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Study on the Influence Factors of Dynamic Modulus and Phase Angle of Dense Gradation Polyurethane Mixture

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Abstract: Polyurethane (PU) mixture is a new pavement material with excellent pavement performance, and most research was focused on the enhancement of pavement performance, but rarely on the dynamic property. This paper studied the factors including gradation, aggregate type, PU type, and PU content, which may influence the dynamic property of the PU mixture. Test results showed that the PU mixture is a kind of linear viscoelastic material, its dynamic modulus and phase angle changed with test temperature and loading frequency, the dynamic modulus would drop by 40%~50% with the temperature raised from 5 °C to 55 °C. All of the factors could affect the dynamic property of the PU mixture which was proved by the analysis of covariance. The effect of gradation did not change with the increase of the nominal maximum aggregate size (NMAS), the dynamic modulus of the PU mixture with limestone was higher than that of the PU mixture with basalt, and the curing speed of PU could affect the ultimate stiffness of the PU mixture, and the increase of the PU content did not help in the increase of the dynamic modulus of the PU mixture. So, more consideration about the selection of gradation, aggregate type, PU type, and PU content should be taken into the design of the PU mixture, which could produce the best pavement structure combination and save more investment.

Keywords: polyurethane mixture; dynamic modulus; phase angle; covariance

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1. Introduction

Asphalt mixtures have viscoelastic a property which is due to the combination of the viscoelastic asphalt binders and the aggregate skeleton [1,2]. At low temperatures, the asphalt binder is in rigid status, the asphalt mixture acts elastically, and the properties of the asphalt mixture are mainly subjected to the asphalt binder. The viscoelastic properties of the asphalt mixture are more affected by the interlocking force between the aggregates than by the asphalt binder when the temperature rises (or frequency falls) because the asphalt binder becomes soft and the asphalt mixture primarily exhibits a viscous behavior. Thus, the aggregate skeleton is primarily subject to the loading stress, as temperature (or frequency) increases [3]. At various temperatures, the viscoelastic behavior of the asphalt mixture is impacted by the aggregate skeleton and asphalt binder.

In the Al−Khateeb model [4], the asphalt mixture is composed of three phases (asphalt binder, aggregate, and air void) in parallel. From this perspective, the properties of the asphalt mixture must be influenced by the three phases, and numerous researchers have looked at the effects of the aggregate gradation and asphalt binder. Ali et al. [5] studied the impact of temperature, frequency, and NMAS on the dynamic modulus and phase angle of eight kinds of asphalt mixture, including wearing and base course mixes, and test results showed that the test temperature and loading frequency could significantly influence the dynamic response of both wearing and base course mixes, but the NMAS factor had an insignificant effect. The study [6] identified that various factors including: aggregate, asphalt content, and reclaimed asphalt pavement (RAP) percentage had significant influence on the dynamic response of asphalt mixtures, and the dynamic modulus of asphalt mixtures is sensitive to the mix constituents. The study [7] reported that asphalt binder could significantly affect the dynamic modulus of asphalt mixtures and concluded that the softer the asphalt binder, the lower the dynamic modulus, and vice versa. This study [8] found that binder grade, air voids, and RAP significantly influence the dynamic modulus of asphalt mixtures. The research [9] concluded that the dynamic modulus of rubber asphalt mixture was affected by factors, i.e., binder, mixture type, temperature, and loading frequency, and temperature and loading frequency had a larger influence on the dynamic modulus of the mixture than the binder, mixture type, etc. Hajibandeh and Shalaby [10] concluded that the dynamic modulus of full-size (standard) and small-scale specimens were considerably influenced by the aggregate gradation and specimen dimension.

The prediction equation employed in the mechanistic empirical pavement design guide (MEPDG) to predict the dynamic modulus of asphalt mixture is a function of aggregate gradation, effective binder content, binder properties, mix air voids, temperature, and loading rate. The dynamic modulus of the asphalt mixture depends on many factors, e.g., aggregate gradation, binder type, aging, construction technology, and volumetric properties [11–15]. For example, Islam et al. [16] demonstrated how the rise in binder content and air void will lead to an increase in the dynamic modulus of an asphalt mixture. According to the research in [17,18], the dynamic modulus of the asphalt mixture is related to the mixture gradation. Solatifar et al. and Su et al. [19,20] concluded that the laboratory-tested dynamic modulus of the asphalt mixture is subjected to binder viscosity, binder content, air voids, and gradation. According to Tan Hung et al. [21], porous asphalt mixtures with fewer air voids exhibited higher dynamic modulus values.

The PU mixture is a complicated mixture that substitutes PU for asphalt binder, its characteristic and mechanical behavior is not fully studied. Based on the above-mentioned documents, many different variables could influence the dynamic modulus of the PU mixture, and those influence variables are still awaiting identification and analysis. This paper aimed at studying the dynamic response characteristics of different PU mixtures, and analyzed the internal PU mixture variables that affect the PU mixture's dynamic modulus and phase angle. The PU content, PU type, aggregate type, and gradation were the variables that were examined in this study. A statistical analysis of covariance was used to link the changes in the mixture variables to the dynamic characteristic of the PU mixture, and the most significant variables would be identified. The asphalt mixture performance tester was adopted to measure the frequency sweep dynamic mechanical properties of different PU mixtures at various test temperatures and loading frequencies.

2. Materials and Methods

2.1. Material and Gradation of PU Mixture

In this paper, four kinds of PU mixtures with dense gradation were adopted, donated as, PUM−10, PUM−13, PUM−16, and PUM−20. Limestone and basalt aggregates were chosen for the mixture design (Xingan Stone Co., Jinan, China). The particle passing percent of the selected gradation was displayed in Figure 1, the X axis in Figure 1 was in the 0.45 power scale, and the Y axis was in arithmetic scale.

In Figure 1, the letters L and B stand for the utilization of limestone aggregates and basalt aggregates, respectively.

Three different types of polyurethane, traditional cure speed PU, slow cure speed PU, and PU dyed with 6179H additive, were used for comparison. The traditional cure speed PU means that the PU would be solidified after about 2−4 h under different cure conditions, the slow cure speed PU means that the PU would be solidified after more than 4 h under the same cure conditions, compared with the traditional cure speed PU, and the PU dyed with 6179H additive is the traditional cure speed PU with color additive. The PU was provided by Wanhua Chemical Group Co., Ltd., (Yantai, China) and the PU is the wet-set type which means that the PU would be solidified under wet conditions.

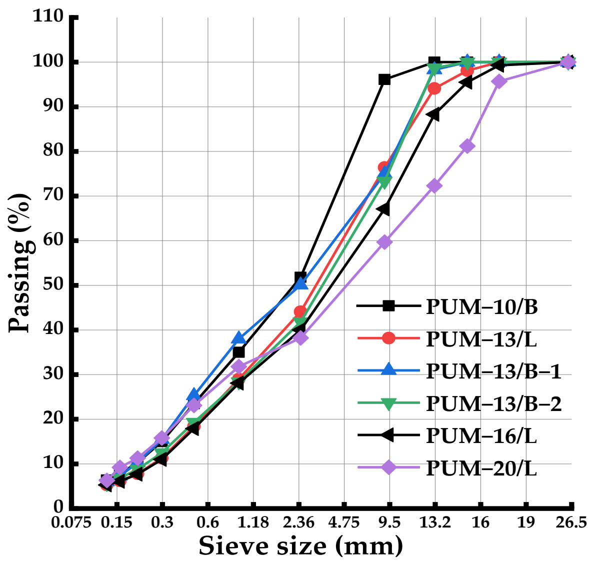


Figure 1. The gradation results of the selected dense gradation.

Mixture information is summarized in Table 1. The indexes of the PU with different cure speeds are shown in Table 2.

Table 1. The mixture gradation design combinations.

