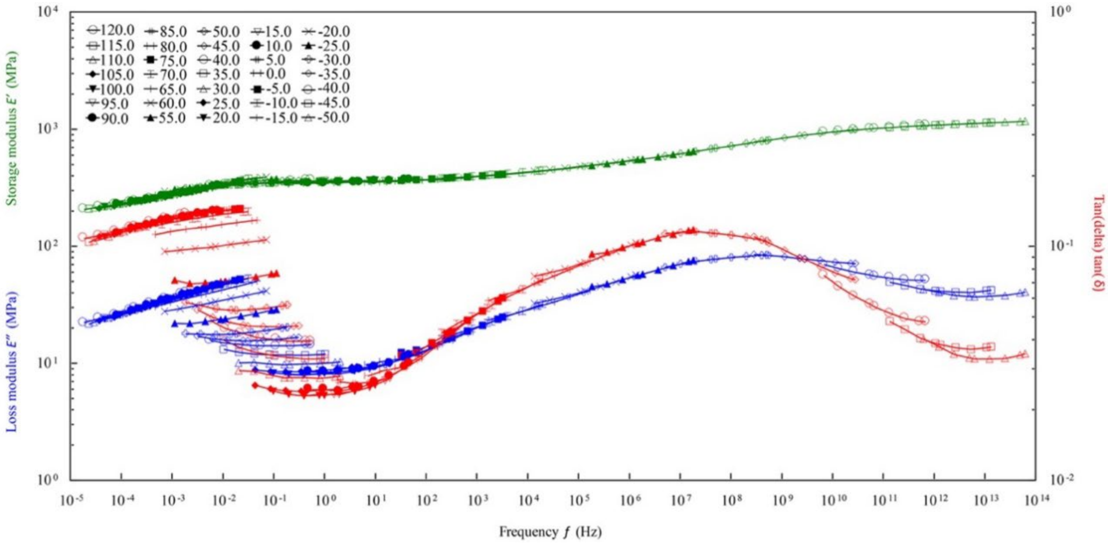


Fig. 8: Master curves for SGE material

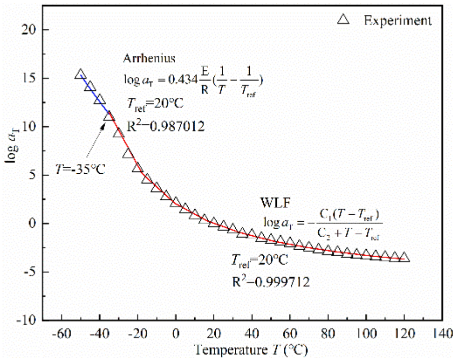


Fig. 9: Shift factor with the temperature for PVE material

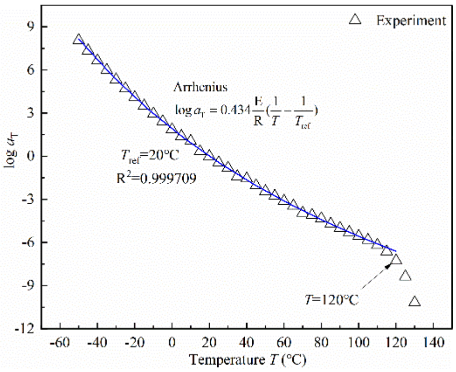


Fig. 10: Shift factor with the temperature for PC material

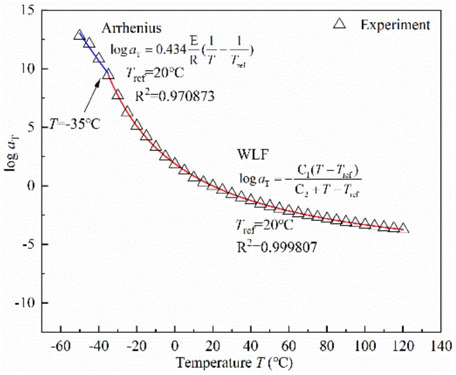


Fig. 11: Shift factor with the temperature for SGE material

Table 3: Parameters of Arrhenius and WLF functions for three types of polymers

Polymer	Arrhenius function		WLF function		
	T_{ref} [°C]	E [J/mol]	T_{ref} [°C]	C_1	C_2 [K]
PVE	20	274453	20	6.9058	88.1971
PC	20	145899	20	-	-
SGE	20	233255	20	7.3773	97.7443

4. Conclusion

Based on the dynamic mechanical thermal analysis, the thermal rheological behavior of the composite interlayer SG, substrate PVE and PC materials were investigated. The results shows that the thermal rheological behavior of composite SGE material is more similar to that of PVE material, but the influence of temperature on polymeric mechanical property declines compared to PVE material. The main transitions for PVE material are glass transition and crystal melting, which occurs -35°C ~ -15°C and 35°C ~ 65°C, respectively. The corresponding temperature ranges for SGE material are -35°C ~ -25°C and 45°C ~ 75°C. But PC material presents the glass transition at 120°C in the range of -50°C ~ 130°C. And the temperature ranges of main transition are influenced by imposed frequency. Besides, PVE, PC, and SGE material follow the complex thermal rheological behavior, which depends on the special mechanical property, temperature range, and time range.

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