This is the Pre-Published Version.

The following publication Yan, C., Yan, J., Zhang, Z., Yu, D., Wang, S., Jiang, X., Ai, C., & Leng, Z. (2024). Screw extrusion process used in the polymer modified asphalt field: A review. Journal of Cleaner Production, 448, 141592 is available at https://doi.org/10.1016/j.jclepro.2024.141592.

Screw extrusion process used in the polymer modified asphalt field: a review

Abstract

Polymer modified asphalt (PMA) has been widely used in asphalt pavement due to its excellent mechanical properties. However most polymer modifiers are not specifically designed for asphalt modification, leading to issues such as incompatibility when blended with asphalt. Meanwhile, the rapid expansion of highway network has led to a growing diversity of demands for polymer modified asphalt, but it is quite challenging to persuade the refineries to adjust their polymers specifically for asphalt modification. Therefore, suppliers are increasingly turning to tailor the polymer modifiers themselves using screw extrusion. Screw extrusion is a manufacturing process that involves using a rotating screw to push the material through an extrusion head to achieve functions like blending, shaping or certain chemical reaction. It is widely used in the polymer field due to its versatility, continuous production capabilities and relatively lower cost. This paper aims to provide an overview of the application of screw extrusion process in the asphalt material field. Based on ingredients and processing purposes, the examined papers are categorized into six applications: i) Plastic compound; ii) Crumb Rubber (CR) compound; iii) Rapid-melting pellet; iv) Nanomaterial compound; v) Grafting; vi) Devulcanization of CR. Furthermore, summary and discussion on the compound formulas and extrusion parameters are provided.

Keywords: Screw extrusion, Modified asphalt, Compound extrusion, Reactive extrusion

© 2024. This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/

Contents

1 Introduction

Asphalt pavement has been widely utilized due to its unique characteristics like smoothness, surface-friction and low-noise. Asphalt pavement was originally paved with plain petroleum asphalt (Y. Ma et al., 2021b). Due to the continuously increasing traffic loads, polymer modified asphalts (PMA) have been proposed and experienced a rapid development during the last few decades (Jiang et al., 2023, 2023). Since 1980s, abundant research articles have been published focusing on the invention, evaluation and application of various polymer modifiers(Yan et al., 2024; Zhang et al., 2023). The mostly mentioned polymer modifiers include polyethylene (PE), polypropylene (PP), ethylene–vinyl acetate (EVA), styrene–butadiene–styrene (SBS), styrene–isoprene–styrene (SIS), and styrene–ethylene/butylene–styrene (SEBS) (Zhu et al., 2014). They are all synthetic polymers, which means they are manually manufactured on a large scale in refineries,

While these synthetic polymers have been found to improve certain pavement properties, none of them were initially designed for asphalt modification. Instead, they were developed for applications in much larger markets such as cloth, medical equipment, and automotive parts. Consequently, this often leads to issues like poor compatibility with asphalt and inferior properties in certain aspects(Noor and Rehman, 2022). For instance, PE-modified asphalt has been proposed as an asphalt binder with outstanding rutting resistance, but it has not been widely used due to its poor storage stability (Liang et al., 2021) and insufficient low-temperature cracking resistance (Du et al., 2020). These deficiencies are attributed to the major difference between PE polymer and asphalt in terms of molecular weight and chemical nature(Y. Ma et al., 2021b) .

As a result of global climate change and rapid increasing traffic load, the implementation of PMA appears to be virtually essential (Lu et al., 2023). Nevertheless, the consumption of polymers in asphalt modification only constitutes a small fraction of global market, rendering it quite challenging to persuade the refineries to adjust the synthetic polymer specifically for asphalt modification. Furthermore, the rapid expansion of highway network has led to a growing diversity of demands for modified asphalt binders, rendering standard (or single) polymer modification no longer sufficient(Lu et al., 2023). Based on these circumstances, there is a growing trend for the contractors/suppliers to modify the existing polymers by themselves to better align with the needs of asphalt modification.

For instance, to alleviate the incompatibility between PE and asphalt, many reported efforts in functionalizing the PE polymer by grating functional groups like maleic anhydride (MAH) (Li et al., 2014). The grafted MAH can chemically interact with asphalt and facilitates the evenly dispersion of PE polymer (Kang et al., 2010). Others also attempted to compound the PE polymer with materials that have a better compatibility with the asphalt, such as Low Density Polyethylene (LDPE) with a high melting index (L. Yu et al., 2022). The resultant compound is named as composite modifier and shows a better workability and compatibility than original PE polymer. Solutions like grafting and composite modifier are more practical and cost-effective than creating brand new polymers.

Screw extrusion process has found its place in the above-mentioned operations, attributed to its capabilities in multi-function, continuous production and relatively lower cost. Screw extrusion is a manufacturing process that involves using a rotating screw to push a material through a die (extrusion head) to achieve functions like blending, shaping or reaction (Gaspar-Cunha et al., 2022). The screw, which is contained within a cylindrical barrel, rotates and conveys the material forward while simultaneously heating and shearing it. As the material is extruded from the die, it takes on desired shape and can be further granulated for subsequent utilization. The barrel of the extruder can be sealed and thus provides a high-temperature and oxygen-free environment to facilitate possible chemical reactions of the extrudate. The shear force provided by the screw also benefits the mixing and reaction of materials. Screw extrusion is widely used for processing various materials, including plastics, rubber, fiber, food and even metals. Currently, more than half of all plastic products, including plastic bags, sheets and pipes are manufactured by extrusion. Major extruders are classified as single-screw or twin-screw (double-screw) type, the former being widely applied to general polymer processing and the latter for compounding purpose (Hyvärinen et al., 2020). A picture and diagram of a typical screw extruder is shown in Figure 1.

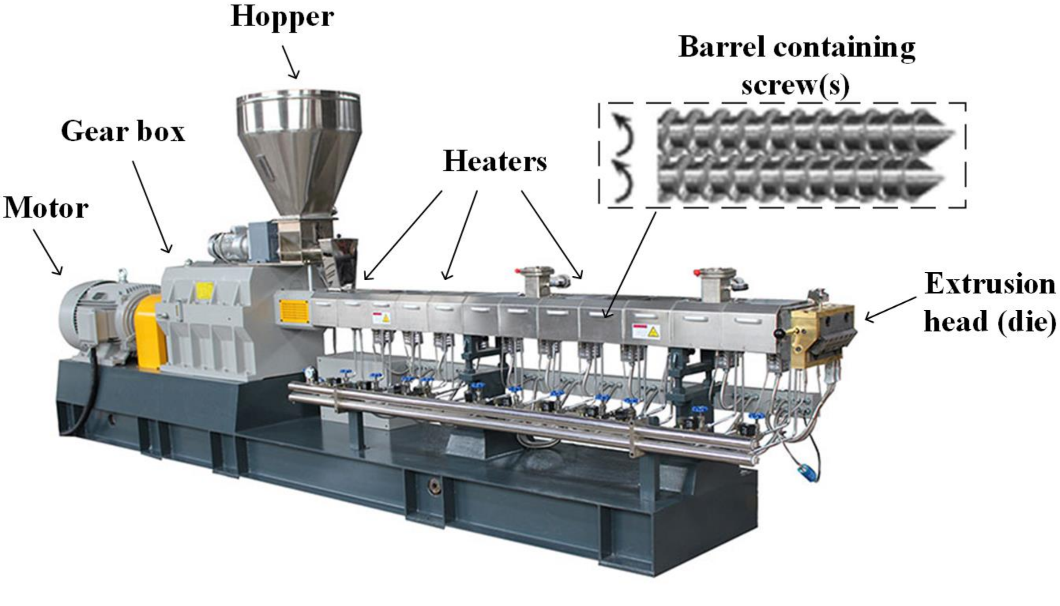


Figure 1 Structure of a typical screw extruder

Generally speaking, extrusion can be divided into two main types: compound extrusion and reactive extrusion. Compound extrusion is a common practice used to achieve melting blending of one or more kinds of materials. It is used by the asphalt suppliers to prepare composite modifiers such as SBS/PE composite, Crumb Rubber (CR)/PE composite, high viscosity modifier (e.g. TPS, short for TAFPACK-SUPER) and etc. Also, through extrusion, the composite modifier can be extruded into different sizes and forms (pellets, strips, films) to facilitate subsequent transportation, storage and production. The difference between compound extrusion and coextrusion should be mentioned as coextrusion is the extrusion of multiple layers of material simultaneously. It utilizes two or more extruders to melt and deliver a consistent volumetric flow of different materials to a single die to extrude. While compound extrusion allows a blended material to be extruded, coextrusion retains the separate materials as different layers in the final product, allowing appropriate placement of materials to achieve various functions such as anti-aging, anti-wearing and strengthening. Currently there has been no report regarding the application of coextrusion in asphalt industry.

Reactive extrusion is the process by which two or more components are compounded and undergo certain chemical reactions (e.g. degradation or grafting) in the extruder. Reactive extrusion enjoys numerous advantages such as continuous production, increased reaction rate and free-of-solvent. Furthermore, the extrusion parameters can be easily adjusted to meet the requirements of different kinds of chemical reactions, rendering it a good choice for both laboratory-scale research and large-scale industrial production. Regarding the application associated with asphalt and modifiers, reactive extrusion is usually used to graft active functional groups to original inertia modifiers (Malus et al., 2023). Another frequent application involves the devulcanization of waste CR. This process has long been a common practice in the reclaimed rubber industry (Formela et al., 2016a), but recently it has gained increasing popularity in the asphalt material field.

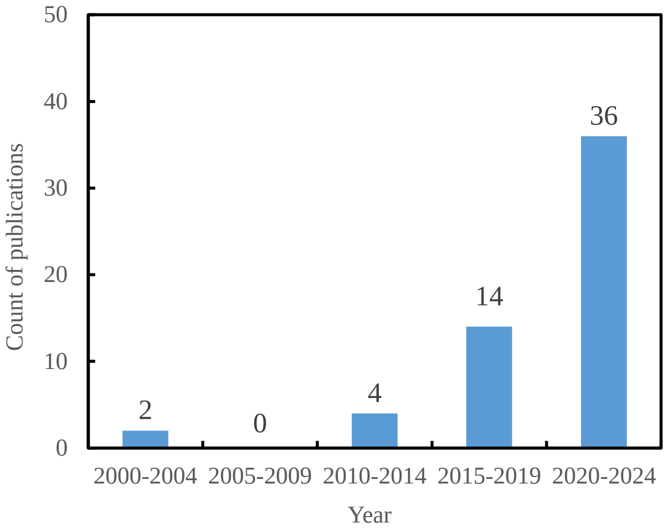


Figure 2 Articles addressing extrusion for asphalt modification published in different years

A total of 51 articles addressing extrusion for asphalt modification are reviewed in this paper, they are sorted by year and the results are shown in Figure 2. A noticeable trend is emerging as this technology gains increasing attention. To the authors best acknowledgement, the majority of articles are using extrusion to tailor asphalt modifiers rather than directly producing modified asphalt. The only exception comes from the research of Tamrin et al. (2023), who directly prepared asphalt mastic via extrusion. They used the lignin made from mahogany sawdust to modify asphalt with fine sand. 300 g sand and 100 g asphalt were blended together and extruded at 150℃, although the authors did not include any images in their publication.

