buildings

MDPI

Article

The Development of a New Thermoplastic Elastomer (TPE)-Modified Asphalt

Rui Dong [1], Aodong Gao [2,3], Ying Zhu [1], Bin Xu [2,3,*], Jierong Du [1] and Shujiang Ping [2,3]

[1] Shandong Hi-Speed Infrastructure Construction Co., Ltd., Jinan 250000, China
[2] Key Laboratory of Transport Industry of Road Structure and Material, Beijing 100088, China
[3] Research Institute of Highway Ministry of Transport, Beijing 100088, China
* Correspondence: zlgk_xu@126.com

Abstract: The use of (recycled) plastics and (waste) vulcanized rubber powder is the main polymer of raw materials, and composite organic additives are selected to fully combine with asphalt components. The physical and chemical reactions between different components are completed in dynamic mixing, establishing a morphology structure similar to thermoplastic elastomers (TPEs), and a thermoplastic highly asphaltized alloy material. TPE-modified asphalt not only significantly improves the high-temperature stability of the base asphalt, but also has the social and economic value of rational utilization of resources and turning waste into treasure. There are very few studies on the preparation of modified high-viscosity asphalt formulations using rubber and plastic as modifiers. In this study, rubber, plastic, and plasticizers were added to the base asphalt, and the TPE modifier formulations were developed through the research of new TPE modifier series and functional formulations, preparation process, and its modified asphalt properties. Meanwhile, the preparation method of the rubber–plastic alloy modifier was determined. The performance of the TPE-modified asphalt was verified through performance verification tests to evaluate the modification effect of the modifier on the base asphalt. The test results showed that the penetration, softening point, ductility, and viscosity indexes of the TPE-modified asphalt developed through the proposed formulation, and it met the specification requirements for high-viscosity modified asphalt. Rubber and plastic modifiers significantly improved the high-temperature stability of the base asphalt. In addition, the rubber–plastic modifier had a significant tackifying effect, with a dynamic viscosity of 60 °C and a Brinell rotational viscosity much greater than asphalt and rubber asphalt. The microscopic mechanism of the newly developed TPE-modified asphalt was analyzed by fluorescence microanalysis. The results showed that the rubber–plastic modifier fully swelled in the asphalt and was uniformly dispersed in the asphalt as a floc. The network structure of activated waste rubber powder-modified asphalt was more uniform and dense, resulting in good performance of the modified asphalt, and stable storage of modified asphalt was obtained. Through appropriate formulation, the comprehensive performance of the TPE-modified asphalt obtained met the requirements of pavement application and construction, providing a good theoretical basis for promoting TPE-modified asphalt.

Keywords: thermoplastic elastomer; scarp rubber/plastic compound-modified asphalt; performance; micro-mechanism

Citation: Dong, R.; Gao, A.; Zhu, Y.; Xu, B.; Du, J.; Ping, S. The Development of a New Thermoplastic Elastomer (TPE)-Modified Asphalt. *Buildings* **2023**, *13*, 1451. https://doi.org/10.3390/buildings13061451

Academic Editors: Huayang Yu and Tao Wang

Received: 27 March 2023
Revised: 5 May 2023
Accepted: 25 May 2023
Published: 2 June 2023

1. Introduction

Currently, various waste rubber products and waste plastic products (commonly known as waste rubber and plastic materials) and other materials are increasing in quantity. The amount of waste rubber and tires produced each year is conservatively estimated to be over 15 million tons. With a production of plastic goods that exceeds 21 million tons yearly and is growing at a rate of around 10% annually. China is another important plastics-producing nation in the world. A large amount of waste gradually intensifies "black pollution" and "white pollution", which inevitably result in more catastrophic social and environmental issues [1].

Currently, the recycling of waste plastics and rubber is an effective way to protect the environment, and is also the sole method for sustainable development. Among them, using waste rubber powder to produce modified asphalt plays an important role in resource conservation and environmental protection [2]. Through a large number of experimental studies and engineering practices, it has been shown that mixing the rubber powder obtained by grinding the rubber tire into petroleum asphalt can improve the high and low-temperature performance, viscoelastic performance, and anti-aging performance of asphalt [3]. A large number of studies on rubber asphalt mixtures have shown that rubber asphalt mixtures have a longer service life compared with ordinary asphalt mixtures, and it can reduce driving noise, slow reflective cracks, improve the adhesion of binder materials with aggregates, improve pavement skid resistance and wear resistance, as well as improve driving comfort, absorb light, and reduce the stimulation of strong light on eyeglasses, among others benefits [4]. On the other hand, with the development of the plastic industry, plastic-modified asphalt already occupies a place in the road material market. Plastics can greatly improve the high-temperature performance of asphalt, while plastic-modified asphalt plays a significant role in improving the high-temperature performance of the mixture. However, plastics do not help improve the low-temperature performance of asphalt, instead plastics reduce the low-temperature performance of asphalt [5].

According to relevant studies, TPE modifiers significantly increase the resilience of asphalt at high temperatures. Styrene-butadiene-styrene (SBS), which is very widely used, is one of the so-called "TPE" materials, or thermoplastic elastomers [6]. Waste rubber and plastic can now be used to change asphalt thanks to advancements in polymer chemistry technology, which have led to steady advances in this field [7]. Especially in the field of additive reinforcement, stability, and uniform dispersion, the development of materials that have not been successfully explored in the past, has now provided better application conditions. In this context, it is necessary to expand the material selection, in recent years, SBS-modified asphalt has been the absolute main variety in the construction of high-grade highways in China [8]. Through the comparison of cost performance of different materials under the new technical status quo and the study of applicable conditions, it is necessary to diversify the application types of modified asphalt and refine their respective application directions [8].

With the development and use of new polymers, the use of rubber asphalt has gradually declined, leading to an increase in its usage for preparation of asphalt, with PE-modified asphalt emerging as a "new player" in the field of modified asphalt technology [9]. The United States has conducted extensive research on linear low-density polyethylene (LLDPE)-modified asphalt. This research has added LLDPE to asphalt to obtain modified asphalt with high tensile strength, cold resistance, and creep resistance. Austria's polyethylene-modified asphalt has obtained a patent, named Novophalt, and is widely used in asphalt pavements around the world [10]. Japan uses waste polyethylene scraps to prepare modified asphalt, greatly improving the flexibility and durability of asphalt at low temperatures, making the road surface free from obvious cracks, fractures, and pits in winter due to severe cold, and easier to lay [11]. At present, one of the most significant problems with PE-modified asphalt is that PE cannot naturally maintain a persistent and uniform dispersion of particles in the asphalt, meaning that it lacks storage stability.

In recent years, researchers have begun to study rubber–plastic composite-modified asphalt. By adding rubber and plastic composite modifier (TPE) to the base asphalt to study the modified asphalt, it was found that the high-temperature stability of modified asphalt is very prominent. Through economic analysis, to illustrate the low cost and economic benefits of rubber–plastic alloy, Fathy et al. conducted further research on rubber–plastic alloy (TPE) and compared and analyzed TPE-modified asphalt with SBS-modified asphalt. It was found that some formulations of TPE-modified asphalt had better high-temperature performance than SBS-modified asphalt, but the addition of TPE would reduce the low-temperature performance of asphalt [12]. Magioli et al. successfully prepared thermoplastic elastomer blends composed of 30% polypropylene and 70% ground rubber tires through dynamic vulcanization process, whether pure or combined with original styrene butadiene copolymer, including different proportions of dicarboxylic peroxide and isophthalimide imide (BMI). This blend exhibited excellent ultimate tensile strength and elongation at break, comparable to other thermoplastic vulcanization systems, and also exhibited good reprocessing properties, which were useful for several potential applications [13]. Nizamuddin et al. studied how the use of innovative compatibilizers can help stabilize recycled rubber–plastic asphalt mixtures during high-temperature storage. At the same time, the storage stability, rheological properties, thermal properties, and physical properties of rubber and recycled low-density polyethylene composite-modified asphalt were studied in the presence and absence of compatibilizers [14].

While studying waste rubber–plastic alloy-modified asphalt, many scholars successfully borrowed the concept of "alloy" and proposed the proposition of preparing rubber–plastic alloy modifiers and rubber–plastic alloy-modified asphalt [15]. Wang et al. studied the technical performance of PE/waste rubber powder-modified asphalt and demonstrated that it is reasonable to analyze and evaluate the technical performance of composite-modified asphalt through the Strategic Highway Research Program (SHRP) binder specification [4]. Mulage prepared modified asphalt using rubber powder and waste plastics (polypropylene and polyethylene), and studied the reaction mechanism of composite modified asphalt [16]. Maw et al. compared and analyzed TPE-modified asphalt with SBS-modified asphalt, and found that some formulations of TPE-modified asphalt had better high-temperature performance than SBS-modified asphalt, but the addition of TPE would reduce the low-temperature performance of asphalt [17]. Reddy et al. further studied and added rubber powder, PE, rock asphalt, and SBR to the base asphalt for composite modification to obtain a high-viscosity modified asphalt. Through road performance verification, it was found that the performance of the OGFC mixture was excellent [18]. Xu et al. prepared three types of rubber–plastic modifiers and modified asphalt, and conducted road performance tests for three types of modified asphalt. Xu et al. mainly conducted research on the road performance of rubber and plastic alloy-modified asphalt, and its conclusions indicate that as a new modified material, rubber–plastic alloy-modified asphalt has no less high-temperature performance than SBS-modified asphalt, but also good low-temperature performance. Based on the component analysis of waste rubber powder and waste plastics, Ki et al. prepared waste rubber–plastic alloy modifiers with different rubber–plastic ratios, analyzed the modification mechanism of waste rubber–plastic alloy modifiers on base asphalt, and tested the technical performance and storage stability of waste rubber–plastic alloy-modified asphalt [19]. The results showed that when the rubber–plastic ratio was 7:3, the waste rubber powder and waste plastic had good compatibility; the blending process of waste rubber and waste plastics and the modification process of base asphalt by waste rubber–plastic alloy modifiers are mainly physical effects; The waste rubber–plastic alloy modifier has good compatibility with the base asphalt, significantly improving the road performance of the base asphalt [20]. Chen et al. studied the effect of raw material quality ratio on the performance of thermoplastic elastomer-modified asphalt. The experimental results indicated that the mass ratio of water-based adhesive powder and SBS had a more important impact on the permeability, softening point and ductility, viscosity, high-temperature storage performance, elastic recovery rate, and dynamic rheological properties of TPE-modified asphalt [21].