Number	Designation	Gradation Type	Aggregate Type	PU Content (%)	PU Type
1	PUM−10/B	PUM−10	Basalt	5.2	Traditional cure speed
2	PUM−13/B−2	PUM−13/2	Basalt	5.2	Traditional cure speed
3	PUM−13/L	PUM−13	Limestone	5.2	Traditional cure speed
4	PUM−16/L	PUM−16	Limestone	4.9	Traditional cure speed
5	PUM−20/L	PUM−20	Limestone	4.9	Traditional cure speed
6	PUM−13/B−1/5.0	PUM−13/1	Basalt	5	Traditional cure speed
7	PUM−13/B−1/5.6	PUM−13/1	Basalt	5.6	Traditional cure speed
8	PUM−13/B−1/5.3(T)	PUM−13/1	Basalt	5.3	Traditional cure speed
9	PUM−13/B−1/S	PUM−13/1	Basalt	5.3	Slow cure speed
10	PUM−13/B−2/H	PUM−13−2	Basalt	5.2	Stained with 6179H additive and Traditional cure speed

B−1 and B−2 represent different basalt aggregate gradations, S represents the slow cure speed PU, H represents the traditional cure speed PU binder stained with 6179H additive, and T represents the traditional cure speed PU.

Table 2. The index of PU with different cure speeds.

Index	Traditional Cure Speed	Slow Cure Speed
Viscosity (25 °C) (MPa·s)	1707	1691
Dry time (30 °C, 90% RH) (min)	70	83
Tensile strength (MPa)	24.5	29.4
Breaking elongation (%)	212	516

2.2. Fabricated Specimens

According to AASHTO: TP−62 (2009), the specimens were compacted using a Superpave gyratory compactor (SGC), and their dimensions were 170 mm in height and 150 mm in diameter. The core specimens used for the dynamic modulus test were cored and sawed into the dimensions of 150 mm in height and 100 mm in diameter, as specified by AASHTO: TP−79, after the specimens were constructed and cured (2010).

The fabricating course is shown as follows: (a) The aggregates and the filler should be desiccant, and the PU mixture should be mixed at room temperature. Therefore, before mixing, the aggregates and the filler had to be kept in a blown oven at 170 °C for about 4 h, then the aggregates and the filler were cooled to room temperature; (b) The PU mixture was mixed for 90 s after the aggregates, filler, and PU binder were added in the correct order to the mixing pot; (c) The PU mixture must be kept at room temperature (below 30 °C) for 1.5 h before compaction; (d) The specimens must be compacted by SGC and compacted 100 times; (e) The specimens must be extracted after compaction, and the specimens were cured for 5 days at 35 °C and 70% RH.

Two replicates of each mixture type were fabricated. The volume index results of the core specimens were listed in Table 3.

Table 3. The volume index results of the core specimens.

Designation	γ_b	γ_t	Air Void (%)
PUM−10/B	2.451	2.574	4.75
PUM−13/B−2	2.419	2.592	6.7
PUM−13/L	2.4	2.523	4.9
PUM−16/L	2.379	2.535	6.15
PUM−20/L	2.412	2.528	4.6
PUM−13/B−1/5.0	2.495	2.661	6.25
PUM−13/B−1/5.6	2.476	2.638	6.15
PUM−13/B−1/5.3(T)	2.499	2.65	5.7
PUM−13/B−1/S	2.406	2.65	9.2
PUM−13/B−2/H	2.449	2.592	5.5

2.3. Dynamic Modulus Test

The asphalt mixture performance tester (AMPT) was adopted for dynamic modulus testing according to the specification of AASHTO: TP−79 (2010). The loading waveform was sinusoidal, and the control mode was the load-controlled uniaxial compression mode. The amplitude of the loading wave was set to maintain the specimen's strain between 75 and 125 uε, which is deemed just to keep the specimen within its viscoelastic range and prevent specimen damage [22,23]. The test temperatures were 5 °C, 15 °C, 25 °C, 35 °C, 45 °C, and 55 °C, while the loading frequencies were set to 25, 20, 10, 5, 2, 1, 0.5, 0.2, and 0.1 Hz [24]. The results of the dynamic modulus and phase angle shown in this paper are the average values of two replicates for each mixture.

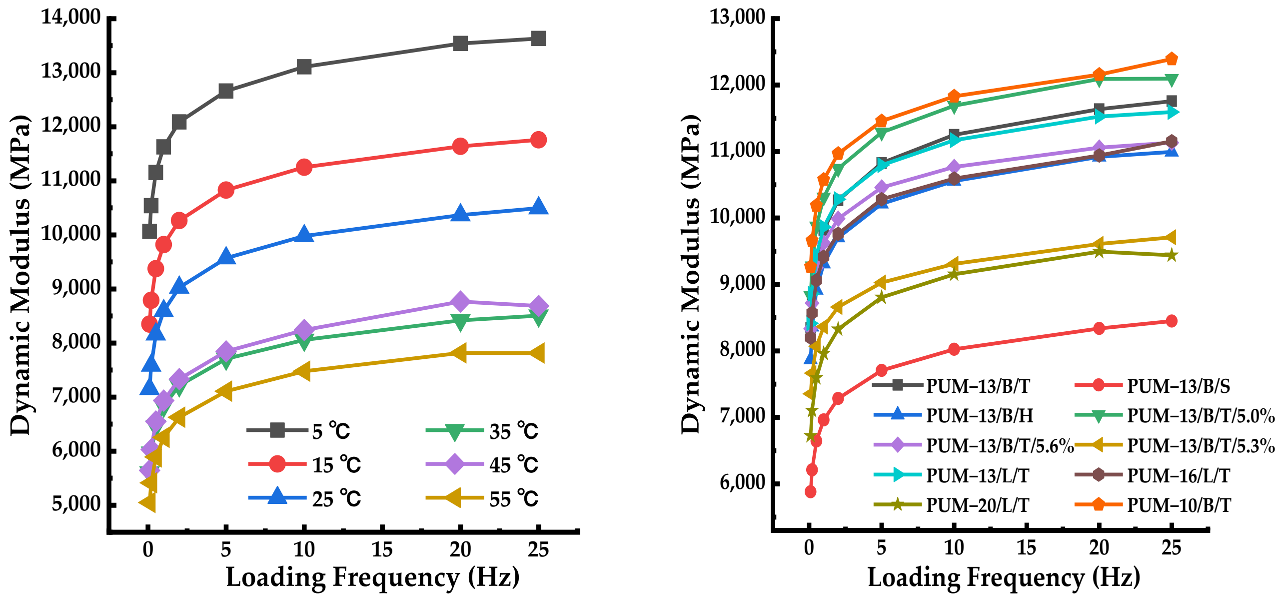
2.4. Statistic Analysis

The SPSS software was used for analyzing the factors utilized in this paper. Additionally, the analysis of covariance (ANCOVA) was used to evaluate the effects of gradation, PU type, PU binder, and aggregate type on the dynamic modulus and phase angle. In the statistical analysis [25,26], gradation, PU type, PU binder, and aggregate type were considered independent variables, whereas temperature and loading frequency were covariates. The dynamic modulus and phase angle were regarded as dependent variables or responses. The statistical analysis with a 5% level of significance (p-value) was used for the results analyzed. When the p-value of any independent variables is less than 5% [27], it means that the independent variable has a significant influence on the dependent variables.

3. Results

3.1. The Dynamic Modulus under Different Temperatures and Frequency

The dynamic modulus results of the PU mixture PUM−13 (fabricated with basalt aggregate and traditional curing speed PU binder) at different test temperatures and loading frequencies arere plotted in Figure 2a. The dynamic modulus of the different PU mixtures at 15 °C is shown in Figure 2b. The dynamic modulus results in this paper were plotted on the normal scale [28].