According to a survey in mainland China, a typical industrial screw extruder costs between 10,000 and 50,000 US dollars, making it an affordable option for most asphalt suppliers. This had led to an increasing trend of using screw extruders to modify and manufacture asphalt modifiers for increasingly diversifying market demands. This paper aims to provide an overview of the application of screw extrusion process in the asphalt material field. After a thorough review, the examined papers are categorized into six applications: i) Plastic compound; ii) CR compound; iii) Rapid-melting pellet; iv) Nanomaterial compound; v) Grafting; vi) Devulcanization of CR. Furthermore, summary and discussion on the formulas and extrusion parameters are provided.

2 Plastic compound

Waste plastic is one of the most significant environmental issues the world encounters (Noor and Rehman, 2022; Zou et al., 2024). Currently the main recycling processing for waste plastic can be classified as four categories, namely re-extrusion, mechanical recycling (e.g. shredding), chemical recycling (e.g. pyrolysis) and energy recovery (burning as fuel) (Wu and Montalvo, 2021). Re-extrusion is the most commonly used process. The output is waste plastic pellets of uniform size and shape. The average size of these plastic pellets is typically between 2 and 5 mm, and one major application of these pellets is for asphalt modification (Salehi et al., 2022). Banfield et al. (2024) suggested that the use of recycled High-density polyethylene (HDPE) allowed for a reduction of 0.5% asphalt binder requirement. Nevertheless, the poor compatibility between waste plastics and asphalt have restrained this practice (Celauro et al., 2021). This incompatibility might be attributed to the density and chemical difference between the plastic and asphalt. Compounding the waste plastic with other materials that have a better compatibility with asphalt might solve this problem. For instance, many prepared the PE-SBS composite modifier via compound extruding. This concept is developed based on two theories. First, the polybutadiene (PB) block of SBS has a similar compatibility with the carbon backbone of PE. Therefore, the introduction of SBS can reduce the crystallinity of PE backbone. Second, the PB segment of SBS have a lot of active olefin bonds, which can chemically bond with asphalt binder and help stabilize the PE particles (Wang, 2022).

Wang (2022) conducted the PE-SBS compound extrusion at 180℃, the PE-SBS composite modifier was extruded with the mass ratio of 8:1, 4:1 and 2:1. After extrusion, he used Fourier Transform Infrared Spectroscopy (FTIR) to confirm no SBS degradation or new functional groups was generated during the process. He also used the tube test (separation test) to examine the effects of extrusion on storage stability. When PE and SBS polymer were individually added in the asphalt, a 30℃ difference in softening point was observed. But the extruded PE-SBS composite yielded a softening point difference smaller than 1.5℃, and the storage stability of the modified asphalt can be further improved with the increase of SBS ratio. Fluorescence Microscopy (FM) also showed that the PE-SBS composite modifier was uniformly dispersed in asphalt without aggregation or separation.

Cheng et al. (2020) prepared PE-SBS composite modifier with a ratio of 4:6. The SBS was commercial product and PE was recycled from shopping bags. The feed speed was 14 rpm and the screw speed was 40 rpm. The temperature from hopper to die was kept in the range of 175℃ to 195℃. This temperature range seems to be a common choice as it guarantees most polymer fluidity without causing serious chain scission to the polymer backbone. After extrusion, the obtained composites were cooled down via water bath and then pelletized for further use. Results indicated that PE-SBS composite modifier dispersed uniformly in the asphalt, but there was still clear phase separation between PE and SBS themselves. This can be alleviated by the addition of 3% treated nano-$CaCO_3$, which was coated by phthalic acid diethylene glycol diacrylate (PDDA). In this case, the nano-$CaCO_3$ was directly added into the asphalt. Nevertheless, nanomaterials can also be compounded with polymers using extrusion to avoid self-agglomeration. This practice will be reviewed in Section 5.

Vamegh et al. (2019) combined PP and SBR in various ratios of 7:3, 5:5 and 3:7. The extrusion was performed using a ZSK-25 Twin-Screw extruder at 80 rpm, 160℃. Afterwards, composites were added in the asphalt binder (penetration 60~70) at dosages of 3%, 4% and 5%. Evaluation indicated that the PP-SBR composite performed better in fatigue resistance than SBS polymer. Among all formulas, 70%SBR+30%PP shows the best performance. On top of this work, the authors further investigated the moisture and rutting resistance of PP-SBR composite modifies (Vamegh et al., 2020). It is reported that by increasing SBR content, the moisture resistance is improved. Among all tested samples, the asphalt mixture containing 5% composites (70%SBR+30%PP) showed the best performance, suggesting it can be considered as an economical alternative for SBS modifier (Figure 3).

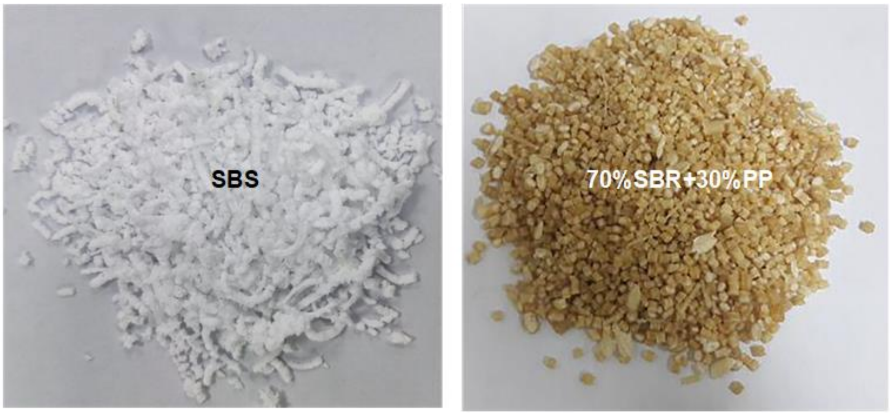


Figure 3 Appearance of SBS and SBR/PP composite modifier (Vamegh et al., 2020)

Based on the literature review it has been found that most plastics used in the asphalt modification are recycled rather than freshly produced. The recycling of waste plastics from separate collection is a well-assessed process only if homogeneous plastics are reprocessed. However this is usually not the case for practical production where a complete separation of all kinds of waste plastics are not economical feasible. Therefore Celauro et al. (2021) sought to explore the feasibility of using the mixed waste plastics (Plasmix) as an asphalt modifier.

Plasmix is the extrudate of a highly heterogeneous mixture of various waste plastics. Figure 4 depicts the Plasmix samples before and after extrusion. Based on a density separation test, its components were divided into light fraction and heavy fraction. The light fraction, characterized by a density lower than that of the water at room temperature, consists of LDPE, HDPE, and a small amount of PP. The heavy fraction mainly consists of polyethylene terephthalate (PET) with a lower content of polystyrene (PS) and trace amounts of metals and paper. The weight ratio between the light and heavy fractions was identified as 20:80. To meet the melting temperature of heavy fractions, the extrusion of Plasmix was conducted at 270°C. It was extruded using a twin-screw extruder produced by Officine Meccaniche Conte, Fondi, Latina, Italy. The feed rate was 6 rpm and the screw speed was 120 rpm. Following extrusion, the resultant filament was pelletized into sizes ranging between 2 and 6 mm.

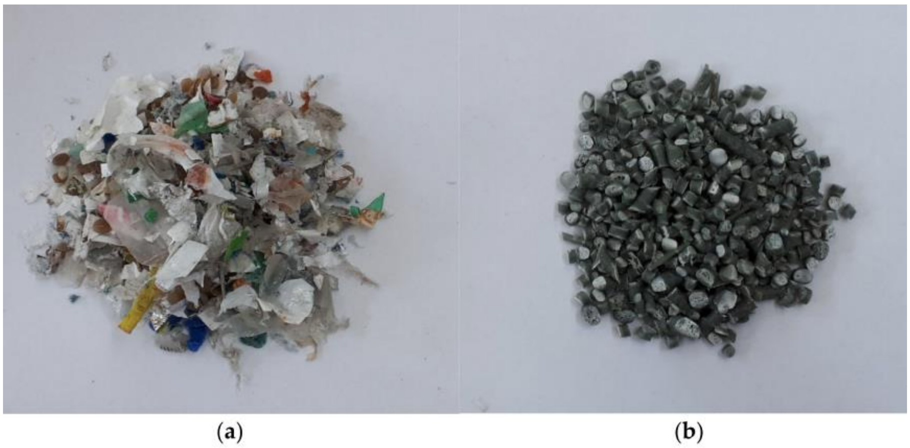


Figure 4 Appearance of plasmix (a) shreds before extrusion (b) pellets after extrusion and granulation (Celauro et al., 2021)

Preliminary test suggests that due to Plasmix's richness in heavy fractions, it failed to effectively mix with the asphalt. Therefore, the authors modified the formula of Plasmix and increased the light fraction by adding extra percentages of waste PE. The light/heavy fraction ratio was thus adjusted to 50/50 and the blend was re-extruded for examination. The re-extruded Plasmix demonstrated a good blending with the asphalt. Results of the mechanical tests prove an increase in performance and that there is a potential of the addition of the Plasmix compound both for asphalt binder and mixture modifications. The study also emphasized the necessity of homogenizing the material via extrusion before elaborated characterization or performance experiments due to the high heterogeneity of Plasmix.

The authors further compared the blending efficiency of extruded Plasmix pellets with unextruded Plasmix shreds. Results showed that shreds had a better blending efficiency than the extruded pellets. This was backed up by Banfield et al's (2024) research which reported the most efficient form to incorporate waste HDPE into asphalt was in flakes. It is believed that the uneven shape and rough edges of the shreds/flaks could help with the aggregate interlock and the physical bonding of the plastic to the asphalt. However, regarding industrial application, it is more practical to use the extruded pellets due to their standard industrial production capacity. Besides, a shred-like appearance can also be achieved using film extrusion or blown film extrusion.