In recent years, some scholars have conducted systematic research on waste rubber powder-modified asphalt. However, there is a gap between the performance of modified asphalt modified with rubber powder alone and that of SBS-modified asphalt [22]. For instance, as the subject of current research, the high-temperature softening point index of SBS-modified asphalt can reach about 80 °C, while rubber powder-modified asphalt usually only reaches about 60 °C; the low-temperature ductility index is also lower than that of SBS-modified asphalt [23]. Judging from the share of rubber powder-modified asphalt and SBS-modified asphalt used in the world, although rubber powder asphalt has many applications, it cannot fundamentally shake the mainstream position of modified asphalt prepared using thermoplastic elastomer SBS [24]. The rubber–plastic alloy TPE material studied in this paper is an extension of the modification of pure rubber powder. From the perspective of technical principles, rubber can impart elasticity to asphalt, while resin can impart rigidity to asphalt, enabling asphalt to have the characteristics of both rubber and resin, thereby enabling rubber–plastic alloy TPE materials to achieve the performance of SBS block copolymer TPE materials.

In this paper, the serialization and functionalization of novel rubber–plastic alloy (TPE) modifiers were studied, as well as the preparation process and properties; the mix ratio of new TPE modifier asphalt mixture was designed; rubber–plastic alloy modifier formulations were developed, the formulation design plans and processing technology plans were then proposed; subsequently, the preparation method of the rubber–plastic alloy modifier was determined. By analyzing the high- and low-temperature performance, temperature sensitivity, aging performance, and rheological properties of the new rubber–plastic alloy-modified asphalt, the theoretical basis for proposing technical standards related to road performance is improved.

2. Materials and Methods

2.1. Materials

2.1.1. Asphalt Binder

Regarding base asphalt, ESSO 70# is used, and its technical indicators satisfy the requirements of heavy-duty asphalt 70# in the current Chinese specification "Technical Specifications for Construction of Highway Asphalt Pavements" (JTG F40-2004), as shown in Table 1.

Table 1. Performance results of base binder.

Test Items		Technical Requirements	Test Results
Penetration (0.1 mm) (25 °C, 100 g, 5 s)		60~80	64
Penetration index		−1.5–1.0	−1.47
Softening point (°C)		≥45	46.0
Ductility (5 cm/min,15 °C) (cm)		≥100	>100
Ductility (5 cm/min,10 °C) (cm)		≥25	54
Dynamic Viscosity (60 °C) (pa.s)		≥160	181
Wax Content (Distillation)(%)		≤2.2	2.0
Solubility (%)		≥99.5	99.98
After aging in film ovens	Weight loss (%)	≤±0.8	0.072
	25 °C, Penetration Ratio (%)	≥61	65
	Ductility (5 cm/min,10 °C) (cm)	≥6	7
Flash Point (°C)		≥260	317
Density 15 °C (g/cm^3)		Actual test records	1.041

2.1.2. TPE Modifier Raw Materials

The waste rubber powder used in the experimental study in this paper is the "MOZHU" brand fine waste rubber powder (80 mesh) produced by Tianjin Tianyuanheng Rubber Products Factory. Its physical indicators are shown in Table 2.

Table 2. Physical properties of waste rubber powder.

Technical Indicators	Measured Results	Technical Standard	Test Method
Residue/%	6.3	<10	GB/T 19208
Relative density/kg/m^3	1.11	1.10~1.30	GB/T 19208
Water content/%	0.48	<1	GB/T 19208

Table 2. *Cont.*

Technical Indicators	Measured Results	Technical Standard	Test Method
Metal content/%	0.004	<0.05	GB/T 19208
Fiber content/%	0.09	<1	GB/T 19208
Natural rubber content/%	33	≥30	GB/T 13249-91
Ash content/%	6.8	≤8	GB 4498-1997
Acetone extract/%	8	≤22	GB/T 3516
Carbon black content/%	29	≥28	GB/T 14837
Rubber hydrocarbon content/%	56	≥42	GB/T 14837

Waste plastic uses recycled plastic bottles to crush linear low-density polyethylene, and the specific technical indicators are shown in Table 3.

Table 3. Physical properties of waste plastic.

Technical Indicators	Measured Results
Density/(g/cm^3)	0.915
Melt index/g/10 min	4.12
Melting peak temperature/%	1.48
MD yield tensile strength/MPa	9.5
MD breaking tensile strength/MPa	48
Gloss/45 °C	44
Haze/%	4.5

The additive was a plasticizer, a white powdery substance that mainly served to increase solubility and reduce viscosity. The stabilizer used in this study was a composite stabilizer consisting of elemental sulfur and a commercial modified asphalt stabilizer, as well as a self-fabricated stabilizer. The stabilizer content in this study was 1.5‰ (percentage of asphalt content). The compatibility agent used was a rubber oil rich in aromatic compounds.

2.2. Test Scheme

This study is based on previous research on rubber powder and plastics-modified asphalts, and the TPE material fabricated from rubber–plastic alloys investigated in this study represents a breakthrough in the modification of asphalt using pure rubber powder or plastic. The so-called new type of rubber–plastic alloy is thermoplastic elastomer (TPE). It is based on the actual situation in China and relies on the abundant resources of waste rubber and plastic materials in the domestic industry. Through process and formulation exploration, a type of highly polymerized "alloy" asphalt material has been developed. Recycled plastics and (waste) vulcanized rubber powder are used as the main polymer raw materials, and recycled plastics and waste vulcanized rubber powder are the main polymer raw materials. During the thermodynamic process, under the action of selected composite organic additives, the components are fully mixed with the asphalt. The physical and chemical reactions between different components are completed in the dynamic mixing process, and different types of reactions should occur simultaneously in the mixture without mutual inhibition. This can establish a synergistic effect between various components or different phases, promoting mutual solubility. Establishing a structural morphology similar to that of thermoplastic elastomers (TPEs), this thermoplastic highly asphaltic alloy material can be extruded, granulated, cooled, and solidified. It is non-adhesive at room temperature and easy to be industrially packaged and transported.

This study selected materials such as waste vulcanized rubber powder (WRP), recycled low density polyethylene (RLDPE), viscosity reducer (compatibilizer), plasticizer (A), organic functional group graft copolymer, and other additives (organic composite additives (SBC)). Adopting the theory of molecular phase structure design technology, a new type of thermoplastic elastomer alloy material was designed, which uses rubber with deep dynamic desulfurization as the soft segment and polyolefin resin as the hard segment.

Firstly, the waste rubber powder was activated to prepare (waste) vulcanized rubber powder (A); then, the formulation was designed based on the analysis and requirements of the modified asphalt properties. A new type of rubber–plastic alloy similar to SBS was then prepared using a melting mixer and a double screw extruder, and the subsequent dry process TPE direct injection technology was studied.

By designing different composition formulas, the wet process serialization and functionalized formulations of modified asphalt systems were studied, as well as on the preparation process and performance of modified asphalt.

2.3. Test Methodology

2.3.1. Raw Material Activation Treatment

Given that the highly crosslinked network structure of waste rubber powder contains three-dimensional crosslinking structures with S–S chemical bonds, it neither melts nor dissolves and is difficult to dissolve and disperse in asphalt. To enhance the compatibility between the various components (including waste rubber powder) in TPE and asphalt, the rubber powder was subjected to a deep desulfurization and activation treatment before processing.

Four types of activators were selected to activate waste rubber powder, namely, petroleum-based (L-A), coal tar-based (L-B), de-link-based (L-C), and vegetable oil-based (S-1) activators. The activation process is the following: the waste rubber powder and activator were mixed in a high-speed mixer first, and then rolled and cooled in a two-roller mixing mill for crushing into fine powder.

2.3.2. Preparation of TPE Modifier

The equipment used for processing the TPE modifier in this paper is the SHJ-20 double screw extruder produced by Nanjing Hanyi Machinery limited company. A specific proportion of activated waste rubber powder, waste plastic, and additives were mixed in a high-speed mixer, and then a double screw extruder was used for reactive blending. The overall mix was extruded and pelletized to make TPE modifier particles. The double screw extruder and TPE modifier particles are shown in Figures 1 and 2.

Figure 1. Double screw extruder.

Figure 2. TPE modifier.

2.3.3. Preparation of TPE-Modified Asphalt

The equipment used for preparing TPE-modified asphalt in this article are a high-speed shear and a blender. Firstly, the TPE modifier was stirred and swelled in the asphalt, then a certain amount of stabilizer was added after being sheared in a high-speed shear mixer, and finally developed in an oven to complete the process. The process of preparing TPE-modified asphalt is shown in Figure 3.

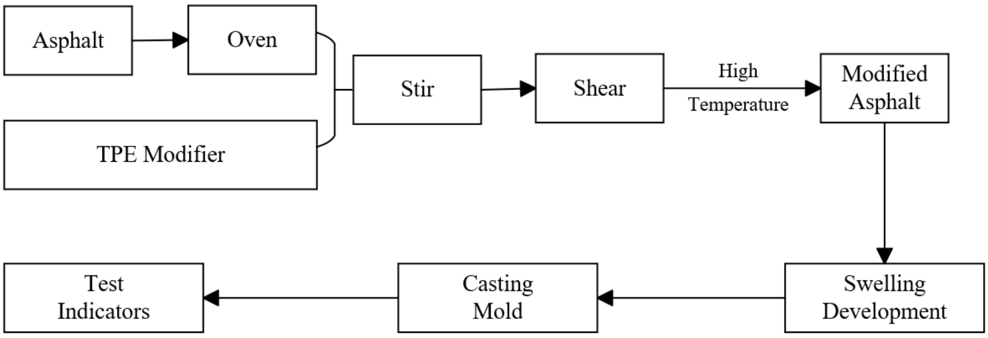

Figure 3. The process of preparing TPE-modified asphalt.