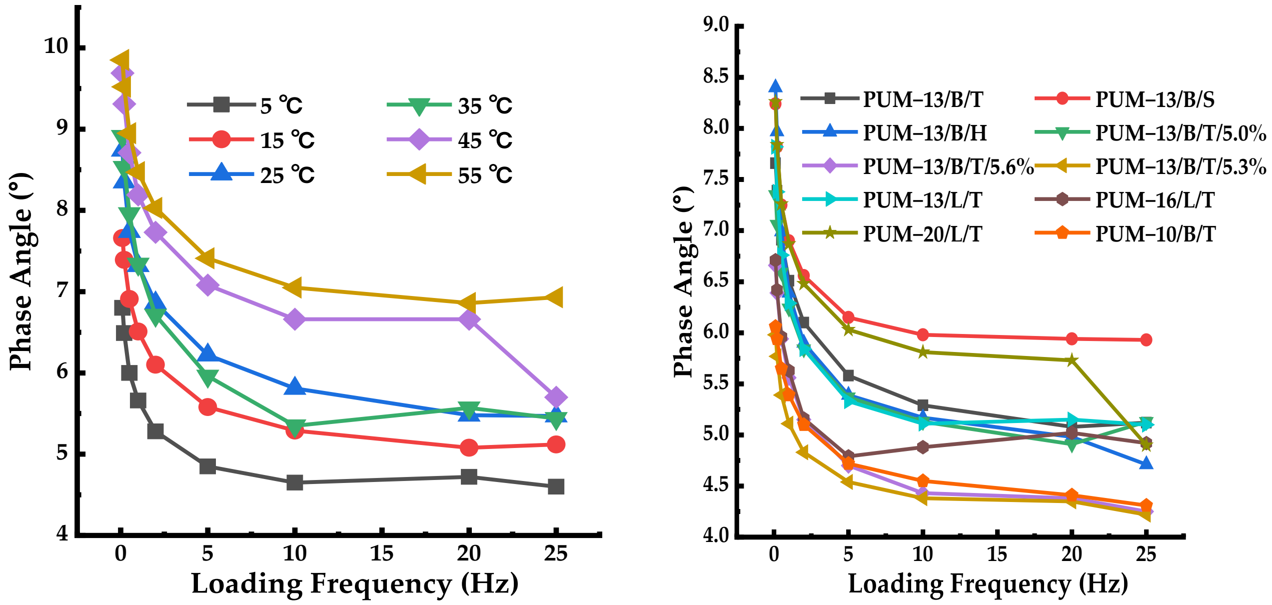


(**a**) (**b**)

Figure 2. Dynamic modulus of the PU mixtures. (**a**) PUM−13 at different test temperatures and loading frequencies. (**b**) Different PU mixtures at 15 °C.

3.2. The Phase Angle under Different Temperatures and Loading Frequency

The phase angle results of PU mixture PUM−13 (fabricated with basalt aggregate and traditional curing speed PU binder) at different test temperatures and loading frequencies are plotted in Figure 3a. The dynamic modulus of different PU mixtures at 15 °C is shown in Figure 3b.



(**a**) (**b**)

Figure 3. The phase angle of the PU mixtures. (**a**) PUM−13 at different test temperatures and loading frequencies. (**b**) Different PU mixtures at 15 °C.

3.3. The Effect of Gradation on the Dynamic Modulus and Phase Angle

The dynamic modulus and phase angle results of the PU mixtures with the same aggregate type and different gradations at different test temperatures and loading frequencies are plotted in Figures 4 and 5.

3.4. The Effect of Aggregate Type on the Dynamic Modulus and Phase Angle

The dynamic modulus and phase angle results of the PU mixtures with the same gradation and different aggregate types at different test temperatures and loading frequencies are plotted in Figures 6 and 7.

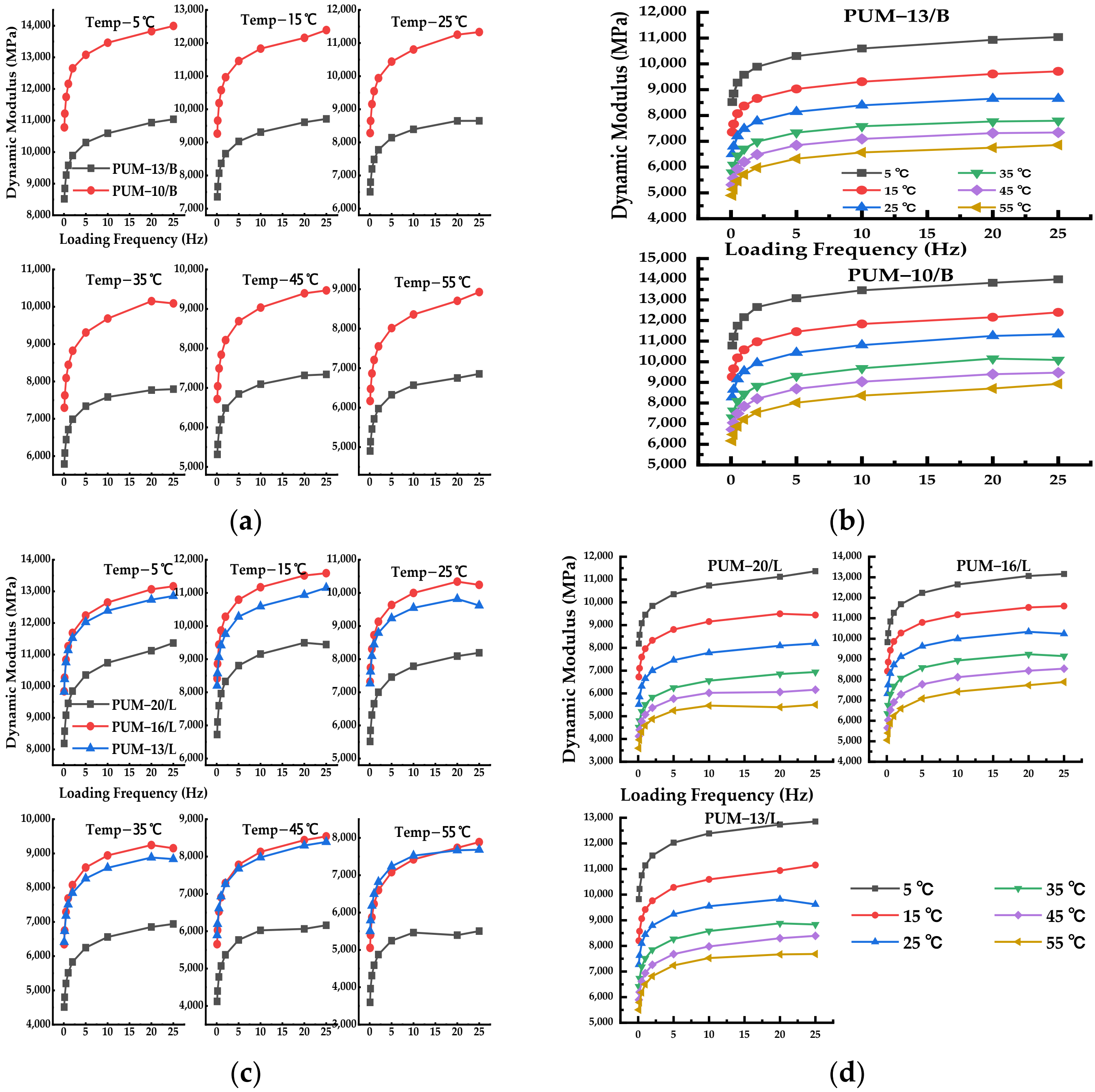


Figure 4. The dynamic modulus of the PU mixtures with the same aggregate type and different gradations. (**a**,**b**) Basalt aggregate, (**c**,**d**) Limestone aggregate.