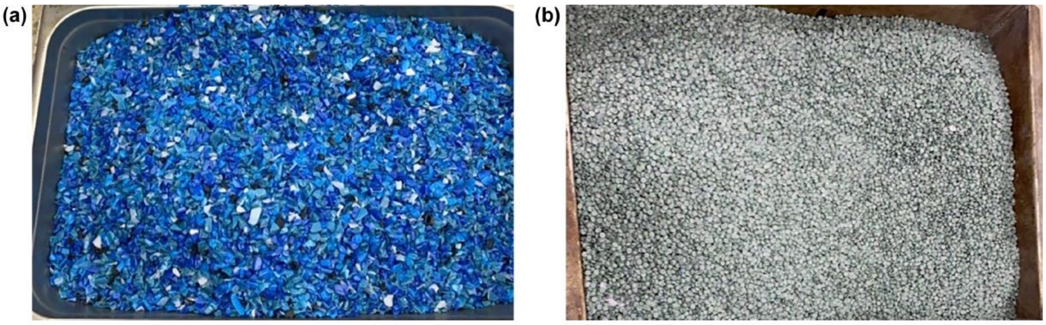


Figure 5 (a) HDPE flakes and (b) HDPE pellets (Banfield and Sanchez, 2024)

3 Crumb rubber compound

CR derived from the scrap tires is another popular waste material which gains a lot of attention in road engineering. The introduction of CR can notably improve the elasticity of asphalt binder, leading to enhanced fatigue and rutting resistance. However, due to the unique three-dimensional chemical network CR possess, it does melt or softens at high temperatures. This makes it quite difficult to dissolve CR into the asphalt binder. The application of extrusion regarding CR can alleviate this issue from two aspects. First, via reactive extrusion, CR can achieve partial devulcanization and its compatibility with asphalt will be improved. Second, via compound extrusion, CR can be mixed with specific polymers to improve compatibility with asphalt. For instance, when plastics are compounded with CR, it improves the high-temperature fluidity and plasticity of the composite modifier, rendering it better workability. As the composite inherent the elastomer nature of CR but exhibit enhanced plasticity, the composite modifier is also named as thermoplastic elastomer (TPE), or rubber-plastic alloy. This section will focus on compound extrusion associated with CR and the devulcanization process will be covered in Section 7.

Wang et al. (2014) tried to stabilize the CR by compounding it with recycled HDPE. The extrusion was conducted at 180℃ using a twin-screw extruder (ZE 25A, made by Berstorff GmbH, Germany). However, results showed that the storage stability of the composite (70%CR+30%HDPE) is not quite satisfactory, with a softening difference of 22℃. Nevertheless, the stability can be significantly improved with a small fraction of LLDPE-g-MA (1%~5%). It is suggested that during extrusion, LLDPE-g-MA induces dipolar interactions between CR and HDPE, which will help these two ingredients combine together and prevent phase separation. By comparing the separation testing results of different formulas (shown in Table 1), the authors further indicate that the density discrepancy among asphalt (1.02 g/cm^3), HDPE (0.94 g/cm^3) and CR (1.15 g/cm^3) also plays an important role in the storage stability. When CR and HDPE are compounded in an appropriate ratio, it results in a similar density to that of asphalt, effectively preventing separation. Conversely, an excessive HDPE content (e.g. 70%) causes the composite modifier to float, leading to subsequent separation.

Table 1 Different formulas and corresponding densities and tube test results (Wang et al., 2014)

No.	Content (%)			Calculated Density (g/cm^3)	Difference in Softening points (°C)
	HDPE	CR	LLDPE-g-MAH		
1	30	70	0	1.08	22
2	30	70	1	1.08	12
3	30	70	3	1.07	3
4	30	70	5	1.07	-2
5	50	50	3	1.04	1
6	70	30	3	1.00	15

Peng et al. (2023) compound CR with PE using a CTE-35 twin screw extruder produced by Kebelon Nanjing Machinery Co., LTD. The extrusion was performed at 160~170°C, with a screw speed of 360 ~ 420 rpm and a barrel residence time of 5 min. Testing results showed that the introduction of PE effectively reduced the high-temperature viscosity as well as construction temperature of the modified asphalt. But the PE content should not be excessive as it would induce the modifier prone to agglomeration and low-temperature cracking. An optimal ratio of CR:PE is recommended as 85:15.

Ma et al. (2021a) assessed the potential of using commercial CR-HDPE composite (waste soaker hose) as an asphalt modifier. The waste soaker hose has a CR:HDPE ratio of 6.8:3.2. The CR is lightly devulcanized prior to the compound extrusion. This process was expected to improve the properties of the modified asphalt through a few mechanisms: First, the lightly devulcanized CR contains carbon black with a layer of decomposed rubber coated on its surface (Wang et al., 2015). This core-shell structured carbon black together with the rubber phase are mixed with melt recycled plastic during the extrusion and will form an entangled network within the asphalt. Second, because carbon black is heavier than asphalt and plastic is lighter, the commingled CR-HDPE composite is expected to show better stability within the asphalt. Results show that the modified asphalt displayed acceptable compatibility of the asphalt and improved rutting and low-temperature resistance of the asphalt mixtures.

Ma et al. further explored the potential of using this waste soaker hose CR-HDPE composites to improve the aging resistance of modified asphalt. To do so, laboratory aging (Wang et al., 2015) and field weather aging (Y. Ma et al., 2023) were both conducted. While laboratory aging focused on thermal oxidation aging, weather aging can cause more severe degradation due to the synergistic effect among oxygen, heat, ultraviolet radiation and moisture. Results show that the CR-HDPE composites demonstrated a considerable improvement of aging resistance to the modified asphalt, indicated by a lower value of complex modulus aging index and carbonyl index. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) revealed that the CR-HDPE composite modified asphalt could sustain more heat before a rapid degradation, which means an enhanced thermal stability. Possible explanation of the increased aging resistance might include the homogenous dispersion of PE particles and the release of carbon black from the devulcanized CR.

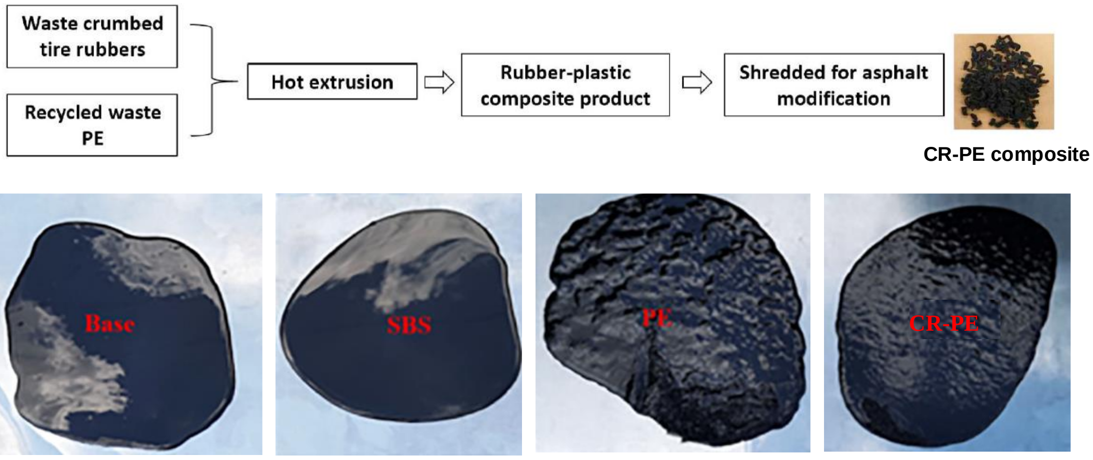
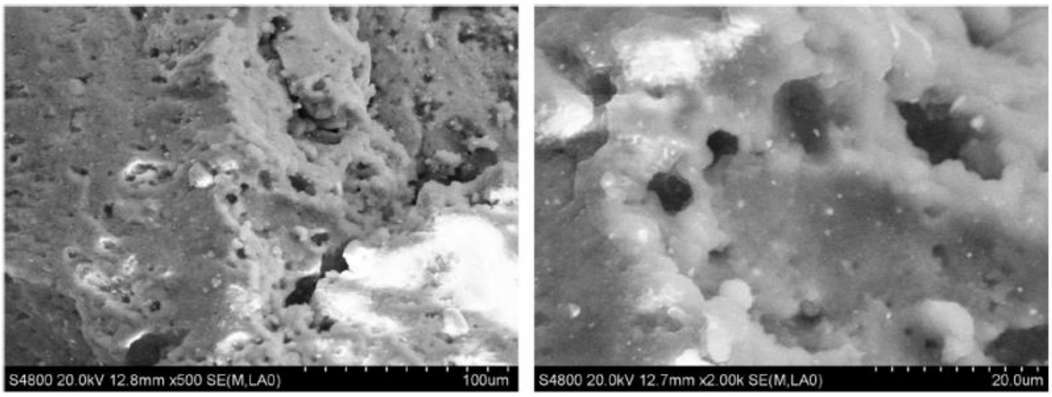


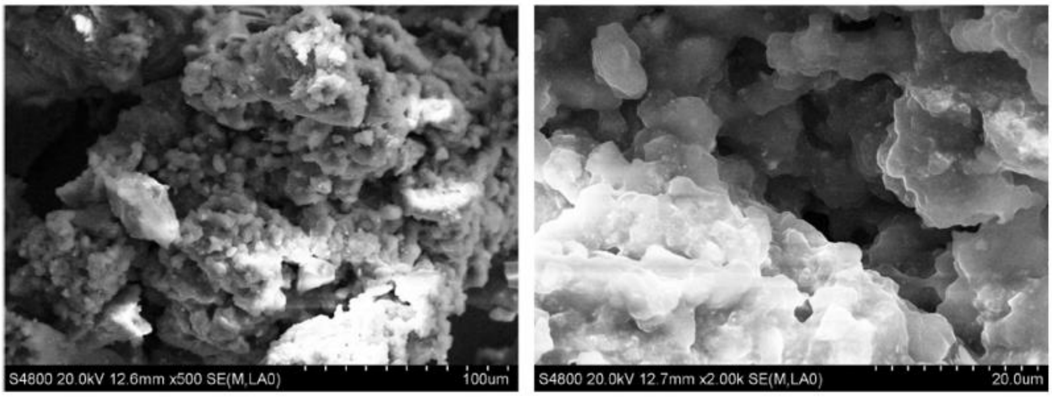
Figure 6 Preparation flowchart of CR-HDPE pellets and corresponding modified asphalt (Ma et al., 2022)

Lightly devulcanization of CR via extrusion can improve the compatibility of CR and boost the aging resistance of the modified asphalt, but it should be noted that excessive extrusion temperature or extrusion time may lead to unwanted degradation of CR, consequently leading to hindered performance. Zhang et al. (2018) used a formula of 70%CR+25%PE and a small fraction of plasticizers to extrude CR-PE composite. The extrusion was conducted at a temperature of 260℃ to achieve degradation of the CR. However, they found the produced CR-PE composite only ranks higher in softening point, but shows inferior results regarding storage stability, ductility and aging resistance (compared with direct blending the modifiers with the asphalt). It is inferred that the extreme extruding temperature of 260℃ have led to aging problems and consequently lower performances.

Liang et al. (2020a) compared the performance of CR-PE composite under ratios of 2:1 and 1:1, and the effects of CR devulcanization was also discussed. Results show that extrusion has a negative influence on the rutting resistance, which might be attributed to the polymer chain scission happened during extrusion. But it improves storage stability of the modified asphalt, which was proven by the tube test. It is seen that the increase of PE in the CR-PE composite increases the rutting resistance. Also, by replacing the conventional CR with devulcanized ones, the asphalt demonstrates weakened rutting resistance with better storage stability. The SEM morphology of devulcanized CR particles show a loosened surface with a mass of porous structures, which might be the reason for devulcanized CR's better compatibility with the asphalt.