2.3.4. Research on the Performance of TPE-Modified Asphalt

According to the requirements of "Standard Test Methods of Bitumen and Bitunimous Mixtures for Highway Engineering" (JTG E20-2011), routine tests such as penetration test, softening point test, ductility test, Brinell viscosity test, and elastic recovery test were conducted on the prepared TPE-modified asphalt. The improvement of modified asphalt in terms of high and low performance was analyzed and compared. In addition, by changing the dosage of the additive, the influence of additive dosage on the conventional performance of TPE-modified asphalt was analyzed. This paper used dynamic shear rheometer and bending beam rheometer to measure relevant indicators to evaluate the rheological properties of TPE-modified asphalt.

The storage stability of the modified asphalt was mainly characterized by the separation test, and evaluated by Δts, the difference of the softening point between the top and bottom. According to the domestic technical standards for modified asphalt, when $\Delta ts \leq 2.5\ ^\circ C$, the stability of the modified asphalt is qualified. On this basis, an optical microscope was also used to analyze the morphology of TPE-modified asphalt at a high temperature by transmission electron microscopy.

3. Results and Discussion

3.1. Waste Crumb Rubber Activation and Modified Asphalt Properties

3.1.1. Activated Crumb Rubber-Modified Asphalt with Mono Activation Agent

Activated crumb rubber-modified asphalt (CRM) is prepared by adding different activators. Its formulation and sample preparation process conditions are shown in Tables 4 and 5.

Table 4. Test formulation table.

		S1	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
No.	**Component**				**phr**			
1	CRM	96.6	96.5	93.2	94.6	91.4	96.6	93.1
2	L-A	3.4	——	——	——	——	——	——
3	L-B	——	3.5	——	——	——	——	——
4	L-B	——	——	6.8	——	——	——	——
5	S	——	——	——	4.3	——	——	——
6	S	——	——	——	——	8.6	——	——
7	L-C	——	——	——	——	——	3.4	——
8	L-C	——	——	——	——	——	——	6.9
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 5. Sample-making process record sheet.

Sample No.	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**
Front roller temperature (start/end), °C	120/122	127/133	115/127	113/120	115/118	118/115	116/120
Rear roller temperature (start/end), °C	110/110	111/117	111/112	117/120	115/117	116/121	115/115
Plasticization time, min	6	5	6	5	5	5	6
Thin pass thickness/times. mm/time	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2
Total dissolving time, min	30	20	17	22	21	15	29
Dissolving quality	good	good	good	good	good	good	good

Note: The front and rear rollers are preheated to 150 ± 5 °C.

An electrically heated twin-roll mill Φ160 is used, the front and rear rollers are preheated to the required temperature, then the already weighed materials are added, the sample is then thin-passed, plasticized, and turned over evenly (the total time of plasticizing is about 15 min). After being sliced and cooled, it is crushed into fine powder.

The obtained activated waste rubber powder is added to the asphalt for modification according to specific process requirements. The performance test results of activated waste rubber powder-modified asphalt are presented in Table 6.

Table 6. Performance test results of different activated WRP-modified asphalt.

Scheme	**Penetration Index/mm**	**Softening Point/°C**	**Ductility /cm**	**Brinell Viscosity/Pa·s**	**Elastic Recovery/%**	**Upper and Lower Softening Point Differ in 48 h**
S1	45	62.2	5.6	1.342	/	6.9
S2	46	70	12.5	3.184	78	1.6
S3	52	59.5	4.7	2.044	68	0.1
S4	43	62.7	5.4	1.546	62	2.6
S5	42	62.3	6.2	2.271	64	0.7
S6	49	60	8.6	3.273	60	7.3
S7	51	61.9	10	3.572	60	2

(1) Effect of WRP activated by various activation agents on asphalt properties

The effect of activator L-A and activator S on the performance of modified asphalt was compared by Scheme S1 and Scheme S4, and the results are shown in Figure 4.

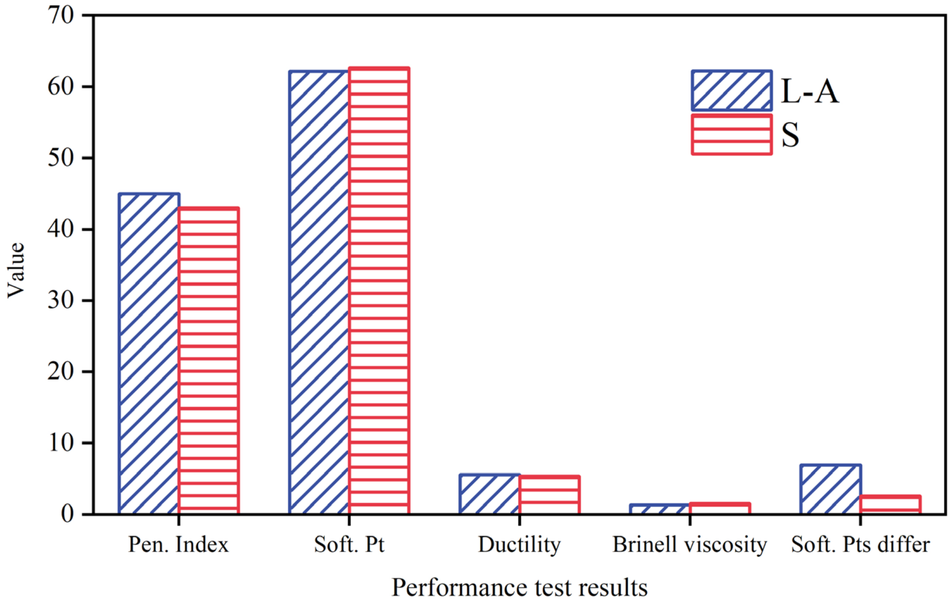

Figure 4. L-A and S activated waste rubber powder-modified asphalt effect comparison.

The comparison in Figure 4 shows that there are not much differences between the modification effects of WRP added with L-A and S on asphalt; however, when the difference between the upper and lower softening points of 48 h is compared, the S-modified asphalt has a lower softening point than that of the L-A-modified asphalt, indicating that the stability of L-A on asphalt is better than that of oil. The effective component of S is a new chemical polymer fabricated from accelerator M and zinc dimethyldithiocarbamate (accelerator ZDMC) dispersed in binary alcohol and in the presence of stearic acid, zinc oxide, and sulfur. S is an effective regenerant for WRP, which can react with the S–S bond in WRP without destroying the C–C bond and breaking the vulcanization network. WRP-modified by S is added to asphalt as a modifier, which has an obvious modification effect on asphalt.

Scheme S3 and Scheme S5 compare the influence of S and L-B on the performance of modified asphalt, and the results are shown in Figure 5. The experimental results show that the difference of the softening point of L-B-modified asphalt is smaller than that of S-modified asphalt, indicating that the stability of L-B-modified asphalt is better than that of S, and the elastic recovery is also larger (nearly 70%). L-B is a black viscous liquid with a special odor. During the experiment, middling coal tar also emits a pungent odor, which has a certain impact on the experimenter's body and is not conducive to the operation of the experiment.

Scheme S2 and Scheme S6 compare the influence of L-B and L-C on asphalt performance, and the results are shown in Figure 5.

L-C is a colorless and odorless mixture obtained from crude oil fractionation. It is a colorless and transparent oily liquid, and its main components are C16~C20 normal alkanes. It can be seen from Figure 6 that the modification effect of L-C is not as good as that of L-B on the whole, and L-B performs much better than L-C in terms of the difference between the ductility and softening point.

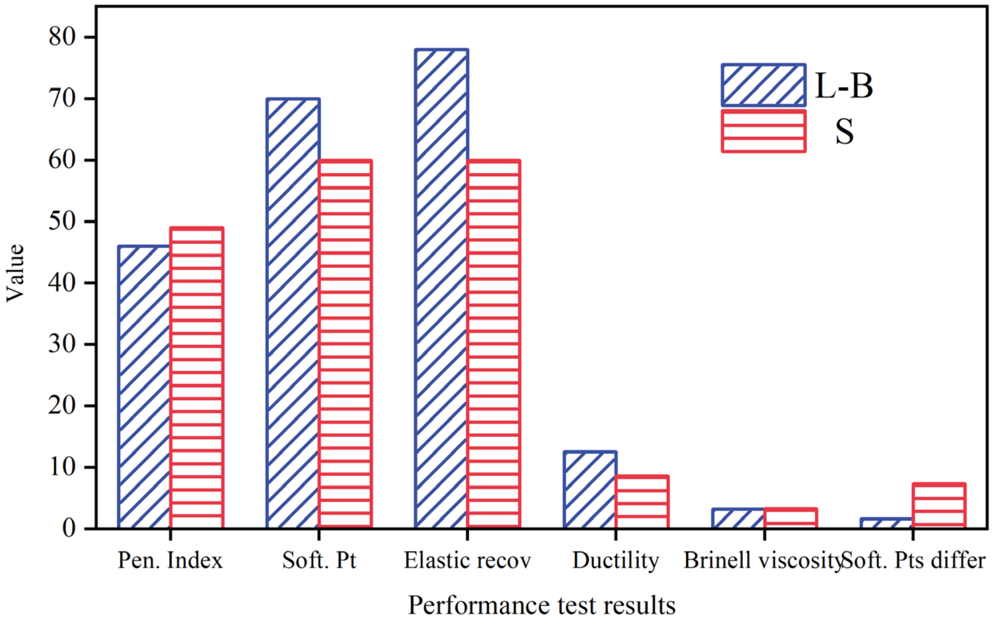

Figure 5. Comparison of the effect of L-B and S activated waste rubber powder-modified asphalt.