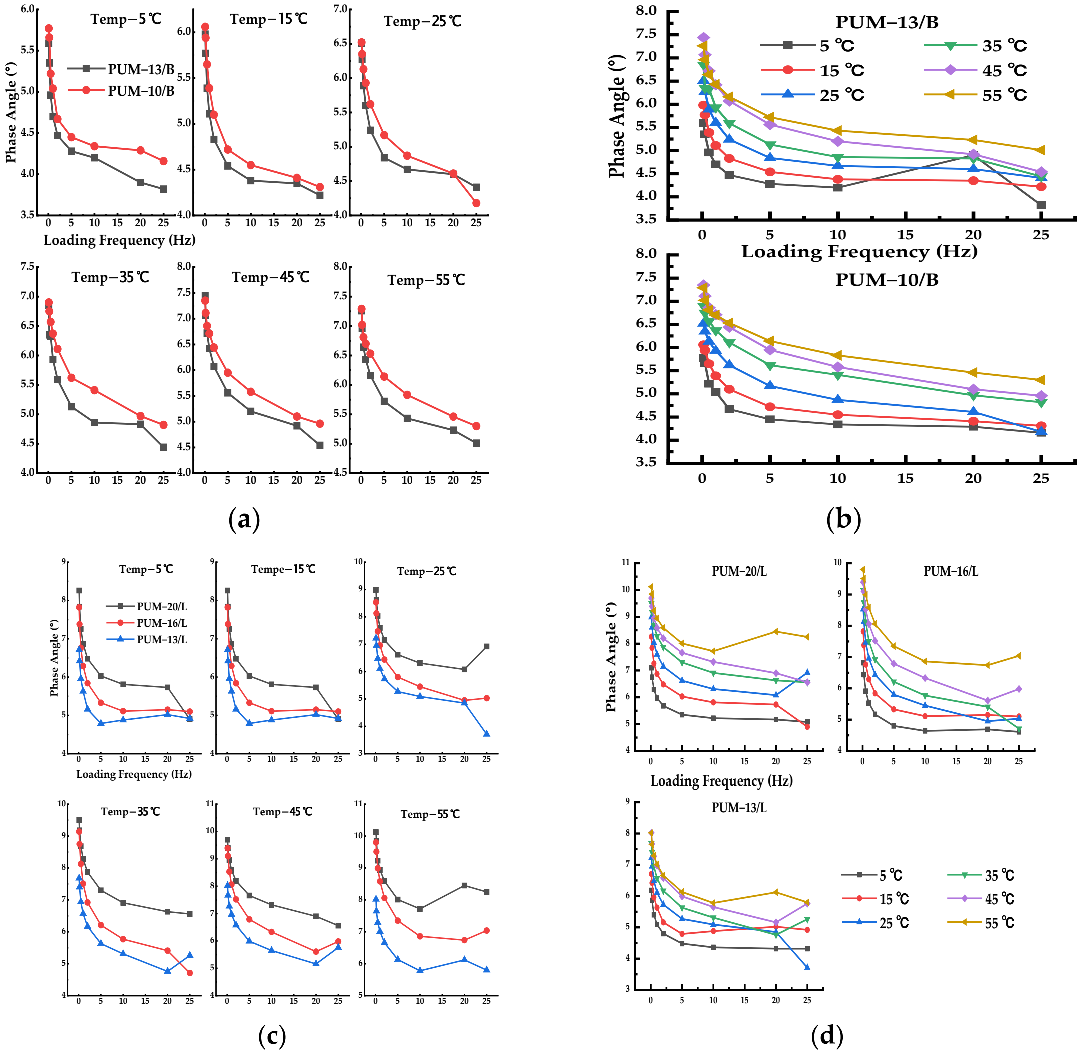


Figure 5. The phase angle of the PU mixtures with the same aggregate type and different gradations. (**a**,**b**) Basalt aggregate, (**c**,**d**) Limestone aggregate.

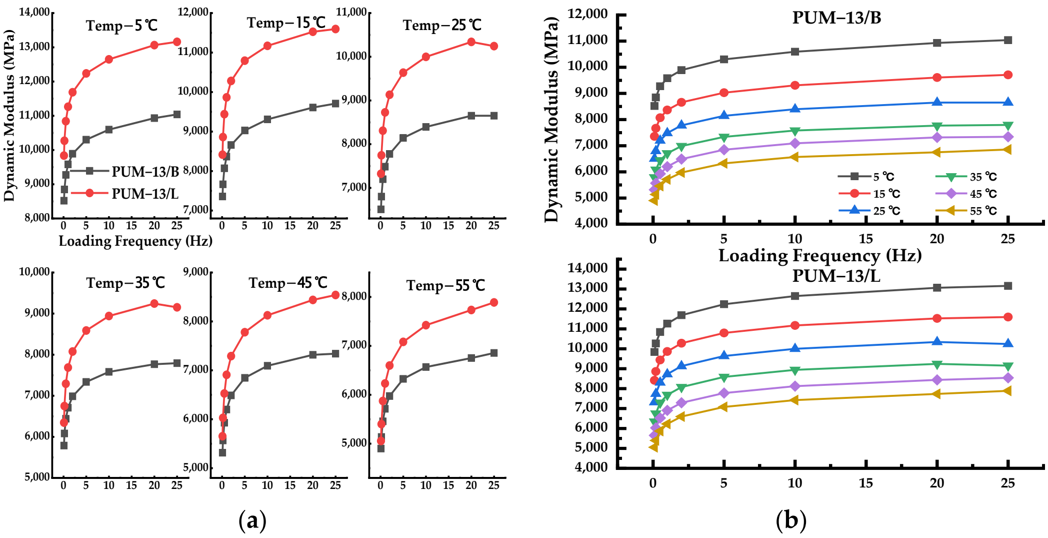


Figure 6. The dynamic modulus of the PU mixtures with the same gradation and different aggregate types. (**a**) dynamic modulus under different test temperatures, (**b**) dynamic modulus with different aggregate types.

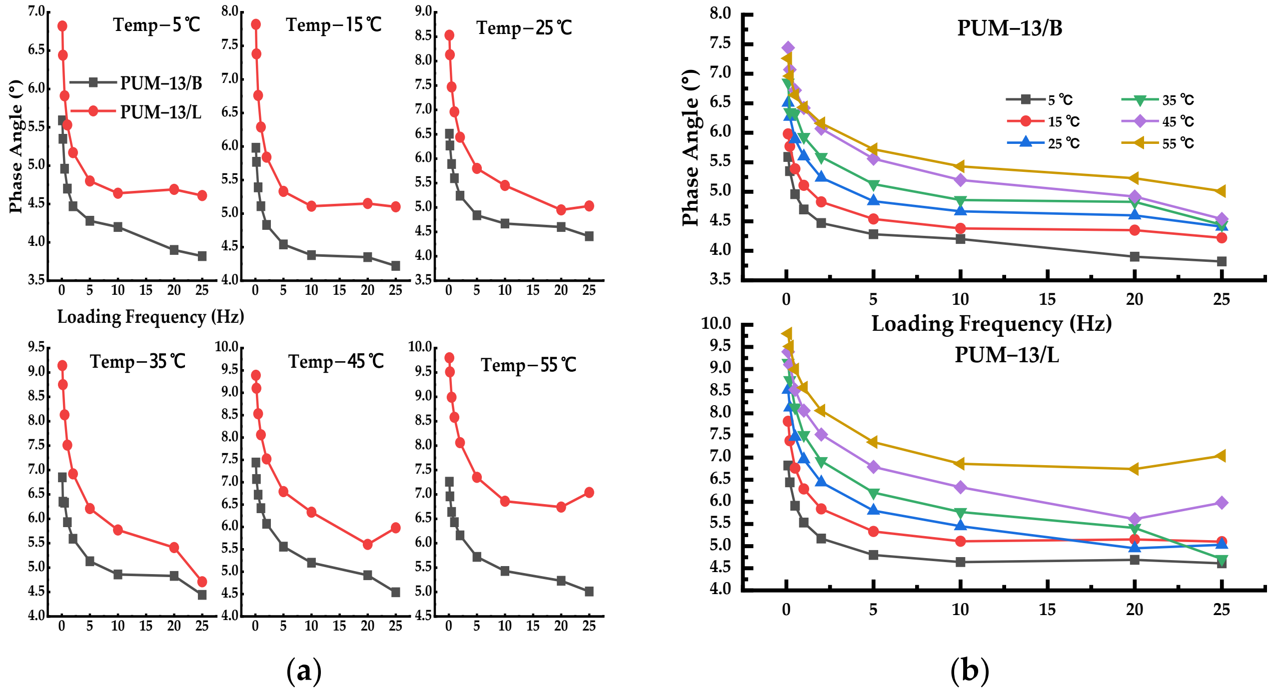


Figure 7. The phase angle of the PU mixtures with the same gradation and different aggregate types. (**a**) phase angle under different test temperatures, (**b**) phase angle with different aggregate types.

3.5. The Effect of the PU Type on the Dynamic Modulus and Phase Angle

The dynamic modulus and phase angle results of the PU mixture with the same gradation and different PU types at different test temperatures and loading frequencies are plotted in Figures 8 and 9.