(a) conventional CR (500x) (b) conventional CR (2000x)



(c) devulcanized CR (500x) (d) devulcanized CR (2000x)

Figure 7 SEM morphology of conventional CR particles and devulcanized CR particles (Liang et al., 2020a)

To facilitate the dispersion of CR-PE within the asphalt, it is also quite common to add plasticizers or compatibilizers. Wang et al. (2015) prepared CR-LDPE, with the presence of waste engine oil as compatibilizer. The oil has a 25℃ viscosity of 46 centi-Poise. A typical formula of CR: LDPE: oil is recommended as 70:30:15. Later Wang et al. (2015) further prepared CR-POE composite modifier using glycidyl methacrylate functionalized polymer (Elvaloy) as a compatibilizer. It is inferred that POE has saturated backbones and show a better aging resistance. But without active functional groups like double carbon bonds, POE can not be easily stabilized in the asphalt, which restrains its industrial applications in the modified asphalt. The authors mutually stabilized CR and POE in the asphalt by extrusion in the presence of Elvaloy. The CR-POE ratio is 7:3 and the Elvaloy content ranges from 0% to 6%. Results show that the extruded CR-POE dispersed more finely in the asphalt than original POE, and the hot storage stability of the modified asphalt was improved. Zhang et al. (2018) added 2% epoxy fatty acid methyl ester, 2% naphthenic oil and 0.5%

fluorocarbon surfactant in the CR-PE composite modifier (70%CR+25%PE). Epoxy fatty acid methyl ester (EFAME) and naphthenic oil are used as plasticizer. Fluorocarbon surfactant is a mold release agent which decrease the Mooney viscosity of the extrudate.

Liang et al. (2020c) evaluated the feasibility of utilization of wax residue, a by-product of Fischer-tropsch synthesis, as compatibilizer for CR-PE composite. It is found that though wax residue may hinder the rutting resistance of asphalt, it improves the storage stability and fatigue performance of the asphalt. Also, a proper wax residue addition would improve the low temperature behavior of the modified asphalt, but excessive dosage should be avoided.

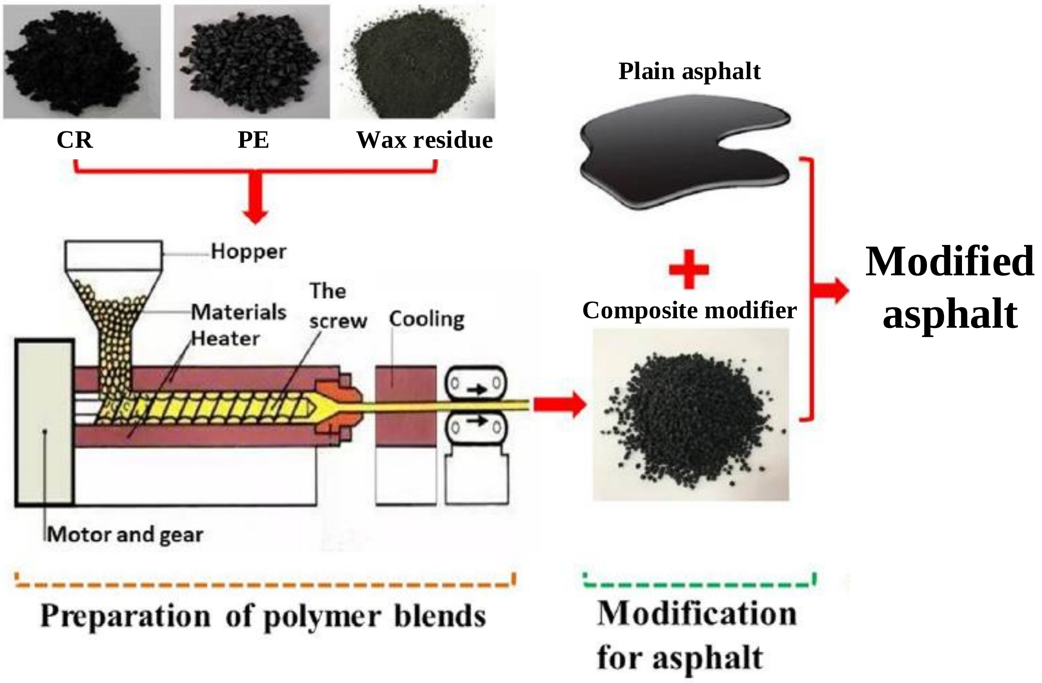


Figure 8 Preparation flowchart of CR-PE-Wax residue composite modifier (Liang et al., 2020c)

4 Rapid-melting pellet for dry-process mixing

Another major function of compound extrusion in the road engineering is to produce rapid-melting pellets/particles/modifiers for dry-process mixing. As mentioned before, conventional modifiers like SBS polymer, plastic and CR are usually incompatible with asphalt due to their large molecular weight and difference in chemical nature. To achieve a homogenous mixing between these modifiers and the asphalt, high-speed shearing or milling must be conducted, which consumes extra time and energy.

Under this circumstance, the rapid-melting pellets are developed by pre-swell the conventional modifiers with considerable portion of plasticizer or solvent. By doing so, the flowability and workability of the treated modifier is significantly improved. Incorporation of these rapid-melting pellets into the asphalt does not require high-speed shearing or milling, saving considerable amount of time and energy. The incorporation can even be performed at the aggregates dry-mixing stage (Figure 9).

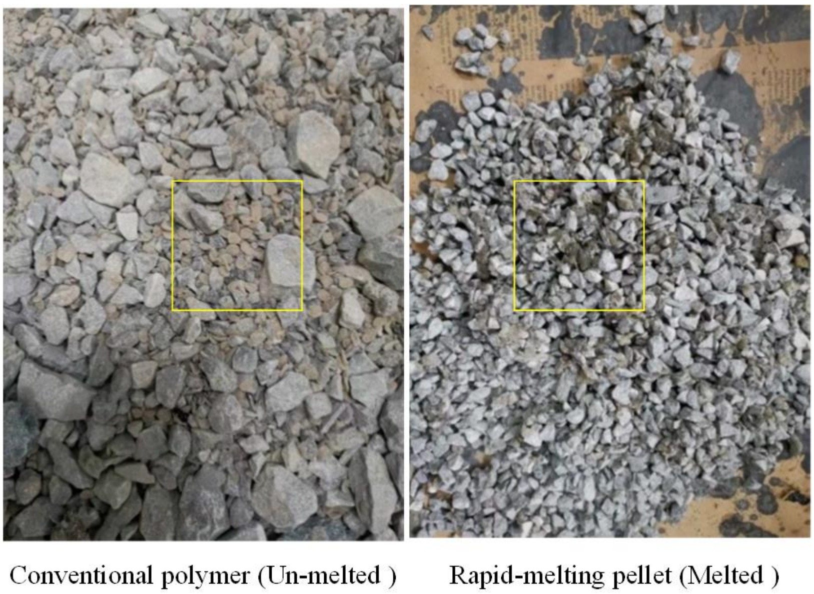


Figure 9 The appearance of conventional polymer and rapid-melting pellets after dry-mix (L. Yu et al., 2022)

The key ingredient of the rapid-melting pellets is usually elastomer modifiers such as SBS and CR, sometimes epoxy resin (Li et al., 2021) is also used. For pre-swell purpose, plasticizers from different sources (aromantic, naphthenic, waste engine oil and etc) are frequently included in the formula. Moreover, low-molecular weight polymers such as petroleum resin, plastics with a high melting index (EVA/LDPE) are also usually adopted to further plasticize the blend. Asphalt itself is also employed as a plasticizer in numerous studies (Grigoryeva et al., 2005; Lievana and Karger-Kocsis, 2004; Z. Zhao et al., 2023a, 2023b).

Zhang and his colleagues (Zhang et al., 2019b, 2019a) have published several articles focusing on the preparation of rapid-melting modifiers and formed a review on this aspect (Yan et al., 2023). They used SBS, EVA, EVA-g-MAH, naphthenic oil and butylated hydroxytoluene (BHT) as raw ingredients to extrude the rapid-melting pellets. The extrusion was conducted with an extrusion head temperature of 180℃ to avoid degradation of the polymers. It is also believed that BHT can improve the oxidation resistance of SBS. It is inferred that EVA has a similar solubility parameter with asphalt, hence by compound extrusion EVA with SBS, the composite would have a better dispersion in asphalt. The organic grafting (EVA-g-MAH) can further improve the compatibility with asphalt. The influence of SBS/EVA ratio and naphthenic oil/SBS ratio were discussed and the results show that the addition of EVA and naphthenic oil benefits the swelling of SBS and improved the workability (measured by melting index), but it may hinder the high-temperature properties like softening point. An optimized formula is recommended as follows: SBS: EVA: naphthenic oil: EVA-g-MAH: BHT in a ratio of 100:25:16:3:5.

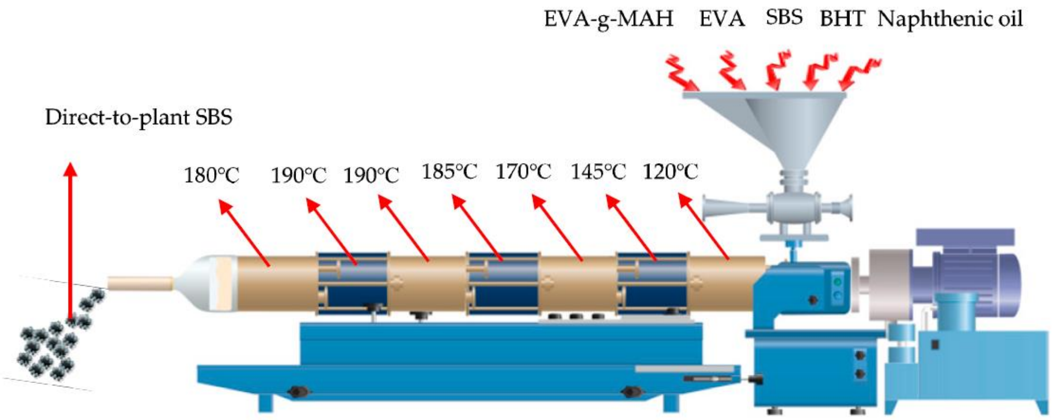


Figure 10 The heating sequence used to prepare rapid-melting pellets (Zhang et al., 2019b)

Like high fluidity EVA, high fluidity LDPE is also a common ingredient for rapid-melting pellet. Melting index is an important parameter for polymer/plastic materials, it can quantify the workability of these materials. The melting index of common PE are in the range of 0.5~2.5 g/min, which render it difficult to uniformly mixed with the asphalt. L. Yu et al. (2022)tried to extrude high-fluidity LDPE (with a melting index of 5 g/min) with conventional LDPE and SBS to prepare rapid-melting pellets. FM, FTIR and GPC characterization show that with the extrusion process and the presence of high melting index LDPE, conventional waste plastic could reach micron-level dispersion in asphalt.