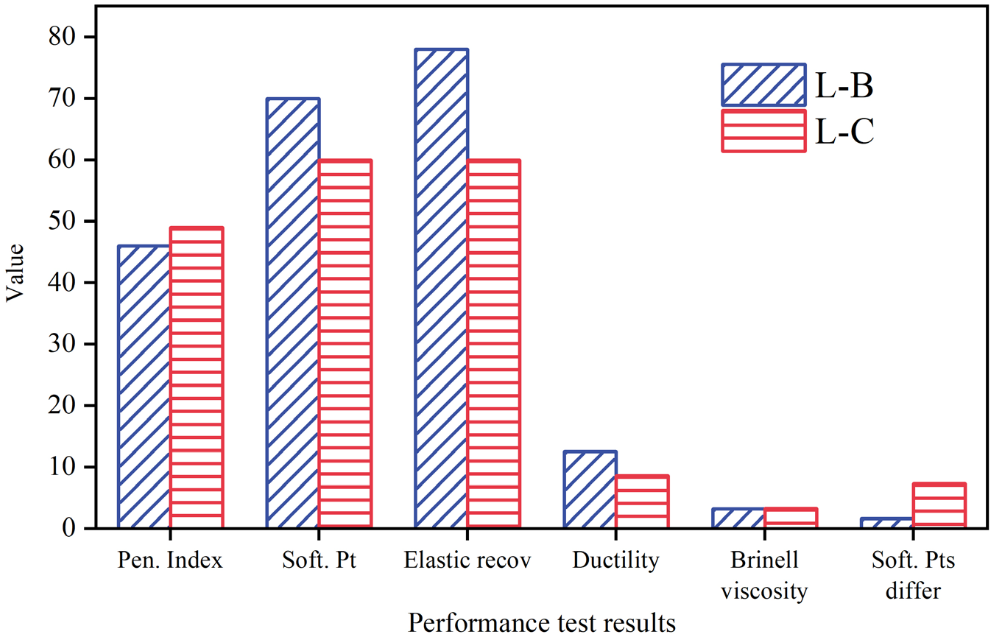

Figure 6. Comparison of L-B and L-C activated waste rubber powder-modified asphalt.

In conclusion, L-B and L-C have better effects on asphalt modification. The modification effect of L-A is not ideal. Finally, it is necessary to conduct more research on S's impact on asphalt ductility.

(2) Effect of activator dosage on asphalt performance

Scheme S6 investigated the effect of L-C on asphalt performance, but the effect is not ideal. In order to further investigate the effect of L-C and increase the amount of L-C, Scheme S7 was designed and compared with Scheme S6. The results are shown in Figure 7.

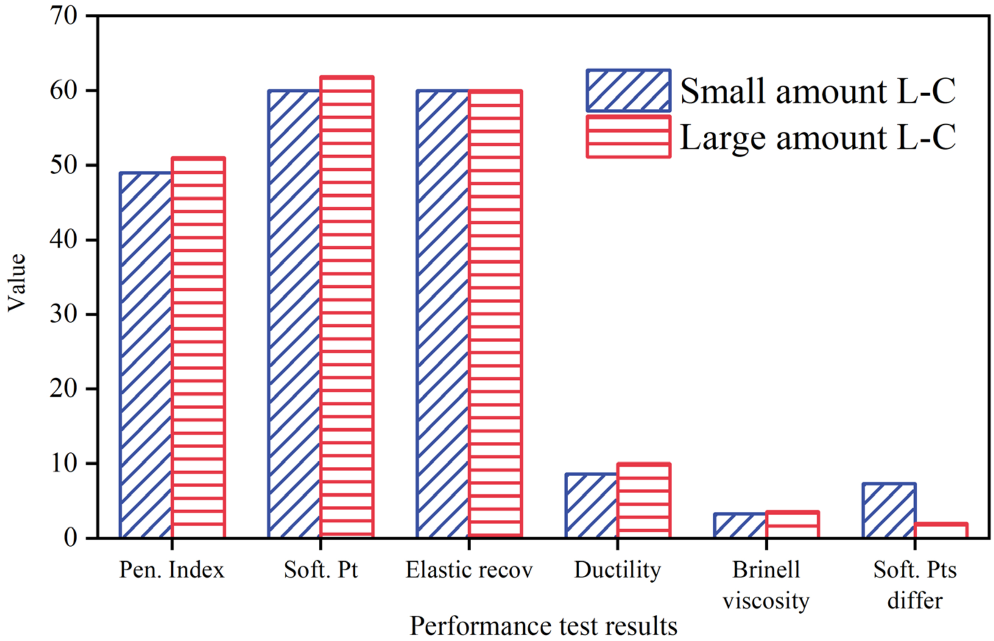

Figure 7. Effect of different L-C dosage on modified asphalt.

As illustrated in Figure 7, with the increase in L-C dosage, the ductility and the Brinell viscosity of asphalt increase, and the difference between the upper and lower softening points decreases, indicating that the stability of asphalt is enhanced, and that the indicators of Scheme 7 met the technical requirements of the specification.

The additive selected in both Scheme S2 and Scheme S3 is L-B; however, the dosage and process for each scheme are different. The two results are compared and illustrated in Figure 8.

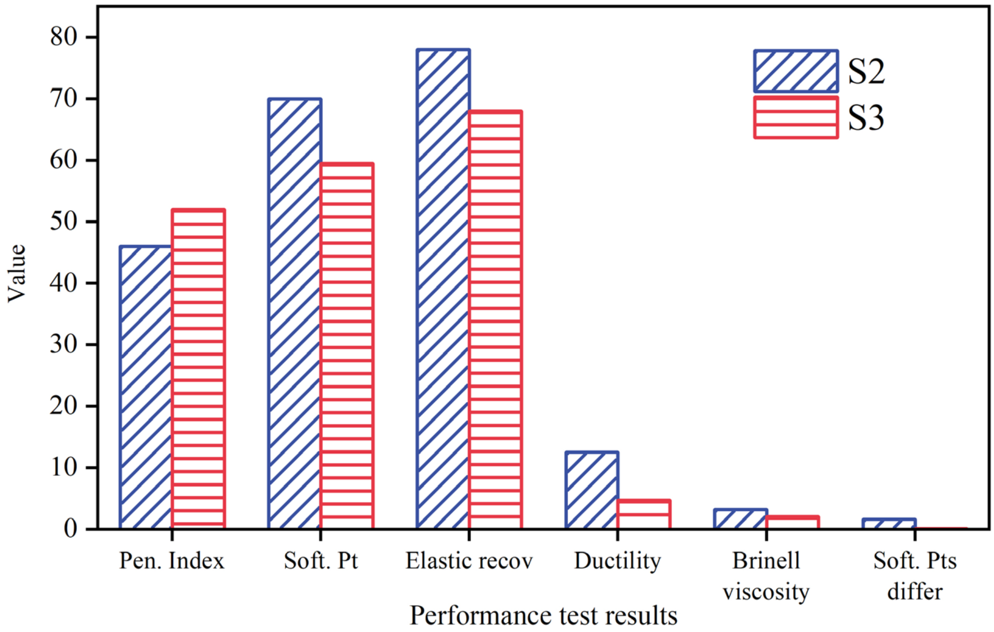

Figure 8. Effect of L-B on modified asphalt.

It can be seen from Figure 8 that in terms of overall performance, the modified asphalt produced by Scheme S2 outperforms that produced by Scheme S3; with the exception of stability, which is not better than that of Scheme 3, all other indicators are better than those in Scheme 3. In Scheme 3, the amount of L-B is more than that in Scheme 2, and the shear time is longer than that in Scheme 2; the shear time mainly reflects on the stability of asphalt, therefore deducing that the more coal tar is not better, and it (the amount of L-B in Scheme S3) reached the requirements of asphalt modification at 3.68 phr.

Scheme S4 is compared with Scheme S5. The additive used in both schemes is S, and the results obtained are shown in Figure 9.

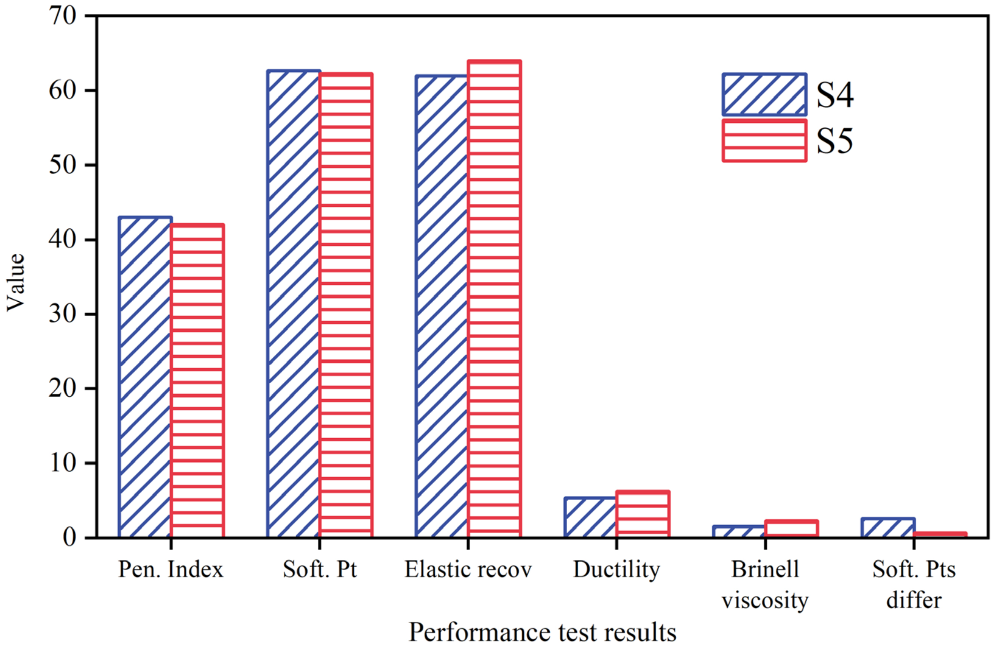

Figure 9. Effect of S on modified asphalt.