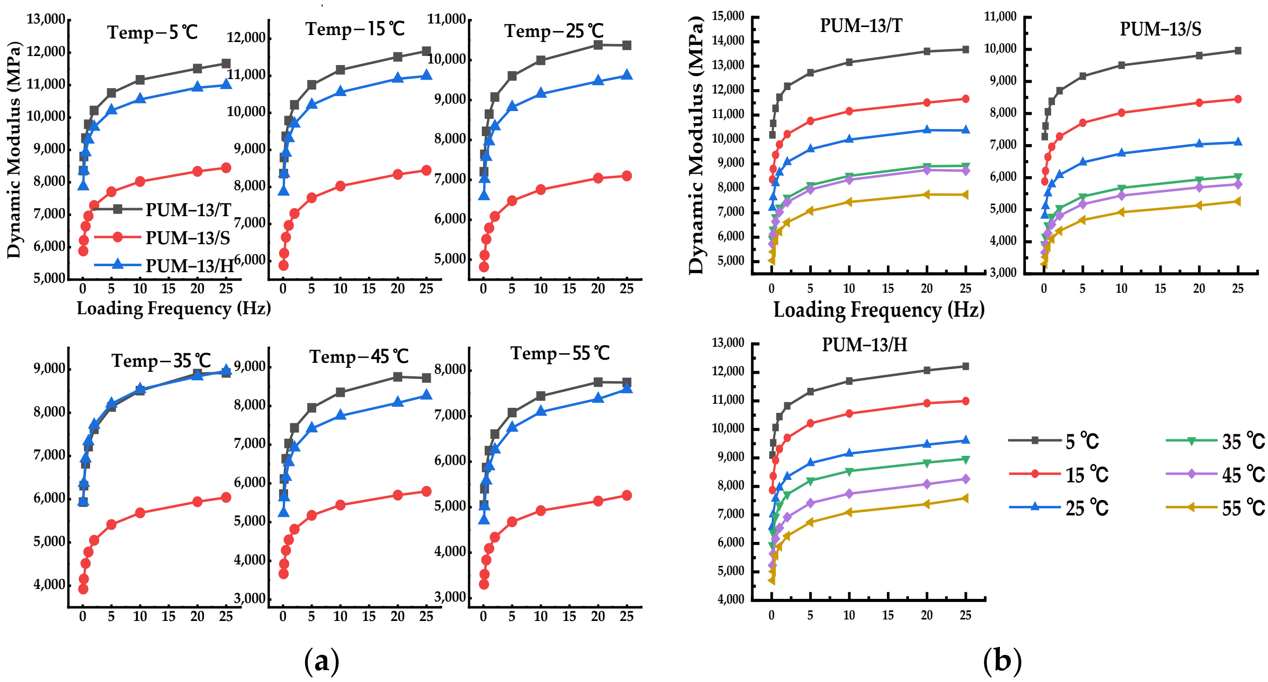


Figure 8. The dynamic modulus of the PU mixtures with the same gradation and different PU types. (**a**) dynamic modulus under different test temperatures, (**b**) dynamic modulus with different PU types.

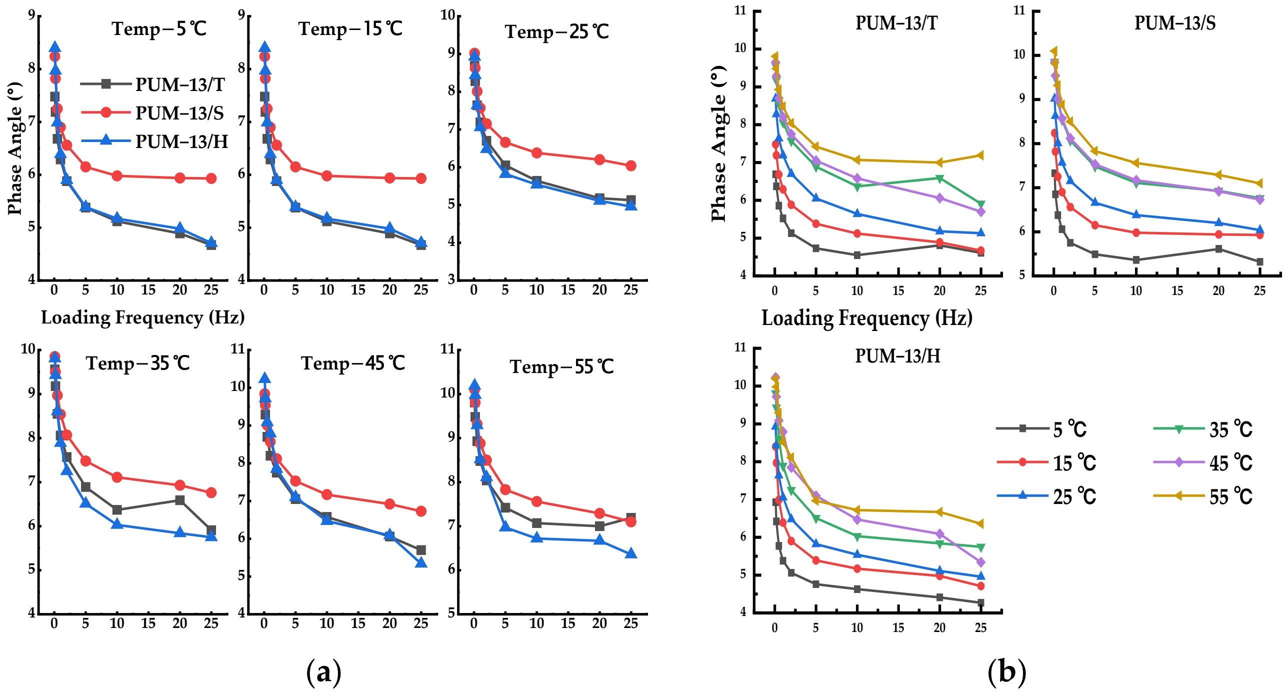


Figure 9. The phase angle of the PU mixtures with the same gradation and different PU types. (**a**) phase angle under different test temperatures, (**b**) phase angle with different PU types.

3.6. The Effect of the PU Content on the Dynamic Modulus and Phase Angle

The dynamic modulus and phase angle results of the PU mixtures with the same gradation and different PU contents at different test temperatures and loading frequencies ae plotted in Figures 10 and 11.

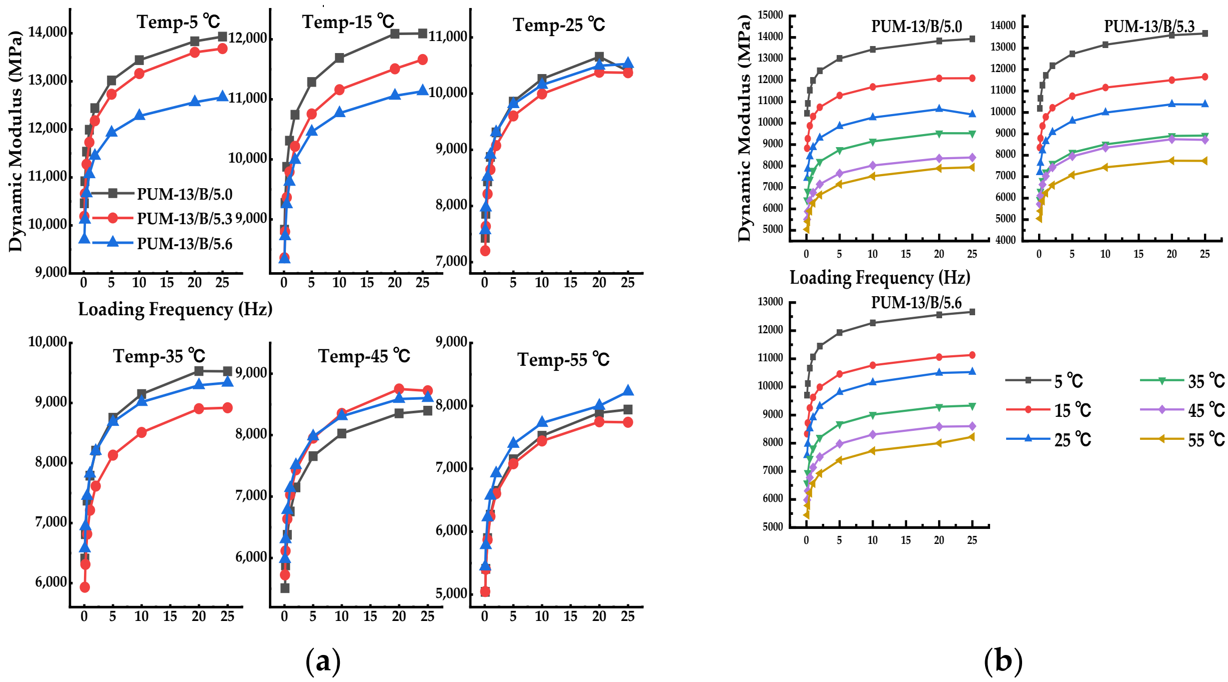
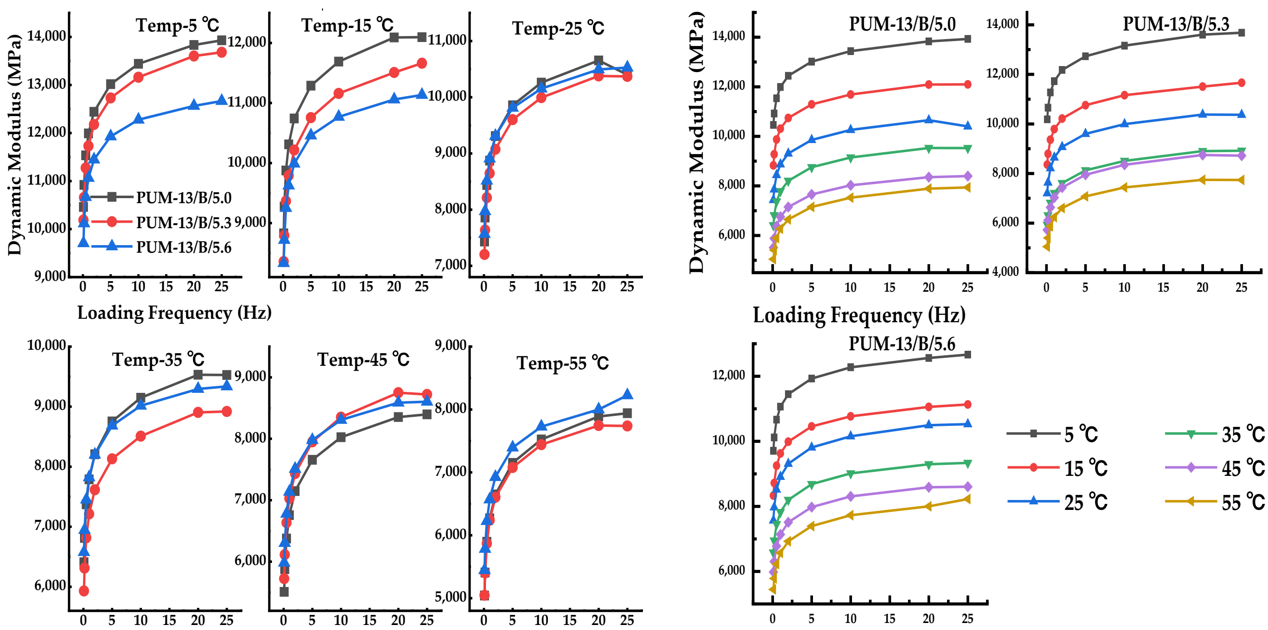