To find an alternative for the famous Japanese TPS rapid-melting modifier, Shi et al. (2020)proposed a low-cost high viscosity modifier formula, using a combination of SBS, C9 resin, naphthenic white oil and talcum powder (79.5:15:5:0.5). First all solid ingredients were grinded into powder and mixed together to attain a uniform blend. The blend was kept in a container at 80℃ for 1h for curing. During which white oil was added and the container is sealed to avoid volatilization of the white oil. After curing, the blend was sent for extrusion. The extrusion was conducted at 160 ℃ using a twin-screw extruder and the screw speed was 600 rpm. Finally, the extruded strip-shaped mixtures were cooled down using a water bath and cut into pellets for further use. This is a typical production for rapid-melting pellets, and the diagram of the process is demonstrated in Figure 11. A similar approach is used by H. Yu et al. (2022), they used a combination of SBS, waste LDPE, C9 resin, aromantic oil and Talcum powder (55:15:15:14.5:0.5). Compared to the work of Shi et al. (2020), the oil content is increased and SBS is partially replaced by LDPE, therefore the cost can be further reduced. L. Chen et al. (2023) have also presented an analog for TPS modifier, where they replaced the C9 resin with terpene-styrene resin. Terpene-styrene resin has a lower melting temperature and stronger polarity, which may lead to better modification effect. The extrusion was conducted at 180℃ with a screw speed of 42 rpm. During the extrusion, dioctyl phthalate (DOP) was also utilized to decrease the viscosity of the hot melt and improve the mixability of different components. The formula consists of SBS: terpene-styrene resin: DOP in a ratio of 64:34:2.

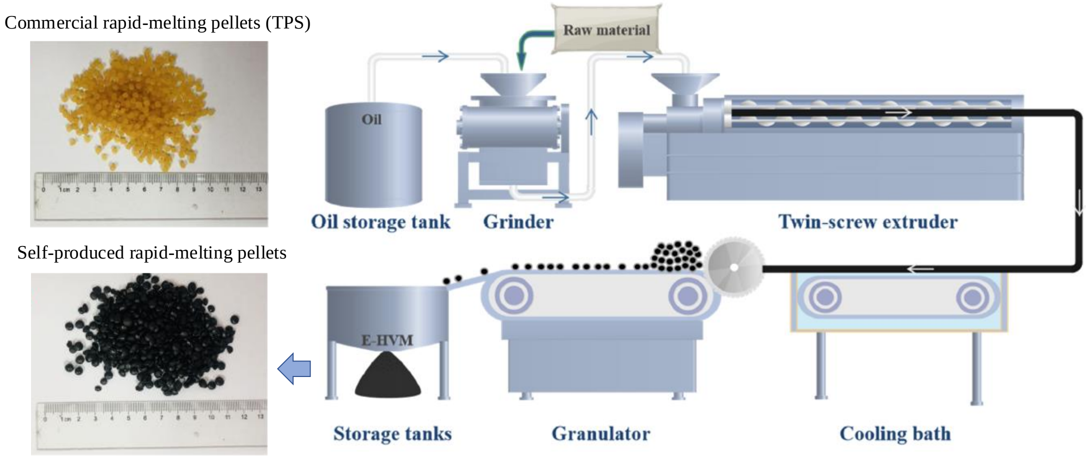
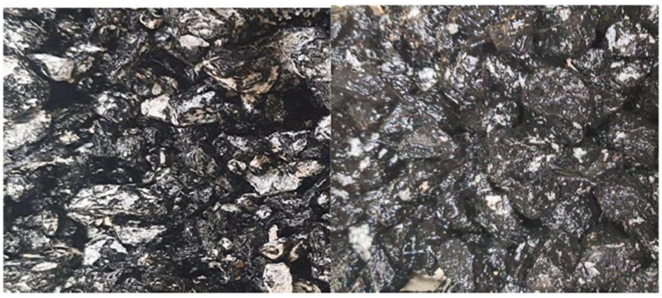


Figure 11 Diagram of typical production process for rapid-melting pellets (H. Yu et al., 2022)

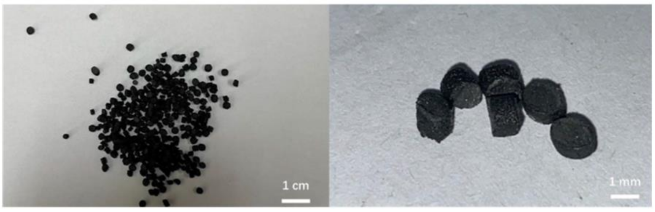
It should be noted TPS itself is also made by melt blending through extrusion. The performance comparison between TPS and self-produced rapid-melting pellet is not quite significant when the detailed formula of TPS is unknow. With the extrusion process, one can easily adjust the formula to achieve certain properties, such as obtaining extraordinarily high-temperature properties with a higher SBS dosage. But this should be balanced with the cost of the formula.

Not all rapid-melting pellets uses SBS as the key ingredient, C. Zhao et al. (2023) and T. Liu et al. (2022) extruded CR with high melting index LDPE to prepare rapid-melting pellets. Based on examination of melting index, a formula of CR: convention LDPE: high fluidity LDPE in ratio of 1:1:1 is recommended. For SBS polymers, an extrusion temperature no more than 190℃ is usually utilized to avoid degradation, but extrusion associated with CR usually requires a much higher temperature to achieve complete or partial devulcanization. They designed an orthogonal testing plan to determine optimal extrusion temperature, extrusion rate and the mesh of rubber particles. Based on the inspection on the dispersion efficiency of the asphalt on the heated aggregate, a devulcanization temperature (not extrusion head temperature) up to 340℃ is determined. This the highest documented temperature among all reviewed literature. Also, an extreme fine rubber particle size of 120 mesh is recommended. T. Liu et al. (2022) choose to perform the CR devulcanization and compound separately to avoid overheat other ingredients at such high temperature during the extrusion. They first devulcanized the CR at 270℃, with a screw speed of 50 rpm. Afterwards, the devulcanized CR was compounded with high fluidity LDPE at 220℃ (CR:LDPE=2:1). Since LDPE is added, the screw rate is increased from 50 to 80 rpm.

(a) Modified pellets in molten state at 140°C (b) Modified pellets in molten state at 160°C



(c) Modified pellets in molten state at 180°C (d) Modified pellets in molten state at 200°C

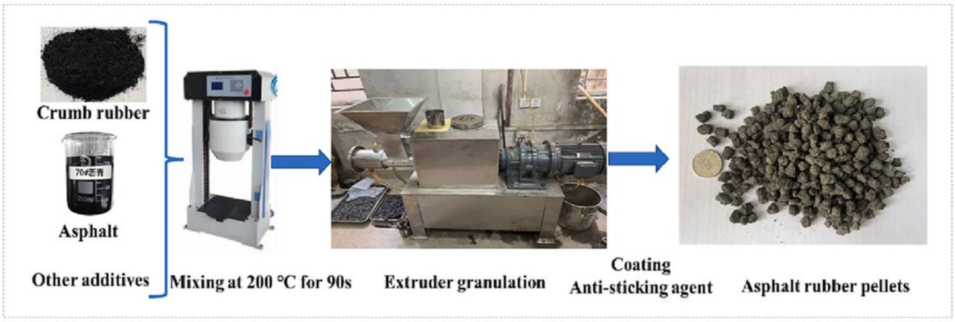


(e) Rapid-melting pellets based on CR and LDPE

Figure 12 Rapid-melting pellets based on CR and LDPE composite (T. Liu et al., 2022; C. Zhao et al., 2023)

Zhao and his colleagues (Z. Zhao et al., 2023a, 2023b) also use CR as the main component to prepare rapid-melting pellets. The novelty is that they used asphalt as the plasticizer. Z. Zhao et al. (2023a) first reported that they manufactured the pellets by combining 50% CR, 40% asphalt (penetration 60~80), and 10% calcium hydroxide together. This formula is mainly based on the granulation efficiency as the authors reported that excessive asphalt content (e.g. 50%) will make the extrudate agglomerate (Figure 13 (b)). During preparation, CR, asphalt and calcium hydroxide were first mixed at 200℃ for 90s to achieve uniform mixing, then the blend was extruded and granulated. Because the extruded pellets are easy to agglomerate, the pellets modifier is sprayed with anti-sticking agent immediately after extrusion to prevent pellets from coagulation. Figure 13 (c) shows the effects of anti-sticking agent. The resultant pellet was compared with industrial modifier PelletPAVE and results suggest that the self-invented pellet shows lower high temperature with superior fatigue and crack resistance. Later Z. Zhao et al. (2023b) published a follow-up study in which they replaced conventional CR with devulcanized CR. By doing so, the rubber ratio of the pellet is increased to 80%,. The recommended ratio for desulfurized CR/asphalt/calcium hydroxide is 8:1:1. SEM shows that desulfurized CR exhibits the rough surface and corners in contrast to the smooth surface of conventional CR. This renders a good fusion between desulfurized rubber and the asphalt, hence the increased rubber ratio in the pellet.

(a) Preparation method of the rapid-melting pellet



(b) Influence of the formula (CR:asphalt:calcium hydroxide) on the appearance of the extrudate

(b) Effects of the anti-sticking agent

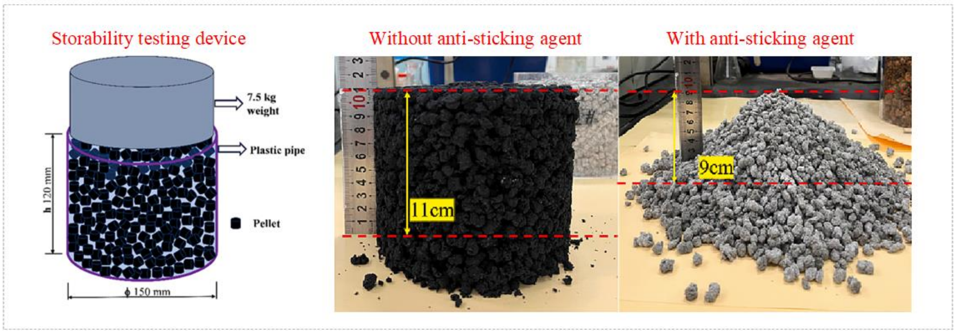


Figure 13 (a) Preparation method of the rapid-melting pellet; (b) Influence of the formula on the appearance of the extrudate; (c) Effects of the anti-sticking agent (Z. Zhao et al., 2023a, 2023b)

5 Nanomaterial compound

Nanomaterials like organic montmorillonite (OMMT), Kaolinite clay, graphene and Carbon Nanotubes (CNTs) have a wide range of applications due to their unique chemical and physical properties. Recently many used these nanomaterials as a potential asphalt modifier for improved properties. However, most nanomaterials tend to self-agglomerate during the mixing with asphalt. Also, since nanomaterials usually have a small density and powder-like appearance, the incorporation of them into either asphalt binder or mixture is quite cumbersome and labor-intense (Figure 14). To solve these problems, numerous studies attempted to pre-mix the nanomaterials with polymer via extrusion to prepare polymer-nanomaterial composite modifiers. By blending the composite modifier with asphalt, a homogenous dispersion of the polymer as well as the premixed nanomaterials can be achieved.