As indicated in Figure 10, the difference in performance between the modified asphalt obtained from Scheme S4 and Scheme S5 are not significant. Ignoring the influence of shear time, when the amount of S is 4.5 phr, the modification effect can be achieved very well, and more is not better.

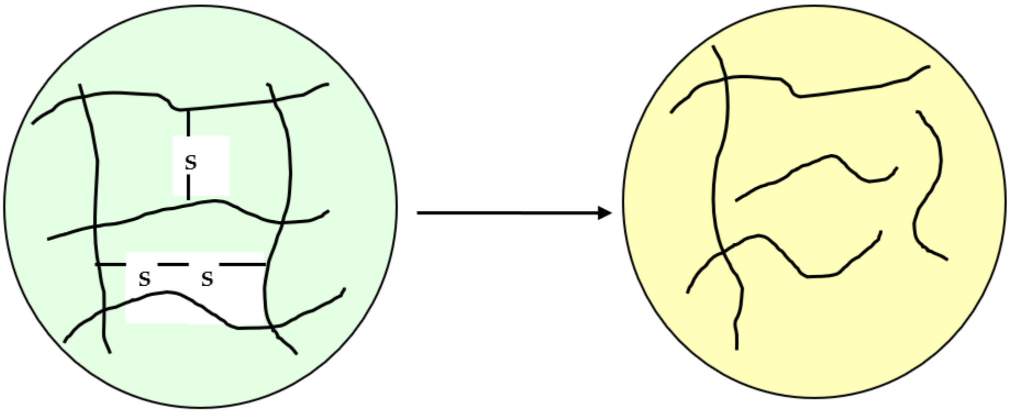

Figure 10. Diagram of waste rubber powder activation.

3.1.2. Properties of Activated Waste Rubber Powder and Modified Asphalt with Complex Activator

The above-mentioned activators were compounded to study the performance index of the modified asphalt. The test formulation is shown in Table 7, and the sample preparation process is established in Table 8. The rubber powder activated by the composite system is used to prepare the modified asphalt, and its performance indicators are shown in Table 9.

Table 7. Test formulation table of modified asphalt.

Formulation No.		**F1**	**F2**	**F3**	**F4**	**F5**	**F6**
No.	**Component**	**Dosage of Each Component/phr**					
1	WRP	93	90.1	86.6	87.4	83.9	87.5
2	L-A	3.3	3.2	3	6.1	6	— —
3	L-B	— —	— —	— —	— —	— —	6
4	L-C	3.7	4	7.8	3.9	7.6	3.9
5	S-1	— —	2.7	2.6	2.6	2.5	2.6
Total		100.00	100.00	100.00	100.00	100.00	100.00

Table 8. Sample-making record sheet.

Sample No.	**F1**	**F2**	**F3**	**F4**	**F5**	**F6**
Front roller temperature (start/end), °C	120/122	127/133	115/127	113/120	115/118	113/118
Rear roller temperature (start/end), °C	110/110	111/117	111/112	117/120	115/117	112/117
Plasticization time, min	6	5	6	5	5	6
Thin pass thickness/times. mm/time	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2
Total dissolving time, min	17	21	15	19	21	16
Dissolving quality	good	good	good	good	good	good

Note: The front and rear rollers are preheated to 150 ± 5 °C.

Table 9. Performance of composite activator activated waste rubber powder.

Sample	**Dosage**	**Preparation Process**	**Pen. Index (25 °C)/0.1 mm**	**Soft. Point/°C**	**Ductility (5 °C)/cm**	**Brinell Viscosity (135 °C)**	**Upper and Lower Soft.Pts Differ in 48 h**
F1	Asphalt /ACR = 92/8	180 °C, 5000 rpm, 30 min	47	61.6	5.6	1.520	1.3
F2	Asphalt /ACR = 88/12	180 °C, 5000 rpm, 60 min	43	66.3	6.7	2.684	3.8
F3	Asphalt /ACR = 88/12	180 °C 5000 rpm, 60 min	43	66	6.7	2.574	3.7
F4	Asphalt /ACR = 88/12	180 °C, 5000 rpm, 60 min	42	65.9	6.7	2.575	2.8
F5	Asphalt /ACR = 88/12	180 °C, 5000 rpm, 100 min	42	65.8	7.3	/	3.3
F6	Asphalt /ACR = 88/12	180 °C, 5000 rpm, 50 min	44	60.5	6.5	2.331	0.4

It can be seen from Table 8 that the composite activation system outperforms the single/mono system, especially regarding the stability of modified asphalt. Other performance changes are not particularly obvious. The following conclusions can be drawn:

(1) Similar to the modified asphalt with single activator system, the modified asphalt with L-B in the composite system has the best stability;
(2) The addition of plant softener S-1 can improve the softening point of modified asphalt;
(3) In the composite system, the change in the content of L-A and S has little effect on the performance of modified asphalt, and the performance index basically does not change with the change in its content;
(4) Compared with other composite systems, the softening point of the modified asphalt system added with L-B is slightly lower.

3.1.3. Study on Activation Effect of Waste Rubber Powder

The waste rubber powder is a highly crosslinked, three-dimensional network structure created from crushed vulcanized rubber that neither melts nor dissolves. The three-dimensional network structure is shown in Figure 10. This crosslinked three-dimensional structure is also difficult to dissolve and disperse in asphalt. However, the traditional regeneration methods, such as the hot oil method and acid method, cause the oxidation and partial thermal cracking of the rubber main chain bond while cutting off the sulfur bond crosslinking mesh, resulting in the decline of its physical properties. Cutting the sulfur–sulfur bond without cutting the carbon–carbon bond maintains the main chain structure of rubber macromolecules to maximize the performance of the original rubber.

The purpose of adding an activator is to reduce the crosslinking of sulfur and modify the surface of waste rubber powder. This can change the surface layer of waste rubber powder from elastic to viscous, and increase its surface reactivity.

XLDS-15 rubber crosslinking density NMR analyzer produced by IIC Innovative ImagingCorp. KG (Germany) was used to determine the crosslinking density of rubber powder. Figure 11 shows the NMR analysis of the crosslinking density of the inactive and activated rubber powder (see Table 10 for the NMR analysis data of the crosslinking density of the activated rubber powder tablet).

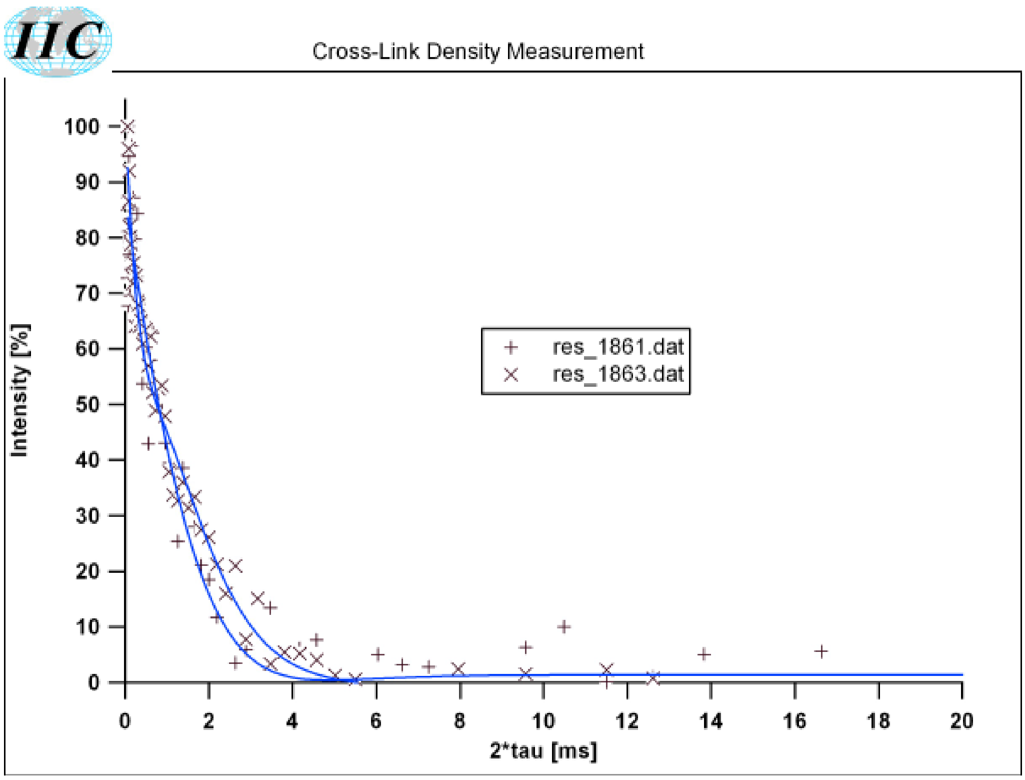

Figure 11. Crosslink density NMR analysis graph.

Table 10. NMR analysis of crosslinking density of activated rubber powder tablet.

	XLD/(10^{-5} mol/cm^3)	A(M_c)/%	T_2/ms	A(T_2)/%
Unactivated rubber powder	13.02	67.78	0.57	24.81
Activated	5.96	66.22	1.16	34.38

Note: XLD: crosslinking density; A (Mc): the area of the crosslinking point, or the number of crosslinking points; T2: movement ability of activity unit; A (T2): area occupied by active units.