Figure 10. The dynamic modulus of the PU mixtures with the same gradation and different PU contents. (**a**) dynamic modulus under different test temperatures, (**b**) dynamic modulus with different PU contents.



(**a**) (**b**)

Figure 11. The phase angle of the PU mixtures with the same gradation and different PU contents. (**a**) phase angle under different test temperatures, (**b**) phase angle with different PU contents.

4. Discussion

4.1. The Dynamic Modulus under Different Temperatures and Loading Frequency

For all test temperatures, the dynamic modulus monotonously increased with the increasing loading frequency and dropped as the test temperature increased [29], indicating that the influence of the dynamic modulus provided by the PU binder weakened as the test temperature ascended. This phenomenon suggests that the PU mixture mainly exhibits elastic behavior at low temperatures but shows viscous behavior at high temperatures. This study noted that the curves of PU mixture PUM−13 tend to flatten out when the loading frequency was higher than 10 Hz. This phenomenon indicated that the PU mixture's dynamic modulus was sensitive to low loading frequency, and the parameter and PU binder both influenced the ultimate dynamic modulus of the PU mixture. This finding is consistent with the regularity of the dynamic modulus of asphalt mixtures, as shown in [3], that the dynamic modulus of the asphalt mixture increases with the increase of loading frequency and decreases with the increase of test temperature.

At low temperatures, the PU mixture exhibits elastic behavior and is mainly subjected to PU binder, so when the temperature rises (or frequency drops), the PU binder softens and exhibits viscous behavior, then leads to the increment of dynamic modulus. At high temperatures, the PU mixture mostly exhibits viscous behavior, and the PU binder's influence on the mixture is diminished while the interlocking force between aggregates in the mixture is more pronounced. Thus, the phenomenon whereby the aggregate skeleton primarily bears the loading stress becomes more apparent with additional increases in temperature (or decreases in frequency), which cause the decline of the dynamic modulus [3,30]. The dynamic modulus of PU mixture PUM−13 would drop by 40%~50% if the test temperature was increased from 5 °C to 55 °C, and would drop by 20~35% if the loading frequency was decreased from 25 Hz to 0.1 Hz. Ali et al. [5] showed that the dynamic modulus of eight kinds of asphalt mixtures would drop by about 40% when the test temperature increased from 21.1 °C to 37.8 °C, and would drop by 67~80% if the loading frequency decreased from 25 Hz to 0.1 Hz. Compared with the asphalt mixtures, the dynamic modulus of the PU mixture was less sensitive to temperature and loading frequency.

As theoretically expected, it can be observed from Figure 2b that the dynamic modulus of all PU mixtures was higher at lower temperatures or had a higher loading frequency, which is the typical behavior of PU mixtures due to their viscoelastic nature.

In terms of variability in the test results, the coefficient of variation (COV) ranged from 9 to 15%, the COV of dynamic modulus would increase with the rising of test temperature, and the COV of different PU mixtures at the same test temperature had no obvious significance. The COV of different PU mixtures would become higher at a relatively low frequency.

Research indicates that the dynamic modulus of the asphalt mixture has a strong correlation with its field rutting resistance [31]. In general, the asphalt mixture will be more resistant to rutting (permanent deformation), the higher the dynamic modulus value [3]. From this aspect, this characteristic demonstrates that the PU mixture with PUM−10 gradation and basalt aggregate had the strongest resistance to rutting (permanent deformation).

4.2. The Phase Angle under Different Temperatures and Loading Frequency

When linear viscoelastic material is subjected to dynamic loading, it presents a phenomenon that the strain response lags behind the loading stress. The degree of this lag, which manifests as a phase angle, was utilized to describe the linear viscoelastic material's viscoelastic properties. For a linear viscoelastic material, it is usual to expect that the phase lag will increase as the frequency drops [32]. At all test temperatures, it is apparent from Figure 3 that the phase lag grows as the loading frequency decreases. This trend in the phase angle of PU mixture PUM−13 proved that the PU mixture is a kind of linear viscoelastic material.

The linear viscoelastic material is more viscous the higher the phase angle value. Therefore, a lower value denotes a more elastic behavior for the linear viscoelastic material [33]. From Figure 3a, it is observed that the phase angle grew as the test temperature rose, indicating that the PU mixture would exhibit more viscous behavior at a higher temperature.

From Figure 3b, it can be inferred that PU mixture with different gradations, aggregate types, and binder contents exhibited a variety of viscoelastic behaviors, and this means that all of the aforementioned variables may have an impact on the viscoelastic behavior of the PU mixture.

According to Witczak's research, the dynamic modulus and the stiffness parameter ($E^*/\sin(\delta)$) of the asphalt mixture has a strong correlation with the rutting resistance of asphalt pavement, and the stiffness parameter of the asphalt mixture can more accurately reflect its rutting resistance at relatively high service temperatures [34]. In general, the asphalt mixture is more resistant to rutting (permanent deformation), the greater the stiffness parameter value [3]. It should be highlighted that the PU mixture with the basalt aggregate and PUM−10 gradation had the highest stiffness parameter ($E^*/\sin(\delta)$), or in other words, the highest resistance to rutting.

4.3. The Effect of Gradation on the Dynamic Modulus and Phase Angle

From Figure 4b,d, the dynamic modulus of each PU mixture with a different aggregate gradation dropped with an increase in test temperature and increased with an increase in loading frequency. At all test temperatures and loading frequencies for basalt aggregates, the dynamic modulus of PU mixture PUM−10 was greater than that of PU mixture PUM−13, and the difference between those two PU mixtures changed slightly as the test temperature and loading frequency changed. For limestone aggregates, the dynamic modulus of PU mixtures PUM−16 and PUM−13 were comparable, with PU mixture PUM−16 having a slightly higher dynamic modulus than PU mixture PUM−13. However, when the test temperature rose, the difference between the two dynamic moduli became negligible. They were both larger than PU mixture PUM−20 at all test temperatures and loading frequencies, and the difference grew larger as the test temperature increased.