Figure 14 The incorporation of nanomaterials into asphalt binder or asphalt mixture (taken by the authors from the field)

OMMT is one of the most utilized nanomaterials for asphalt modification. It is a type of mineral that consists of layers of tetrahedral silicate sheets and octahedral hydroxide sheets with the nanoscale lamellar structure. It can be used for the modification of asphalt since the large surface of the montmorillonite platelets creates a gas barrier which slows down the diffusion of oxygen through the asphalt and thus retard oxidation(Belke et al., 2017). However, due to the higher viscosity of asphalt and higher surface energy of the nanomaterials, it is quite difficult to evenly disperse pure OMMT within the asphalt. Fang et al. (2013) prepared PE-OMMT composite modifier using a SHJ-35 twin-screw extruder (Nanjing, China) with a extrude temperature of 150℃ and screw speed of 90 rpm. Four different PE:OMMT ratios of 600:50, 600:100, 600:150, 600:200 are evaluated. The structure and morphology of how OMMT dispersed within the WPE was examined using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The results are shown in Figure 15.

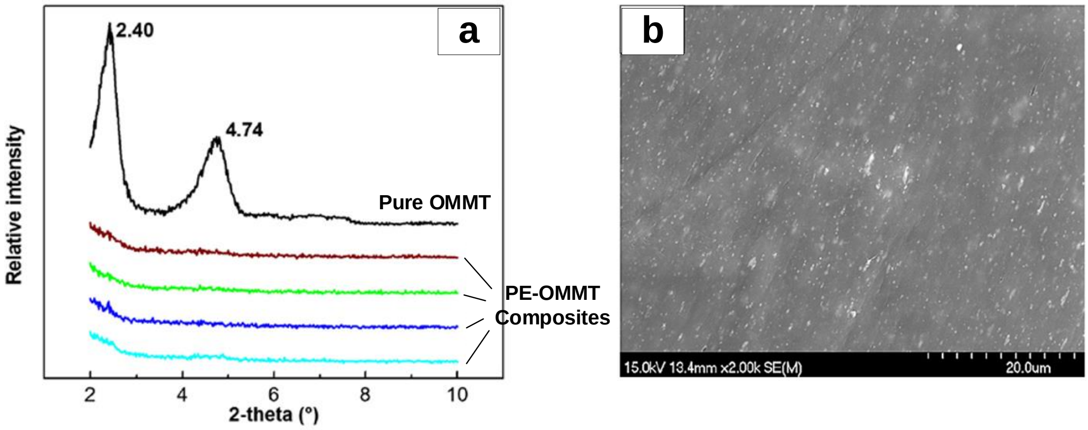


Figure 15 Characterization on the PE-OMMT composite: (a) XRD results, (b) SEM results (Fang et al., 2013)

Based on the Bragg formula, the calculated interlayer spacing of OMMT are 3.7 nm and 1.9 nm, corresponding to the XRD peaks at 2.40° and 4.74° for pure OMMT. However for the composite, there is no obvious XRD peaks for all four OMMT ratios, indicating that the interlayer spacing of OMMT in the composite is more than 4.4 nm (corresponding to the lower XRD measuring limit of 2.0° used in this article). This suggests that OMMT lamellas are exfoliated and dispersed in the PE matrix. This was further confirmed by the SEM observations, where the light particles are OMMT and darker phase is PE matrix. The exfoliation of OMMT in PE matrix can prevent the agglomeration of nanosized OMMT, thereby promoting dispersion of the OMMT in the asphalt. By incorporating the PE-OMMT into the asphalt, the swollen of PE particles are improved and the hot storage stability of the modified asphalt is enhanced.

Following the same method, Fang et al. (2014) further compounded the OMMT with waste poly vinyl chloride (PVC). Based on XRD, a similar conclusion was made that OMMT has peeled off in the process of extrusion, forming exfoliated or partially exfoliated structure. It is inferred that the formation of an exfoliated structure increases the surface area of OMMT, facilitating the insertion of the asphalt and PVC molecules into OMMT structure. Also, the exfoliated structure of OMMT results in numerous polar branches on PVC molecular chain inserted among the OMMT lamella. This is caused by the polarity of free radical chains and the large surface energy of OMMT. Therefore, the activity of PVC molecular chain is intensified and leads to better swollen and dispersion of PVC. Nevertheless, excessive OMMT addition (1.4% of the modified asphalt) should be avoided as it may cause self-agglomeration.

Fang et al. (2015) later also reported preparing composite modified asphalt by directly blending PE and OMMT with the asphalt instead of compound them beforehand. It is documented that the modification effectively improves the hot storage stability of the modified asphalt. But unfortunately, the products prepared by direct blending and compound extrusion were not compared.

Kaolinite Clay (KC) is another silicate mineral resembles OMMT. Ouyang et al. (2005) prepared SBS-KC composite (100:30) using a two-rod mill. A two-rod mill can achieve a similar blending function to extrusion, despite using different mechanical processes. Two-rod mill involves the utilization of two counter-rotating rolls, where the material is compressed, mixed and shaped into uniform sheets or strips. Unlike plastics, SBS is quite vulnerable to thermal oxidation and may degrades confronting high temperatures. Therefore, different treating temperatures of 130, 140, 150, 170 and 190℃ were evaluated. It is seen that increased temperature will cause notably degradation to the SBS and the resultant SBS-KC composite yields weakened mechanical properties and reduced molecular weight (Table 2). An odor is also noticed at preparing temperatures above 150℃, attributed to the degradation of SBS. Thus, a preparation temperature no more than 140℃ is recommended by the authors. With an appropriate content of SBS-KC composite addition (less than 2%), the stability of the modified asphalt is improved. This is attributed to two reasons. First, the active surface allows KC to chemically interacts with SBS. Second, while SBS is lighter (0.95 g/cm^3) and KC (2.57 g/cm^3) is heavier than the asphalt (1.02 g/cm^3), the of SBS-KC composite has a similar density (1.13g/cm^3) with asphalt, and this can slow down the floating of SBS polymer.

Ouyang's colleague, Wang et al. (2003) prepared an SBS-carbon black composite using the two-rod mill. The mixing was conducted at 145 °C for 5 min and an SBS:CB ratio of 100:50 is recommended by the authors. The corresponding modified asphalt exhibited improved storage stability. This is because carbon black has an active surface which can interacts with different kinds of rubber materials. SBS, as is a kind of thermoplastic rubber, can also interact and bond with the carbon black. Also, when SBS and carbon black are mixed together, the density difference between SBS and asphalt is reduced and thus the separation is slowed down.

Table 2 Mechanical properties and molecular weight of SBS/KC composite at different extrusion temperatures (Ouyang et al., 2005)

Item	Temperature					
	Before extrusion	130℃	140 ℃	150 ℃	170 ℃	190 ℃
Tensile strength (MPa)	/	20.4	19.8	13.0	11.8	3.7
Ultimate elongation (%)	/	690	740	830	980	320
Modulus at 300% (MPa)	/	3.7	3.9	3.5	3.4	3.5
Hardness, Shore A	/	83	83	83	83	82
M_n	816000	/	74800	/	48000	/
M_w	872000	/	82500	/	79800	/
Polydispersity	1.07	/	1.10	/	1.66	/

CNTs are a type of one-dimensional quantum material with light weight and perfect hexagonal structures. The radial dimension of CNTs is nano-scaled while its axial dimension is micron-scaled. Many researches have demonstrated that CNTs strengthened the interface of composites and shows certain anti-aging functions (Wang et al., 2017). Despite the high cost of CNTs, there has been a trend of using CNTs of an asphalt modifier. J. Chen et al. (2023) premixed CNTs with SBS polymer using extrusion and prepared corresponding modified asphalt. Examinations indicate the dispersion of SBS-CNTs was notably improved compared with directly blending of SBS and CNTs. Also, the introduction of CNTs improved the high-temperature performance (measured by Hamburg rutting test) of the asphalt without compromising its low-temperature performance.

Wang et al. (2017) investigated exactly how CNTs improves the dispersion of SBS by exploring the effect of CNTs on the morphology of SBS modified asphalt. To do so, three different mixing techniques of incorporating CNTs were adopted and compared (coded as Nano-SBS 1, Nano-SBS 2, and Nano-SBS 3). For Nano-SBS 1, SBS was first crushed into powders and mixed with CNTs at room temperature, guaranteeing that CNTs were coated on the surface of SBS without serious self-aggregation, the coated SBS was then mixed with the asphalt via conventional high-speed shearing. For Nano-SBS 2, CNTs were first dispersed in furfural extract oil using ultrasonic bath, then the solution was added to the pre-prepared SBS modified asphalt. For Nano-SBS 3, CNTs and SBS were premixed at 180°C via extrusion and then the composite was used to prepare modified asphalt. FM (Figure 16) shows that

Nano-SBS 3 (extrusion process) shows the strongest SBS polymer network with a unique “orange-skin” morphology, indicating SBS phase and asphalt phase have achieved adequately mixing. This explains why Nano-SBS 3 yields the best storage stability and high temperature properties (measured by dynamic viscosity and softening point). The results from the molecular dynamic simulation showed that SBS intertwined or surrounded CNTs to improve their interaction. Saturate, aromatic, and resin were absorbed into the tube of CNTs. Therefore, CNTs had a positive action on the interaction between SBS and asphalt because they acted as a bridge to link the different phases, finally reinforcing the interface of SBS-PMBs.

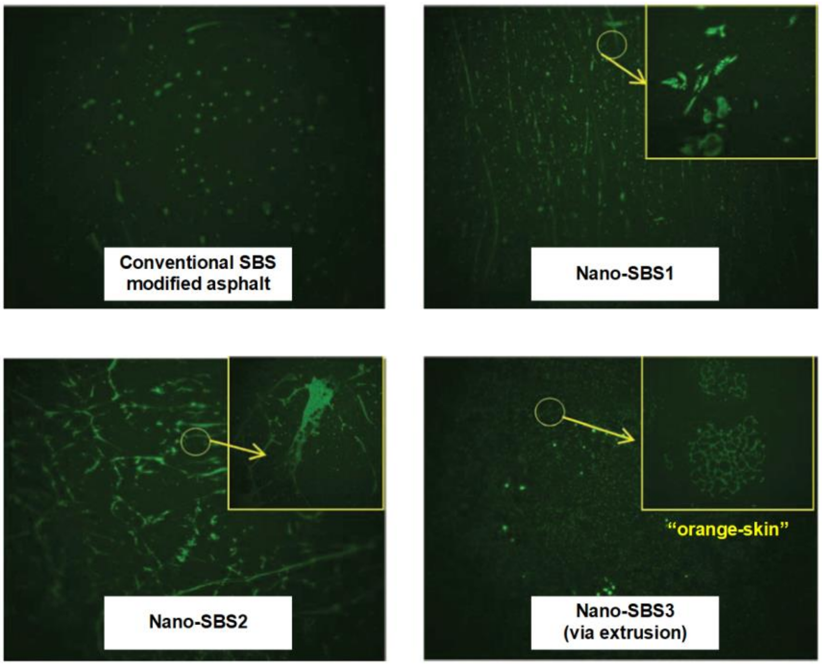


Figure 16 FM images of modified asphalt prepared by different techniques (Wang et al., 2017)

J. Liu et al. (2022) evaluated the properties of asphalt modified by a commercial PP-graphene nanoplatelet (GNP)-carbon black composite. It is prepared via extrusion and the ratio of PP: graphene: carbon black is 95:2.5:2.5. The results of composite modifier and directly adding PP and graphene are compared and the composite modifier yields better performances in terms of intermediate and low-temperature properties. The authors inferred that different incorporation methods have formed different micro structures in the asphalt matrix. The possible mechanism is illustrated in Figure 21. The modified asphalt formed by the direct incorporation of PP, graphene and carbon black (method #2) mainly relied on the strong adsorption of graphene, which adsorbed certain PP molecules on the laminated surface. However, this effect is limited due to the graphene’s agglomeration tendency. Therefore, there is no major difference in the mechanical performance between the PP/graphene/carbon black modified asphalt and conventional PP-modified asphalt.