The NMR crosslinking density analysis of activated waste rubber powder showed that the crosslinking density decreased and the area of crosslinking point decreased, indicating that the number of crosslinking points in the waste rubber powder decreased. The number of crosslinking points of activated waste rubber powder decreases, the restriction of network structure on the movement of molecular chain decreases, the small molecular chain segment increases, the movement ability of small active units increases, and the number increases, in other words, T2 increases. Due to the reaction between the activator and the macromolecule of the waste rubber powder, a part of the crosslinking bond of the rubber powder was interrupted, and the network structure was destroyed, resulting in a relatively large number of small movement units, meaning that some free molecular chain segments appeared, corresponding to the increase in A (T2). The above analysis shows that the activation of waste rubber powder effectively breaks the sulfur–sulfur bonds in the three-dimensional network structure of waste rubber powder, increases its reactivity, and the fracture of the molecular chain is also conducive to the dispersion of waste rubber powder in asphalt.

3.1.4. Activated Waste Rubber Powder-Modified Asphalt Microstructure Analysis

In the waste rubber powder-modified asphalt system, there is only partial adsorption and phase dissolution between the waste rubber powder and asphalt, rather than a complete melting. This kind of system belongs to the thermodynamic unstable system, which is prone to separation between two phases, thus causing segregation as shown in Figure 12. The fluorescence microscope of waste rubber powder-modified asphalt shows that the waste rubber powder is black, and the field of vision is dark.

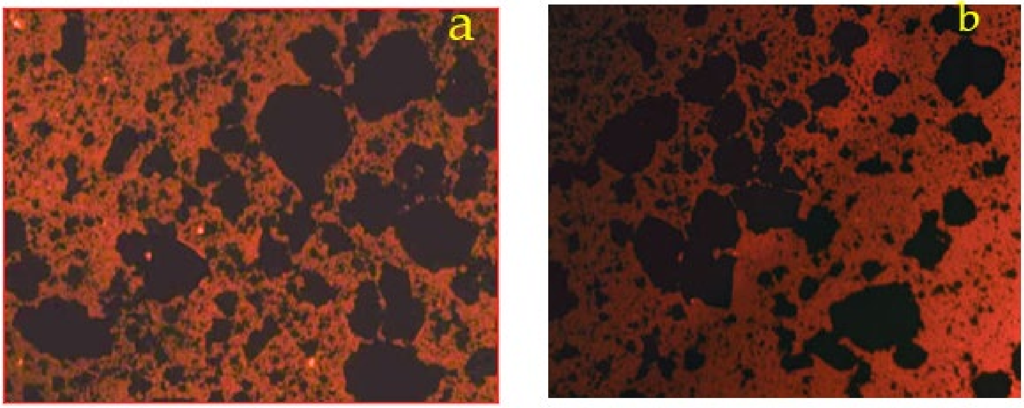

Figure 12. Fluorescence micrograph of waste rubber powder-modified asphalt (400×): (**a**) 15% waste rubber powder + SK70; (**b**): 12% waste rubber powder + SK70.

The activated waste rubber powder is dispersed in the asphalt by physical methods such as shear machine high-speed mixing and shearing. The activated waste rubber powder has a strong interaction with the asphalt, which limits the cohesion and flexibility of the asphalt and reduces its sensitivity to temperature.

Figure 13 shows the fluorescence micrograph of activated waste rubber powder-modified asphalt. Compared with Figure 12, it can be seen that in the activated waste rubber powder-modified asphalt system, the surface of waste rubber powder is swelled by the light components of asphalt, and the waste rubber powder particles are evenly dispersed. The activated waste rubber powder-modified asphalt prepared by activated waste rubber powder is shown in Figure 13a. The surface of the rubber powder swells, but it penetrates less into the interior. With the addition of the activator, asphalt penetrates the rubber powder, and the rubber powder particles are smaller. In the interface area between asphalt and rubber powder, the rubber powder is translucent.

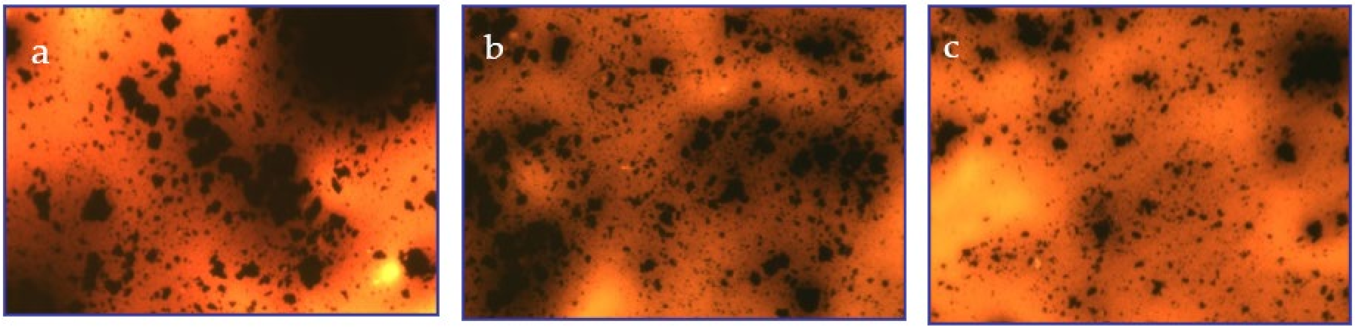

Figure 13. Fluorescence micrograph of activated waste rubber powder-modified asphalt (400 times). (**a**) 15%S3 + SK70; (**b**) 15%F6 + SK70; (**c**) 15%F4 + SK70.

3.2. Selection and Determination of Organic Functional Group Graft Copolymer

In waste rubber-based thermoplastic elastomer (polymer alloy), some organic composite additives are often selected to establish the physical and chemical interaction between different components (rubber and plastic). Therefore, based on the activation of waste rubber powder, the selection of organic chemical additives and the effect of modified asphalt properties were studied.

The organic functional group graft copolymers selected three kinds of P grafts and one kind of styrene block thermoplastic elastomer styrene butadiene block copolymer (SBC). The formulation is shown in Table 11 below. The preparation process is as follows: a Φ 160 electrically heated twin-roll plasticizing machine, the front and rear rollers are preheated to the suitable temperature, the weighed materials are added, thin-passed, plasticized, and turned over evenly (the total plasticizing time is controlled at about 15 min). After cutting and cooling, crushing and grinding into fine powder, they are then passed through 80 sieves for use. The sample preparation process is listed in Table 12.

Table 11. Test formulation.

Formulation		**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**
No.	**Component**	**Quantity, phr**						
1	WRP	67.9	67.9	67.9	89.1	94.1	78.5	59.5
2	RLDPE	29.1	29.1	29.1	9.9	4.9	8.7	31.4
3	P-A	3	——	——	1	1	1.1	0.6
4	P-B	——	3	——	——	——	——	——
5	P-C	——	——	3	——	——	——	——
6	SBC	——	——	——	——	——	11.7	8.5
Total		100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 12. Sample-making process record sheet of modified asphalt.

Sample Number	**T1**	**T2**	**T3**	**T4**	**T5**	**T6**	**T7**
Front roller temperature (start/end), °C	140/142	147/143	135/147	143/140	145/148	148/145	146/145
Rear roller temperature (start/end), °C	140/140	131/137	151/142	137/140	145/147	146/141	145/145
Plasticization time, min	6′15″	4′	6′	5′20″	5′05″	5′42″	6′20″
Thin pass thickness/times. mm/time	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2	0.5/2
Total dissolving time, min	30′	20′	17′54″	22′	21′	15′39″	29′
Dissolving quality	Good	Good	Good	Good	Good	Good	Good

Note: The front and rear rollers are preheated to 150 ± 5 °C.

3.2.1. Effect of Organic Functional Group Graft Copolymer on the Properties of Modified Asphalt

The function of organic functional group graft copolymer is to closely combine waste rubber, waste plastics, and additives in the alloy as an intermediary, improve the compatibility of rubber and plastic alloy and base asphalt, and improve the interfacial properties of rubber and plastic alloy particles and base asphalt. Three kinds of organic functional group graft copolymers were selected and their modification effects were compared. The experimental scheme and comparison results are shown in Tables 13 and 14. It can be seen that the difference between the softening points of the three modified asphalts above and below 48 h is large, the ductility is also too low, and the indexes of penetration, softening point, and Brinell viscosity meet the technical requirements of the specification. In the optics of improving the ductility of modified asphalt, reducing the proportion of RLDPE is one method.

Table 13. Different interface modifier agent modification process conditions.

Scheme	Formulation	Interface Modifier	TPE Amount w /%	Shear Time /min
T1	Waste rubber powder	P-A	8	30
T2	(WRP):Recycled plastics	P-B		
T3	(RLDPE):Interface modifier = 70:30:3	P-C		

Table 14. Comparison of modification effects of different interface modifiers.

Scheme	Penetration Index/mm	Softening Point/°C	Ductility /cm	Brinell Viscosity/Pa·s	Upper and Lower Soft.Pts Differ in 48 h
T1	45	64.3	3.6	2.285	31.3
T2	49	64.2	3.4	1.871	29.4
T3	48	64.7	4	1.993	22.9

3.2.2. Effect of WRP/LDPE Ratio on the Performance of Modified Asphalt

Scheme T4 and Scheme T5 were designed to investigate the effect of different ratios of WRP/LDPE on the performance of modified asphalt. See Tables 15 and 16 for the comparison of experimental schemes and results.

Table 15. Experimental schemes of different rubber/plastic ratios.

Scheme	WRP/RLDPE	PE-A /Fen	Amount of TPE w /%	Shear Time /min
T4	90/10	1	15	60
T5	95/5			

Note: Fen is the unit for modifiers in this paper.

Table 16. Comparison of the effects of different rubber/plastic ratios on the performance of modified asphalt.