According to the discussion above, the dynamic modulus of the PU mixture with basalt aggregates was not considerably impacted by the change in gradation. For the PU mixture with limestone aggregates, the trend reversed. The dynamic modulus of PU mixtures did not change with the change in the nominal maximum aggregate size of different gradations in a simple form. This phenomenon indicated that each PU mixture should be tested before application, and the structure combination should be selected carefully and based on the demand of the project. For instance, the structure combination of PUM−13 gradation (basalt aggregate) for the upper layer and PUM−16 gradation (limestone aggregate) for the lower layer had a higher dynamic modulus than other combinations.

From Figure 5a, it can be inferred that the phase angle of PU mixtures PUM−13 and PUM−10 were comparable, and the variation was negligible at low loading frequencies (<5 Hz) and grew slightly as loading frequencies increased. As the loading frequency increased, the phase angle of the PU mixture reduced. Figure 5b presented that the phase angle was close under low temperatures (<35 °C), and the variation grew as the test temperature rose. The phase angle of the PU mixture with limestone aggregate ranked as follows, PUM−20 > PUM−16 > PUM−13, and the difference became bigger with the increase of test temperature, as shown in Figure 5c. According to Figure 5d, as the test temperature rose, the phase angle of PU mixtures with limestone aggregates increased.

The gradation had a negligible impact on the phase angle of PU mixtures with basalt aggregates, especially at low loading frequency (<5 Hz) and test temperature (<35 °C). With a decrease in loading frequency and a rise in test temperature, the phase angle rose for PU mixtures with limestone aggregates. So, the gradation could influence the viscoelasticity of the PU mixture with limestone aggregate, and for the PU mixture with basalt aggregate, but the influence was less evident for the PU mixture with basalt aggregate.

The dynamic modulus and phase angle results were analyzed statistically using the analysis of covariance (ANCOVA). When the test temperature and loading frequency were controlled, the statistical analysis aimed to determine if gradation appeared to have an impact on the dynamic modulus and phase angle of the PU mixtures.

The response examined was the dynamic modulus and phase angle of the PU mixtures. Independent variables included the three PU mixtures with limestone aggregates as fixed factors (PUM−20/L, PUM−16/L, PUM−13/L gradation) and the two PU mixtures with basalt aggregates as fixed factors (PUM−13/B, PUM−10/B gradation), respectively, and two testing variables as covariates (temperature and loading frequency). The ANCOVA results are summarized in Table 4 and detailed below. The determination of the conditions under which samples are statistically different, was conducted using a 95% significance level. The variables have statistically significant effects on the dynamic modulus and phase angle if the computed *p*-value (i.e., significance level) is less than 0.05, otherwise, it can be considered that the compared groups are statistically equivalent [35].

Table 4. Statistically significant effect of the aggregate gradation in the dynamic modulus and phase angle.

Aggregate Type	Variables	Effect on Dynamic Modulus	Effect on Phase Angle
Limestone	Aggregate gradation	Yes (p = 0.000)	Yes (p = 0.000)
	Temperature	Yes (p = 0.000)	Yes (p = 0.000)
	Loading frequency	Yes (p = 0.000)	Yes (p = 0.000)
	Overall	Yes (p = 0.000)	Yes (p = 0.000)
Basalt	Aggregate gradation	Yes (p = 0.000)	Yes (p = 0.002)
	Temperature	Yes (p = 0.000)	Yes (p = 0.000)
	Loading frequency	Yes (p = 0.000)	Yes (p = 0.000)
	Overall	Yes (p = 0.000)	Yes (p = 0.000)

The dynamic modulus and phase angle of the PU mixtures with various aggregate gradations were significantly influenced by temperature and loading frequency as variables because the *p*-values were less than 0.05 (p = 0.000), according to the significance values. Therefore, the dynamic modulus and phase angle of the PU mixtures with different aggregate gradations were significantly predicted by the temperature and loading frequency.

When the effects of temperature and loading frequency were taken into account, the effect of aggregate gradation on the dynamic modulus and phase angle of the PU mixtures was significant, with p = 0.000 and 0.002, respectively. The model as a whole was still significant, therefore it is possible to conclude that these variables (aggregate gradation, temperature, and loading frequency) significantly influence the dynamic modulus and phase angle of the PU mixtures, as the *p*-value for the corrected model was less than 0.05 (p = 0.000).

Compared with the test results in [5], the NMAS had an insignificant influence on the dynamic modulus and phase angle of eight kinds of asphalt mixtures, including wearing and base course mixes.

4.4. The Effect of Aggregate Type on the Dynamic Modulus and Phase Angle

From Figure 6, it is vital to obtain that the dynamic modulus of the PU mixtures with basalt and limestone aggregates both increased with the rising of loading frequency and decreased with the rising of test temperature. The dynamic modulus of the PU mixture with limestone aggregate was larger than that of the PU mixture with basalt aggregate, and the difference weakened with rising test temperature.

It can be learned from Figure 7 that the phase angle of the PU mixture with limestone aggregate reduces with the rising loading frequency and increases with the increasing test temperature. This trend contrasted with that of the PU mixture with basalt aggregate, which was shown in Figure 5b. The phase angle of the PU mixture with limestone aggregate was larger than that of the PU mixture with basalt aggregate, this trend means that the PU mixture with limestone aggregates displayed more viscous properties than the PU mixture with basalt aggregates, which indicated that the interlock of limestone aggregates was weaker than that of basalt aggregates.

The limestone aggregate could enhance the dynamic modulus of the PU mixture compared with the basalt aggregate, which did not comply with the anticipation. So, the application of limestone in a PU mixture became more economical with higher resistance to deformation. However, further criteria, such as sliding resistance, must be taken into consideration when selecting the aggregate type for the upper layers.

In this section, the dynamic modulus of a PU mixture with PUM−13 gradation and limestone was plotted against that of a PU mixture with PUM−13 gradation and basalt in Figure 12. The plot displayed a nearly linear distribution of data along the line of equality (LOE). The closer the data point is to the LOE, the effect of aggregate type on the dynamic modulus of the PU mixture is less significant. So, the aggregate type could significantly affect the dynamic modulus of the PU mixture.

How closely a fitting model's unconstrained linear trend line matches the line of equality is an indicator of its overall bias. In other words, it shows how the unconstrained intercept and slope are close to 0 and 1, respectively. The closer the intercept is to 0 and the slope is to 1, the lower the bias will be [36].

The equation (y = a*x + b) was used to fit the trend line of the data. The final equation was $y = 1.3211*x - 1248.42069$ and the R^2 was 0.99733. From the final equation, it can also be concluded that the aggregate type may have an impact on the dynamic modulus of the PU mixture.

The two PU mixtures with limestone and basalt acted as independent factors, while two testing variables acted as covariates (temperature and loading frequency). The ANCOVA results are presented in Table 5.

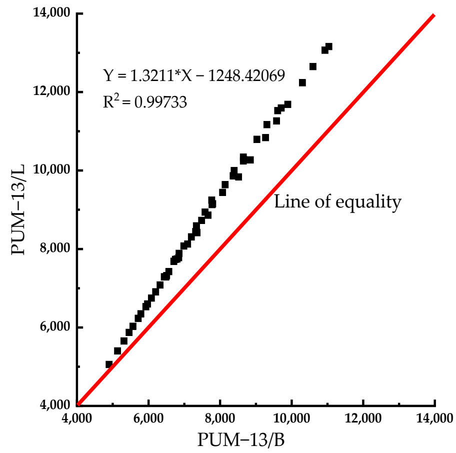


Figure 12. The line of equality about the dynamic modulus of the PU mixture with the same gradation and different aggregate types.

Table 5. Statistically significant effect of aggregate type in the dynamic modulus and phase angle.

Variables	Effect on Dynamic Modulus	Effect on Phase Angle
Aggregate type	Yes (p = 0.000)	Yes (p = 0.000)
Temperature	Yes (p = 0.000)	Yes (p = 0.000)
Loading frequency	Yes (p = 0.000)	Yes (p = 0.000)
Overall	Yes (p = 0.000)	Yes (p = 0.000)

Looking at the significance values, the temperature and loading frequency as covariates significantly affected the dynamic modulus and phase angle of the PU mixtures with different aggregate types, because the p-values were less than 0.05 (p = 0.000).