In contrast, via extrusion (method #1), PP, graphene and carbon black was fully integrated, exhibiting a structure of part of graphene nanosheets embedded in PP blocks and others closely adsorbed on PP spheres, which possessed both the stiffness of PP and the toughness, thermal conductivity, and lubrication properties of graphene. Meanwhile, this endows PP with great toughness and less possibility of crystallization. Consequently, this unique structure, further enlarged the spatial distance of the graphene nanosheets and increased the contact area and strength of the interface between graphene and PP, thus potentially improving the strength of the composite.

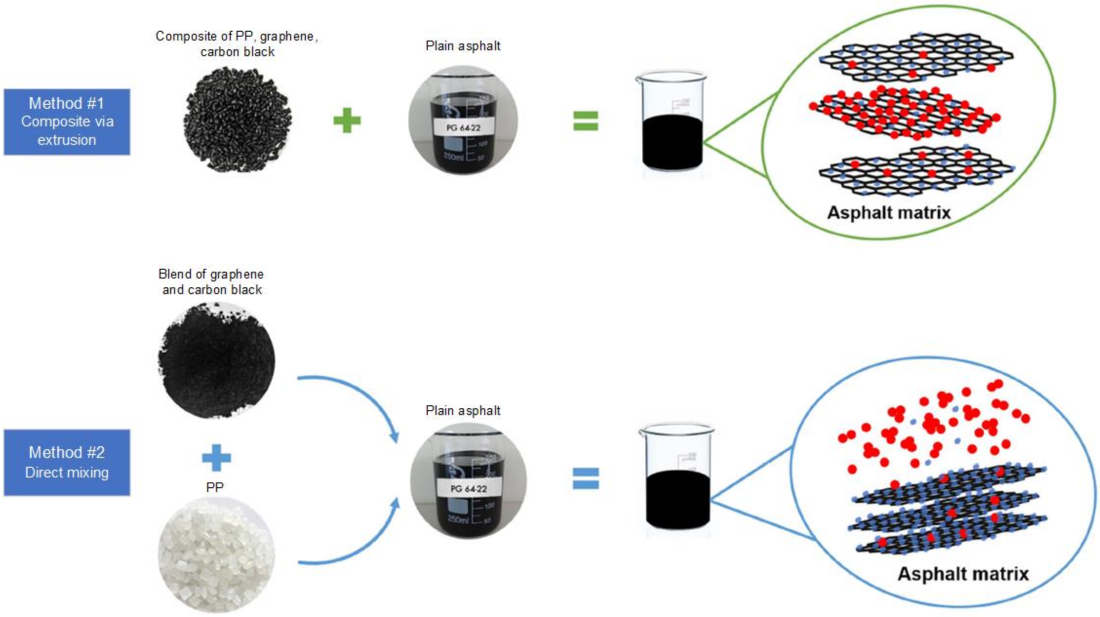
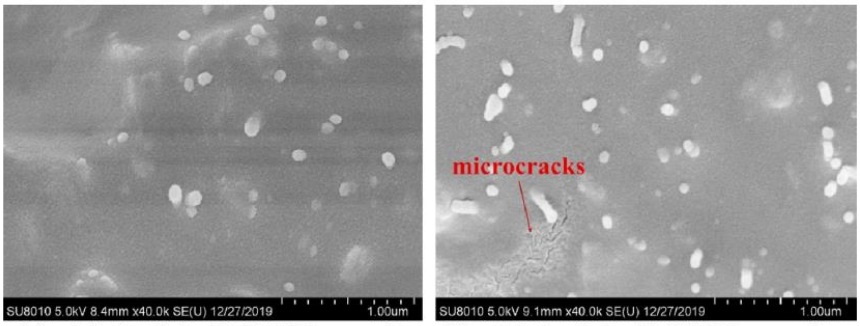
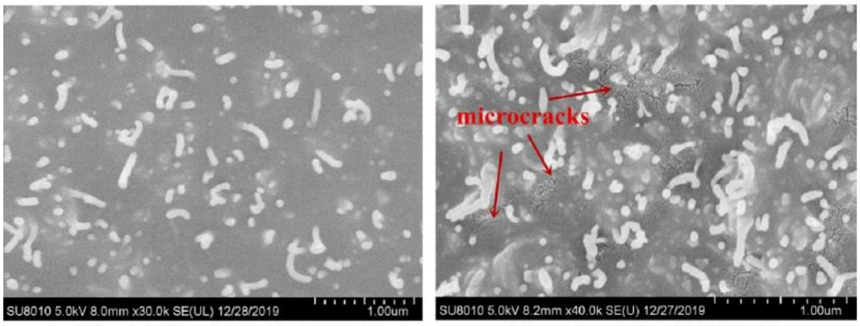


Figure 17 Illustration of interaction mechanisms of two different incorporation methods (J. Liu et al., 2022)

Xin et al. (2020) and Liang et al. (2020b) evaluated a commercial PE-CNTs composites supplied by JCNANO Company, Nanjing, China. It is in the form of black pellets and was prepared by compound extrusion with PE and CNTs and PE (80:20). It has a density of 0.952 g/cm^{-3} and melting point of 145℃. SEM (Figure 18) shows that when CNTs and PE are directly added in the asphalt, CNTs were mostly dispersed in asphalt matrix, whereas for the premixed PE-CNTs composite, most CNTs were incorporated inside the bulk PE. Considering the high strength of CNTs, direct blending of PE and CNTs will lead to better high-temperature properties. The advantage of PE-CNTs composites is that once the PE matrix is dispersed homogeneously in asphalt, the CNTs is evenly dispersed simultaneously. Also, after aging, lots of micro-cracks occurred in the morphology of asphalt for directly added CNTs and PE. This may be caused by the evaporation of light component of asphalt fractions. For PE-CNTs composite modified asphalt, fewer micro-cracks are observed after aging. This implies that the dispersed PE-CNTs composites can absorb some of the light asphalt component, which retards the evaporation of light asphalt fractions during aging. That suggests PE-CNTs composite modified asphalt has a better antiaging performance. The authors further (Liang et al., 2020b) conducted more performance evaluation tests and reported that PE-CNTs composite modified asphalt also showed better moisture resistance and storage ability. This is explained by that CNT bridges the interface between PE phase and asphalt, enhancing the bonding between interfaces. Xin, Liang and their colleagues (C. Ma et al., 2023; Su et al., 2023; Xin et al., 2022a, 2022b) later published a series of articles focusing on using CNTs based composite as flexible sensors for traffic monitoring. Polymers like epoxy and polystyrene microspheres are selected as carrying matrix for CNTs. The introduction of CNTs renders the polymer blend conductive and thus can be used as a flexible traffic monitor. Nevertheless, the blend of the polymer and nanomaterials are not achieved by extrusion but mostly via solution method.



(a) original asphalt with CNT/PE composites (b) original asphalt with CNT/PE composites



(c) original asphalt with CNT+PE (d) aged asphalt with CNT+PE

Figure 18 SEM images of asphalt modified with PE-CNTs composite and prepared by directly blending with PE and CNTs. (Xin et al., 2020)

Fiber is another light-weight modifier that encounters blending and stability issues like nanomaterials. Zhang et al. (2016) once used waste LLDPE with PAN-based carbon fiber (PANCF) to modify asphalt. The LDPE was recycled from waste bags and the PANCF was short-cut with an average length of 5 mm. The modification was achieved using different methods including direct blending, solution method and extrusion method. In the extrusion process, PE and PANCFs were mixed and extruded at 170 °C to prepare composite modifier. It is found that the modification by PE and short-cut PANCFs can obviously improve high temperature performance and resist deformation of the modified asphalts. PE and short-cut PANCFs are best dispersed into asphalt by the extrusion method. In the modified asphalts prepared by the extrusion method, a network is well formed by PANCFs and PE, which prevents segregation and improves the hot storage stability and high temperature performance.

6 Grafting of functional groups

Adding functional groups to original inertia polymer is a quite common process in the polymer industrial field (Li et al., 2003). Functionalized polymer is of great importance for application as compatibilizers in polymer blends, as adhesion promoters for polymer and composites and as bonding agents for polymer and metal (Moad, 1999). Plastics usually show a high tendency to crystallize at ambient temperatures. When using plastics as asphalt modifier, it may lead to phase separation and deteriorated road performances. Inspired by the work in polymer filed, asphalt scientists are using grafted plastics as modifiers to achieve better compatibility and improved bonding/flexibility. MAH is the most utilized functional groups for asphalt. Some other frequently used functional groups include ester and epoxy (e.g. GMA, MAA) (Jun et al., 2008). However those functional groups are more commonly incorporated with the asphalt modifier using solution process instead of extrusion process.

Ma et al. (2016) grafted MAH onto waste PE to prepare a functionalized asphalt modifier (PE-g-MAH) via reactive extrusion. 1000 g of waste PE pellets, 7.5 g of MAH and 5 g of Dicumyl peroxide (DCP) were first mixed at room temperature and then extruded at 175℃. Grafting is usually started from forming free radicals through subtraction of hydrogen atoms from the polymer chain through the initiator radicals, followed by the addition of the unsaturated MAH monomer to react with the radicals. Hence during extrusion, initiator (e.g. DCP) which generates radicals is frequently adopted. After extrusion, the grafting degree is confirmed using FTIR. To do so, the extrudate was first dissolved in refluxing xylene with excess acetone. By this procedure the un-grafted MAH was separated from the desired PE-g-MAH. The precipitated sample was filtered, washed and dried under vacuum at 80℃ for 24 h. Then the purified sample was sent for FTIR characterization. The results are shown in Figure 19. Absorption peaks at 1868 cm^{-1}, 1790 cm^{-1} and 1715 cm^{-1} are due to different vibrations of carbonyl functional group. Since PE does not possess carbonyl, the existence of such functional group confirms the successful grafting of MAH. The influence of DCP content (0~3 %) and MAH content (0~2%) were discussed. Because there are multiple interaction routes between DCP, MAH and PE, it is necessary to increase the content of DCP and MAH simultaneously to increase the grafting degree. An excessive DCP content might lead to crosslinking rather than grafting, and thus should be avoided.

The influence of extrusion temperature was also investigated. It is found that extrusion temperature affects the grafting through two aspects (Table 3). Firstly, it increases the melting index of the polymer blend and facilitate the extrusion efficiency. Second, an extreme temperature may lead to a rapid decomposition of the DCP initiator, causing a high concentration free radicals and increased ratio of side reactions (decreased grafting degree). A balance should be made between these two factors. The authors recommended that the grafting reaction should be controlled at 160℃~195℃. With a suitable extrusion temperature and well-balanced DCP/MAH ratio, the prepared of PE-g-MAH as an asphalt modifier, can notably improve the rutting resistance of the asphalt binder.