Scheme	Penetration Index/mm	Softening Point/°C	Ductility /cm	Brinell Viscosity/Pa·s	Elastic Recovery /%	Upper and Lower Soft.Pts Differ in 48 h
T4	42	65	8.7	11.497	69	3
T5	42	63	8.5	9.933	63	2

It can be seen from Table 15 that when the plastic content is reduced, the difference of softening point of modified asphalt is significantly reduced, and the stability is greatly improved. The rubber and plastic alloy used in Scheme T4 and Scheme T5 accounts for 15% of the asphalt, and the rubber powder content is much higher than that in Scheme 8–10. The ductility of the modified asphalt is also significantly improved; however, the Brinell viscosity is higher.

3.2.3. Effect of Additive SBC

In order to further improve the effect of rubber–plastic alloy-modified asphalt, 13.6% content of SBC (based on 100% content of total WRP and RLDPE) is added on the basis of Scheme T4 and Scheme T5, and Scheme T6 and Scheme T7 are designed respectively. Other conditions remain unchanged (see Table 17 for the formulation).

Table 17. Modification effect of additive SBC on asphalt.

Scheme	WRP /LDPE	SBC	Pen. Index/mm	Soft. Point/ °C	Ductility /cm	Brinell Viscosity/Pa·s	Elastic Recovery /%	Upper and Lower Soft.Pts Differ in 48 h
T4	90/10	no	42	65	8.7	11.497	69	3
T5		yes	44	66.1	10.1	14.800	72	0.6
T6	95/5	no	42	63	8.5	9.933	63	2
T7		yes	42	68	14.7	14.275	82	0.7

Figures 14 and 15 show the performance comparison between SBC added and SBC unadded. The two figures show that the addition of SBC significantly improves the stability of the system, reduces the difference between the softening point above and below 48 h, and increases the softening point, ductility, and elastic recovery. This suggests that the addition of SBC improved the blending of RLDPE and the system as well as the low-temperature performance of asphalt. However, it can also be seen that the Brinell viscosity of the system increases, which has a great impact on the construction conditions of asphalt.

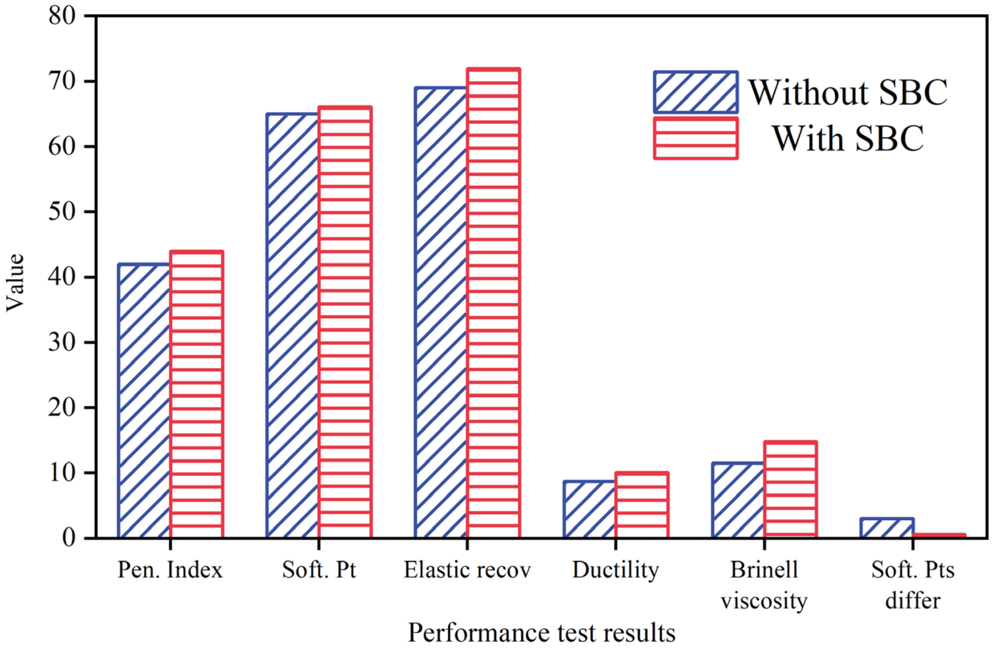

Figure 14. Effect before and after adding SBC when WRP/LDPE = 90/10.

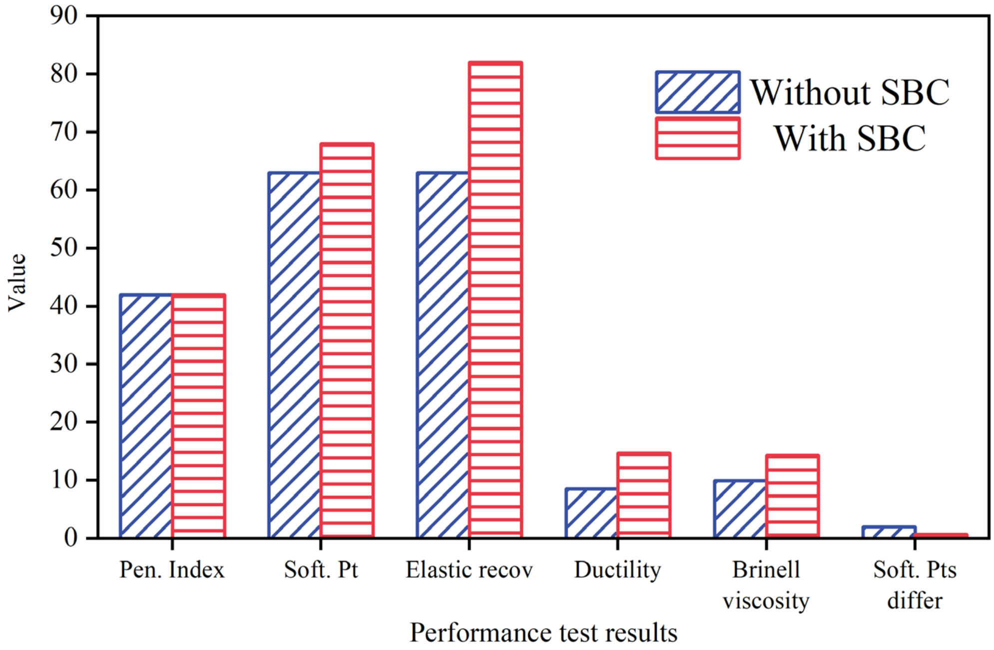

Figure 15. Effect before and after adding SBC when WRP/LDPE = 95/5.

3.2.4. Viscosity-Reducing Effect of Plasticizer A on Asphalt

In order to solve the problem of excessive Brinell viscosity of rubber–plastic alloy-modified asphalt, plasticizer A (plasticizer A is a mixture of cracked polyethylene and long-chain alkyl acid in a certain proportion) was selected, and the design scheme investigated the viscosity reduction effect of plasticizer A.

With plasticizer A as the variable, the modified system prepared by Scheme T7 was selected, and 1 fen (T8) and 1.5 fen (T9) of plasticizer A were added in the shear process of modified asphalt. The specific formulation and results are shown in Tables 18 and 19.

Table 18. Test formulation of plasticizer.

Scheme	Formulation	TPE Amount w/%	Shear Time /min	Plasticizer A/Modification System/%
T7	WRP:RLDPE:P-A:SBC = 95:5:1:13.6	15	60	0
T8				1
T9				1.5

Table 19. Viscosity reduction effect of plasticizer A.

Scheme	Pen. Index /mm	Soft. Point /°C	Ductility /cm	Brinell Viscosity /Pa·s	Elastic Recovery /%	Upper and Lower Soft.Pts Differ in 48 h
T7	42	68	14.7	14.275	82	0.7
T8	46	62.7	9.2	4.312	68	0.8
T9	46	64	11.5	3.992	70	−0.5

It can be seen from Figure 16 that the viscosity reduction in modified asphalt is obvious when adding 1 fen of plasticizer A, but with the increase in the proportion of A, the viscosity reduction is no longer obvious. The long-chain alkyl acid in plasticizer A can soften the combination of S segment in SBC and RLDPE in modified asphalt, so the viscosity of modified asphalt is reduced, but the softening point is also reduced, resulting in the weakening of the high-temperature performance of modified asphalt. The cracked polyethylene in plasticizer A can not only further reduce the viscosity of the system, but also improve the high-temperature performance of modified asphalt raw materials. The combination of the two can reduce the viscosity of modified asphalt while maintaining the original performance of asphalt.

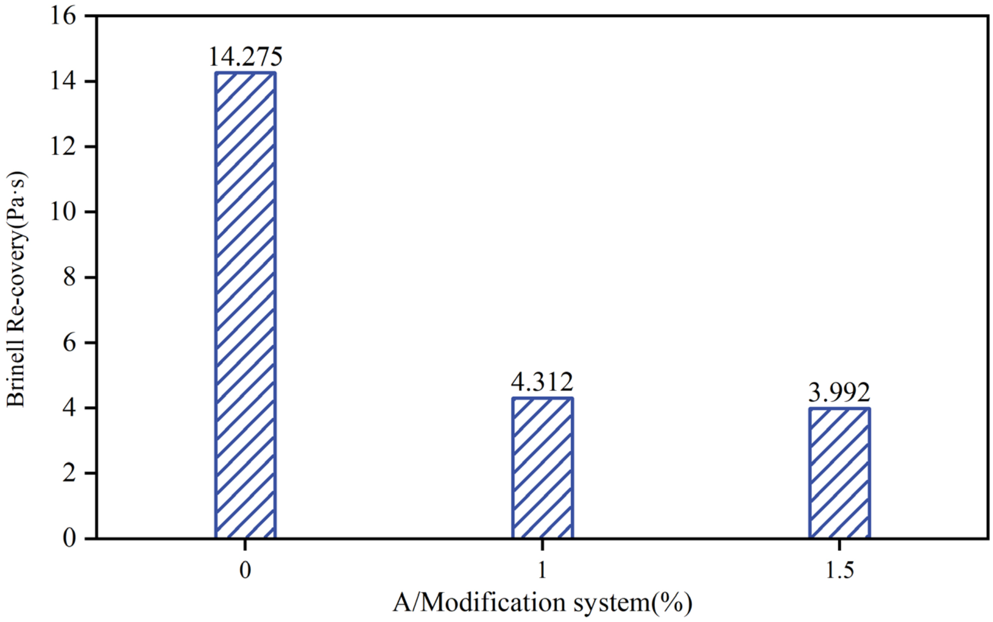

Figure 16. Viscosity-reducing effect of plasticizer A.