Even when the effects of temperature and loading frequency were excluded, the effect of aggregate types on the dynamic modulus and phase angle of the PU mixtures was significant, with p = 0.000. Because the model as a whole was still significant and the p-value for the corrected model was less than 0.05 (p = 0.000), it is possible to conclude that these variables (aggregate type, temperature, and loading frequency) significantly affect the dynamic modulus and phase angle of the PU mixtures.

4.5. The Effect of the PU Type on the Dynamic Modulus and Phase Angle

From Figure 8, it can be observed from the plots that each of the PU mixtures with different PU types followed the same trend mentioned above, which is that the dynamic modulus would rise with an increase in loading frequency and fall with an increase in test temperature. The dynamic modulus of the PU mixtures ranked as PUM−13/T > PUM−13/H > PUM−13/S. Therefore, the PU type influenced the PU mixture's dynamic modulus.

The difference in PU type will influence the viscoelasticity of the PU mixture in the same PU mixture with fixed gradation and aggregate type, which mostly reflects the change of dynamic modulus and phase angle. In comparison to the PU mixture with the slow cure speed PU binder, the PU mixture with the traditional cure speed PU binder had a greater dynamic modulus. This also proved that different PU binders brought different viscoelastic properties to the same mixture. The findings mentioned above demonstrate that the PU binder was the source of the PU mixture's viscoelastic property. The dynamic modulus of the PU mixture might change depending on the type of PU employed, the phase angle of the PU mixture only relied on the viscoelastic property of the PU binder.

It can be inferred from Figure 9 that the phase angle of PU mixtures with different PU types followed the same trend mentioned above. According to Figure 9, the phase angles of PUM−13/T and PUM−13/H were comparable, with the difference becoming somewhat bigger as the temperature rose. They were both smaller than that of the PU mixture PUM−13/S. Thus, the viscoelasticity of the PU mixture was not affected by the 6179H additive, but it was affected by the PU's cure speed.

The three PU mixtures (PUM−13/T, PUM−13/S, and PUM−13/H) with different PU types as fixed factors acted as independent variables, while two testing variables (temperature and loading frequency) served as covariates. The ANCOVA results are presented in Table 6 and are detailed below.

Table 6. Statistically significant effect of the PU type on the dynamic modulus and phase angle.

Variables	Effect on Dynamic Modulus	Effect on Phase Angle
PU type	Yes (p = 0.000)	Yes (p = 0.000)
Temperature	Yes (p = 0.000)	Yes (p = 0.000)
Loading frequency	Yes (p = 0.000)	Yes (p = 0.000)
Overall	Yes (p = 0.000)	Yes (p = 0.000)

The dynamic modulus and phase angle of the PU mixtures with different PU types were significantly influenced by temperature and loading frequency as covariates because the p-values were less than 0.05 (p = 0.000), according to the significance values. Therefore, the temperature and loading frequency were significant predictors of the dynamic modulus and phase angle of the PU mixtures with different PU types.

The influence of the PU types on the dynamic modulus and phase angle of the PU mixtures was significant, with p = 0.000, when the influences of temperature and loading frequency were excluded from the calculation. Since the model, as a whole, was significant and the p-value for the corrected model was less than 0.05 (p = 0.000), it can be inferred that these variables (PU type, temperature, and loading frequency) significantly influence the dynamic modulus and phase angle of the PU mixtures.

4.6. The Effect of the PU Content on the Dynamic Modulus and Phase Angle

As can be seen from Figure 10, the dynamic modulus of the PU mixture with 5.6% PU binder had the lowest value at low temperatures, the difference became insignificant as the temperature rose. At high temperatures, the dynamic modulus of the PU mixture with different PU binder contents had similar values. This could be explained by the fact that the rising PU binder content did nothing to help the PU mixture's dynamic modulus increase. The dynamic modulus should be taken into consideration when determining the optimum PU binder content. The dynamic modulus of the PU mixture with different PU binder content followed the trend of the dynamic modulus decreasing with rising temperature and increasing with growing loading frequency.

Depending on Figure 11, it can be seen that the phase angle of the PU mixture with different PU binder contents increased as the test temperature rose, and dropped as the loading frequency grew. The phase angle of the PU mixtures with 5.0% and 5.3% PU binder were close and both higher than that of the PU mixture with 5.6% PU binder, this could be attributed to the increasing PU content's potential to aggravate strain response lag.

The three PU mixtures (5.6%, 5.3%, and 5.0%) with different PU content served as fixed factors for the independent variables, and two testing variables (temperature and loading frequency) served as covariates. The ANCOVA results are described below and summarized in Table 7.

Table 7. Statistically significant effect of the PU content in the dynamic modulus and phase angle.

Variables	Effect on Dynamic Modulus	Effect on Phase Angle
PU content	No (p = 0.177)	Yes (p = 0.000)
Temperature	Yes (p = 0.000)	Yes (p = 0.000)
Loading frequency	Yes (p = 0.000)	Yes (p = 0.000)
Overall	Yes (p = 0.000)	Yes (p = 0.000)

According to the significance values, the temperature and loading frequency as covariates significantly affected the dynamic modulus and phase angle of the PU mixtures with different PU contents, because the *p*-values were less than 0.05 (p = 0.000). Therefore, the temperature and loading frequency strongly predicted the dynamic modulus and the phase angle of the PU mixtures with different PU contents.

The effect of PU contents on the dynamic modulus was non-significant with p = 0.177 even after the effects of temperature and loading frequency were excluded, but the effect on the phase angle was significant with a *p*-value of 0.000. The model as a whole was significant and the *p*-value for the corrected model was less than 0.05 (p = 0.000), it can be concluded that these variables (PU content, temperature, and loading frequency) significantly influence the dynamic modulus and phase angle of the PU mixtures.

5. Conclusions

In this study, the PU mixtures with different gradations, aggregate type, PU type, and PU content were subjected to a dynamic modulus test. The effect of gradation, aggregate type, PU type, and PU content on the dynamic modulus and phase angle of the PU mixtures were compared and discussed, and the statistical method of analysis of covariance (ANCOVA) was introduced into the analysis of the effect of the different variables. Based on the aforementioned discussion, we could draw the following conclusion:

(1) For PU mixtures, the dynamic modulus followed the trend that it would generally be increased with the increasing loading frequency and decreased with the increasing test temperature; however, the tendency was reversed for the phase angle. This regularity was consistent with that of asphalt mixtures;

(2) The PU mixture is a kind of linear viscoelastic material which would exhibit elastic properties at low temperatures and exhibit viscous properties at high temperatures;

(3) The PU mixture with PUM−10 gradation and basalt exhibited the greatest deformation resistance;

(4) The dynamic modulus of the PU mixture would drop by 40%~50% if the test temperature was increased from 5 °C to 55 °C, and drop by 67%~80% if the loading frequency decreased from 25 Hz to 0.1 Hz. Compared with the asphalt mixtures, the dynamic modulus of the PU mixture was less sensitive to temperature and loading frequency;

(5) The dynamic modulus and phase angle of the PU mixture were considerably influenced by the gradation, and the influence trend did not follow the increase of nominal maximum aggregate size. The structure combination should be selected carefully and based on the demand of the project;

(6) The aggregate type affected the dynamic modulus and phase angle of the PU mixture, and the dynamic modulus of the PU mixture with limestone was larger than that of the PU mixture with basalt. The selection of aggregate type for the PU mixture, particularly the upper layer, must be based on more factors, such as skidding resistance;

(7) The cure speed of the PU binder could also impact the dynamic modulus and phase angle of the PU mixture, and further considerations, such as the construction window period and ultimate stiffness, should be taken into account when choosing the PU type;

(8) The viscoelastic characteristic of the PU mixture may be greatly impacted by the PU content. The dynamic modulus test should be taken into account when determining the optimum PU binder content since the dynamic modulus and phase angle of the PU mixture did not change linearly with the growing PU content and the rising PU content did not help in the rise of stiffness of the PU mixture.

In this paper, the effect of gradation, aggregate type, PU type, and PU content was compared and analyzed, but only the AC gradation and two kinds of aggregate types were involved in this paper. It is still necessary to study more gradation types and aggregate types. The impact of the variables on the changing trend of the dynamic modulus and phase angle was discussed, and the effect on the master curve should be researched in further study.

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