4. Conclusions

In conclusion, the analysis of GPC data for crumb rubber-modified asphalt and extracted asphalt leads to the following conclusions:

(1) Investigation and analysis were carried out on the infrared and thermal analysis characteristics of crumb rubber and waste plastic, and based on this, a design method for rubber–plastic alloys used in modified asphalt was proposed. The theory of molecular phase structure design technology was used to design an SBS-like waste rubber–plastic alloy material structure based on the extracted infrared and thermal analysis data of waste rubber–plastic materials. A new thermoplastic elastomer alloy material was invented, which uses rubber with deep dynamic desulfurization as the soft segment region and polyolefin as the hard segment region;

(2) The formulation and preparation processes of the rubber–plastic alloy were studied indoors, and the technical scheme adopted included graft modification of the rubber–plastic alloy with activated waste rubber powder and organic functional group graft copolymer. In the experiment, a mono activator and a composite activator were used to activate the waste rubber powder, and a comparative study of their properties was carried out. The results showed that after adding the activator, the waste rubber powder expanded significantly in the asphalt, with smaller and more uniformly dispersed particles. The network structure of the modified asphalt with activated waste rubber powder was more uniform and dense, resulting in improved performance and storage stability of the modified asphalt;

(3) This study made a reasonable formulation of waste rubber powder, waste plastic, organic functional group graft copolymer, desulfurization and activation agents, and viscosity-reducing agents, and adjusted the processing technology. A new type of thermoplastic elastomer rubber–plastic alloy material was obtained through reactive blending technology. By formulating and adjusting the ratio of waste rubber pow-

der and waste plastic, rubber–plastic alloy materials suitable for different practical engineering requirements can be obtained;

(4) The optimal process conditions for modifying asphalt with a rubber–plastic alloy were obtained through exploration of the process conditions: shear temperature of 160–170 °C, rotating speed of 3000 r/min, and shear time of 30 min. Through this research, it was discovered that the prolongation of shearing time has the greatest impact on the performance of modified asphalt, and the method of prolonging shearing time can be used to prepare modified asphalt with more stable storage.

Author Contributions: Conceptualization, R.D. and A.G.; methodology, Y.Z.; software, Y.Z.; validation, B.X., R.D. and S.P.; formal analysis, R.D. and J.D.; investigation, Y.Z.; resources, J.D.; data curation, Y.Z.; writing—original draft preparation, B.X.; writing—review and editing, S.P.; visualization, R.D.; supervision, B.X. and J.D.; project administration, A.G.; funding acquisition, R.D. All authors have read and agreed to the published version of the manuscript.

Funding: 2017 Shandong Provincial Transportation Technology Plan.

Data Availability Statement: The relevant data has been reflected in the paper, and there is no additional data available for sharing.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, S.; Wang, Q.; Wu, X.; Zhang, Y. Asphalt modified by thermoplastic elastomer based on recycled rubber. *Constr. Build. Mater.* **2015**, *93*, 678–684. [CrossRef]
2. Wang, T.; Xiao, F.; Zhu, X.; Huang, B.; Wang, J.; Amirkhanian, S. Energy consumption and environmental impact of rubberized asphalt pavement. *J. Clean. Prod.* **2018**, *180*, 139–158. [CrossRef]
3. Li, J.; Xing, X.; Hou, X.; Wang, T.; Wang, J.; Xiao, F. Determination of SARA fractions in asphalts by mid-infrared spectroscopy and multivariate calibration. *Measurement* **2022**, *198*, 111361. [CrossRef]
4. Wang, T.; Xiao, F.; Amirkhanian, S.; Huang, W.; Zheng, M. A review on low temperature performances of rubberized asphalt materials. *Constr. Build. Mater.* **2017**, *145*, 483–505. [CrossRef]
5. Zhang, Z.; Sun, J.; Jia, M.; Ban, X.; Liu, H. Effects of Polyurethane Thermoplastic Elastomer on Properties of Asphalt Binder and Asphalt Mixture. *J. Mater. Civ. Eng.* **2021**, *33*, 04020477. [CrossRef]
6. Rosa, C.D.; Auriemma, F. Structure and physical properties of syndiotactic polypropylene: A highly crystalline thermoplastic elastomer. *Prog. Polym. Sci.* **2006**, *31*, 145–237.
7. Anagha, M.G.; Chatterjee, T.; Picchioni, F.; Naskar, K. Exploring the influence of electron beam crosslinking in SEBS/TPU and SEBS-g-MA/TPU thermoplastic elastomer blends. *J. Appl. Polym. Sci.* **2022**, *139*, 51721. [CrossRef]
8. Xu, P.; Zhu, Z.; Wang, Y.; Cong, P.; Li, D.; Hui, J.; Ye, M. Phase structure characterization and compatibilization mechanism of epoxy asphalt modified by thermoplastic elastomer (SBS). *Constr. Build. Mater.* **2022**, *320*, 126262. [CrossRef]
9. Rynne, O.; Lepage, D.; Aymé-Perrot, D.; Rochefort, D.; Dollé, M. Application of a Commercially-Available Fluorine-Free Thermoplastic Elastomer as a Binder for High-Power Li-Ion Battery Electrodes. *J. Electrochem. Soc.* **2019**, *166*, A1140–A1146. [CrossRef]
10. Zou, X.; Zhang, W.; Gu, Y.; Fu, X.; Zhang, Z.; Ge, Z.; Luo, Y. A study on the effect of four thermoplastic elastomers on the properties of double-base propellants. *RSC Adv.* **2020**, *10*, 42883–42889. [CrossRef]
11. Behnood, A. Morphology, rheology, and physical properties of polymer-modified asphalt binders. *Eur. Polym. J.* **2019**, *112*, 766–791. [CrossRef]
12. Fathy, E.S.; Elnaggar, M.Y.; Raslan, H.A. Thermoplastic elastomer based on waste polyethylene/waste rubber containing activated carbon black: Impact of gamma irradiation. *J. Vinyl Addit. Technol.* **2018**, *25*, E166–E173. [CrossRef]
13. Magioli, M.; Sirqueira, A.S.; Soares, B.G. The effect of dynamic vulcanization on the mechanical, dynamic mechanical and fatigue properties of TPV based on polypropylene and ground tire rubber. *Polym. Test.* **2010**, *29*, 840–848. [CrossRef]
14. Nizamuddin, S.; Giustozzi, F. The role of new compatibilizers in hybrid combinations of waste plastics and waste vehicle tyres crumb rubber-modified bitumen. In *Plastic Waste for Sustainable Asphalt Roads*; Woodhead Publishing: Cambridge, UK, 2022; pp. 165–178.
15. Xiao, Z.; He, W.; Ying, S. Current trends in energetic thermoplastic elastomers as binders in high energy insensitive propellants in China. *Sci. Technol. Energ. Mater.* **2014**, *75*, 37–43.
16. Mulage, K.S.; Patkar, R.N.; Deuskar, V.D.; Pundlik, S.M.; Kakade, S.D.; Gupta, M. Studies on a Novel Thermoplastic Polyurethane as a Binder for Extruded Composite Propellants. *J. Energ. Mater.* **2007**, *25*, 233–245. [CrossRef]

17. Wagner, M.A.; Hadian, A.; Sebastian, T.; Clemens, F.; Schweizer, T.; Rodriguez-Arbaizar, M.; Carreno-Morelli, E.; Spolenak, R. Fused filament fabrication of stainless steel structures—From binder development to sintered properties—ScienceDirect. *Addit. Manuf.* **2021**, *49*, 102472.
18. Reddy, T.S.; Nair, J.K.; Satpute, R.S.; Gore, G.M.; Sikder, A.K. Rheological studies on energetic thermoplastic elastomers. *J. Appl. Polym. Sci.* **2010**, *118*, 2365–2368. [CrossRef]
19. Ilya, K.; Andrey, D.; Dmytro, H.; Ekaterina, V.; Vladislav, K.; Oleg, T. Development thermoplastic elastomer-based fiber-metal laminate for vibration damping application—ScienceDirect. *Mater. Today Proc.* **2020**, *30*, 393–397. [CrossRef]
20. Wilkinson, P.J.; Weaver, M.C.; Kister, G.; Gill, P.P. Styrene-Ethylene/Butylene-Styrene (SEBS) Block Copolymer Binder for Solid Propellants. *Propellants Explos. Pyrotech.* **2021**, *47*, e202100142. [CrossRef]
21. Chen, Z.R.; Cao, D.W.; Zhao, W.Z.; Wang, B.X.; Zhang, H.Y. Study on Properties of Modified Asphalt by the Thermoplastic Elastomer (TPE) Compound. *Adv. Mater. Res.* **2012**, *598*, 404–408. [CrossRef]
22. Xing, C.; Li, M.; Liu, L.; Lu, R.; Liu, N.; Wu, W.; Yuan, D. A comprehensive review on the blending condition between virgin and RAP asphalt binders in hot recycled asphalt mixtures: Mechanisms, evaluation methods, and influencing factors. *J. Clean. Prod.* **2023**, *20*, 136515. [CrossRef]
23. Cong, P.; Guo, X.; Mei, L. Investigation on rejuvenation methods of aged SBS modified asphalt binder. *Fuel* **2020**, *279*, 118556. [CrossRef]
24. Zhang, J.; Su, W.; Liu, Y.; Gong, J.; Xie, H. Laboratory investigation on the microstructure and performance of SBS modified epoxy asphalt binder. *Constr. Build. Mater.* **2020**, *270*, 121378. [CrossRef]