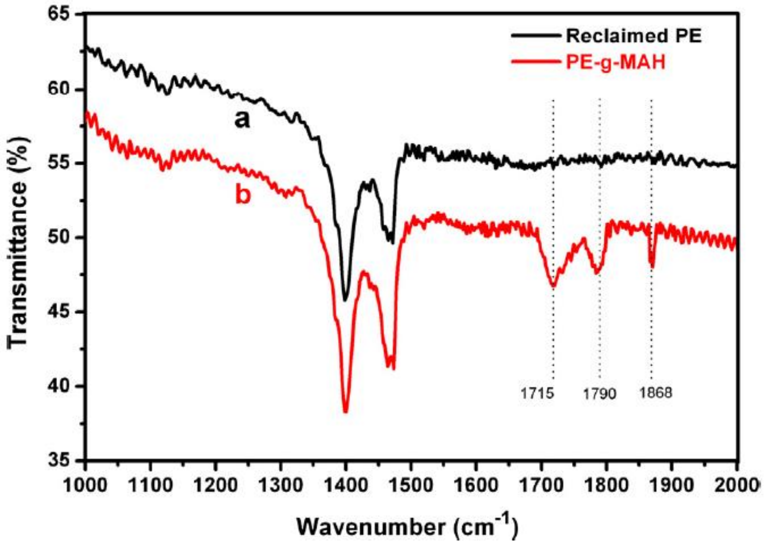


Figure 19 FTIR spectra of waste PE and PE-g-MAH (Ma et al., 2016)

Table 3 Effects of temperature on melting index and grating degree (Ma et al., 2016)

Temperature (℃)	Melting index (g/10 min)	Grafting degree (%)
155	2.34	0.67
165	2.96	0.72
175	4.3	0.79
185	6.54	0.82
195	8.41	0.77

Malus et al. (2023) grafted functionalized propylene (FPP) with poly(styrene-co-maleic anhydride) (SMA) using both solution process and reactive extrusion. They compared the efficiency of these two methods and found out solution process has a higher efficiency. Nuclear Magnetic Resonance (NMR) characterization shows while solution process yields a 57% conversion rate, reactive extrusion shows a 38% conversion rate. Nevertheless, the authors indicated that the solution process is quite complicated and labor-intensive, and their future study will be focusing on improving the reactive extrusion to obtain products with similar properties as those produced in a solution.

X. Xu et al. (2022) used Haake torque rheometer to achieve thermal-and-mechanochemical recycling of waste polypropylene into asphalt modifier with warm-mix functions. Recycled PP and different amounts of DCP (1‰, 3‰, and 5‰) were mixed at 180℃ with a shear speed of 40 rpm for 5min. 1.5% MAH and 5~20% epoxidized soybean oil (ESO) were also included in the mixing in another related study (Xu et al., 2023). The final product was collected and granulated for asphalt modification. It is believed that DCP can chemically degrade PP, resulting in better flowability. Grafting of MAH and ring-opening reactions of ESO also happened during the mixing. ESO can fully participate in the grafting reaction between PP and

MAH, leading to an increase in the molecular weight and hardening of the molecular structure. Evaluation on the modified asphalt shows that the treated PP can reduce the asphalt production temperature by 20~40℃ and improve the deformation and fatigue resistance. An optimal DCP dosage of 3‰ and ESO dosage of 5% are recommended.

Vargas et al. (2013) investigated the application of LDPE-g-MAH, HDPE-g-MAH and bimodal high density polyethylene (BHDPE)-g-MAH in asphalt. Though the specific procedure of the reactive extrusion is not documented, they reported that grafted polymers allow for an improvement in the miscibility between polymer and asphalt, while non-grafted polymers were not readily miscible with asphalt. Other than plastics, Vargas et al. (2015) grafted SBS, SIS and SEBS with MAH. The grafting is conducted at 160℃ in a twin-screw conical counter-rotating Haake Rheocord Extruder 90, with an L/D ratio of 24:1, working at a screw speed of 70 rpm. Benzoil peroxide was used as the initiator. To avoid gelation, the grafted MAH content is less than 2%. The properties of the original and grafted polymers are summarized in Table 4. It is seen that grafting leads to a slight increase in molecular weight as well as an increase in polydispersity. This indicates that the grafting mainly occurs on the secondary or tertiary carbons and few backbone-scission has occurred.

Table 4 Properties of the original and grafted polymers

Polymer	MAH (%)	$T_{g,PS}$ (℃)	$T_{g,PMID}$ (℃)	$\delta H_{Tm\beta}$ (J/g)	M_w (10^4 g/mol)	D
SBS	-	92	- 89	-	7.133	1.096
SIS	-	90	- 74	-	8.168	1.038
SEBS	-	70	- 72	10	7.166	1.086
SBS-g-MAH	0.4	92	- 86	-	8.207	1.210
SIS-g-MAH	0.8	87	- 65	-	9.468	1.820
SEBS-g-MAH	2	65	- 61	8.7	9.184	1 .283

From the FM images shown in Figure 20, it is inferred that grafted polymers improve the morphology and interaction between the mixture components while the original polymers (SBS, SIS and SEBS) present a poor polymer distribution. The mechanical properties (penetration, softening point, G*) of the asphalt modified by grafted polymers are also better than their non-grafted counterparts. In a subsequent study, Vargas et al. (2023) further blend the grafted polymers with montmorillonite clay. It is believed that the functionalized group can develop strong interactions with clays to generate reactive nanoclay-polymer layers, which can further improve the binder properties.

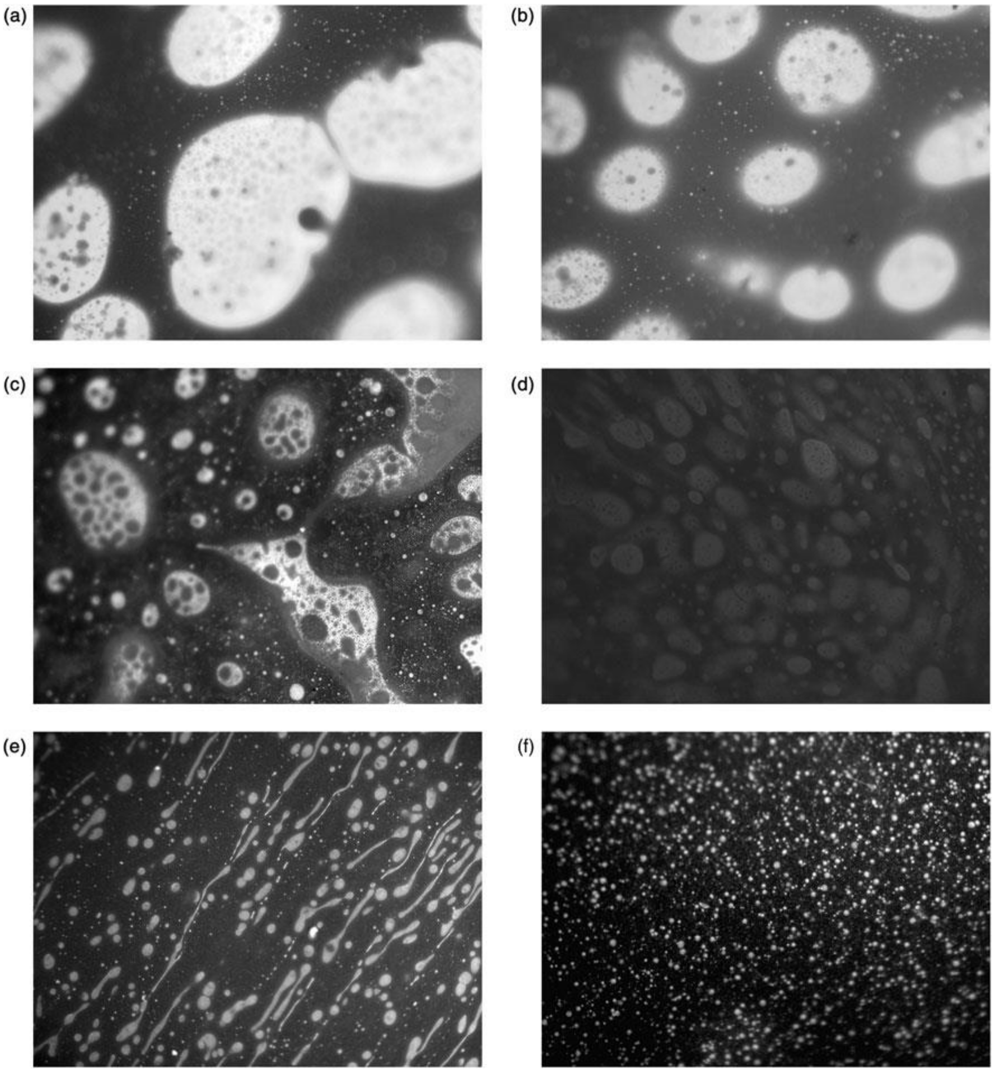


Figure 20 FM images of modified asphalt: (a) SBS, (b) SBS-g-MAH, (c) SEBS, (d) SEBS-g-MAH, (e) SIS and (f) SIS-g-MAH. (Vargas et al., 2015)

7 Devulcanization of crumb rubber

Waste CR possess a unique three-dimensional chemical network, posing a great challenge for the recycling and reutilization of this material (Wu et al., 2016). This crosslinked chemical network is the main cause for the incompatibility and consequent poor storage stability of conventional rubberized asphalt, which limits the further utilization of this technology (Jin Li et al., 2022). To appropriately utilize CR as an asphalt modifier, it is necessary to devulcanize it to a certain degree and thus improve its compatibility with asphalt. Many attempts have been explored to achieve partial devulcanization of CR, and extrusion appears to be one of the most promising ones. It has numerous advantages like high production efficiency, continuous operation and controllable pollution, which means the toxic exhaust emitted during the devulcanization can be centrally disposed, attributed to the enclosed barrel of the extruder. It should be noted that extrusion has long been a common practice in the production of reclaimed rubber (a cheap substitute of fresh rubber during manufacture of new rubber products) (Formela et al., 2016a), only recently picking up the attention among asphalt field scientists.

Jin Li et al. (2022) composed diagrams of how extrusion works to achieve CR devulcanization (Figure 21). When CR is fed to the extrusion, it will be heated up to 180℃~300℃ via heaters and shearing friction. The heat as well as strong shear force will lead to the breakage of C-C/C-S/S-S bond inside CR, which leads to both devulcanization and degradation of the CR. The idea is to achieve selective scission of crosslinks (devulcanization) with negligible backbone scission (degradation). This shall produce devulcanized CR with high mechanical properties and good compatibility with the asphalt. During extrusion, the barrel can be sealed and thus the toxic exhaust can be collected through a single outlet and disposed centrally. Decrosslinking agent are also frequently employed during the extrusion to accelerate the process. The most commonly used decrosslinking agent include organic disulfides, such as 2, 2’-dibenzothiazole disulfide, and dixylyl disulfide.

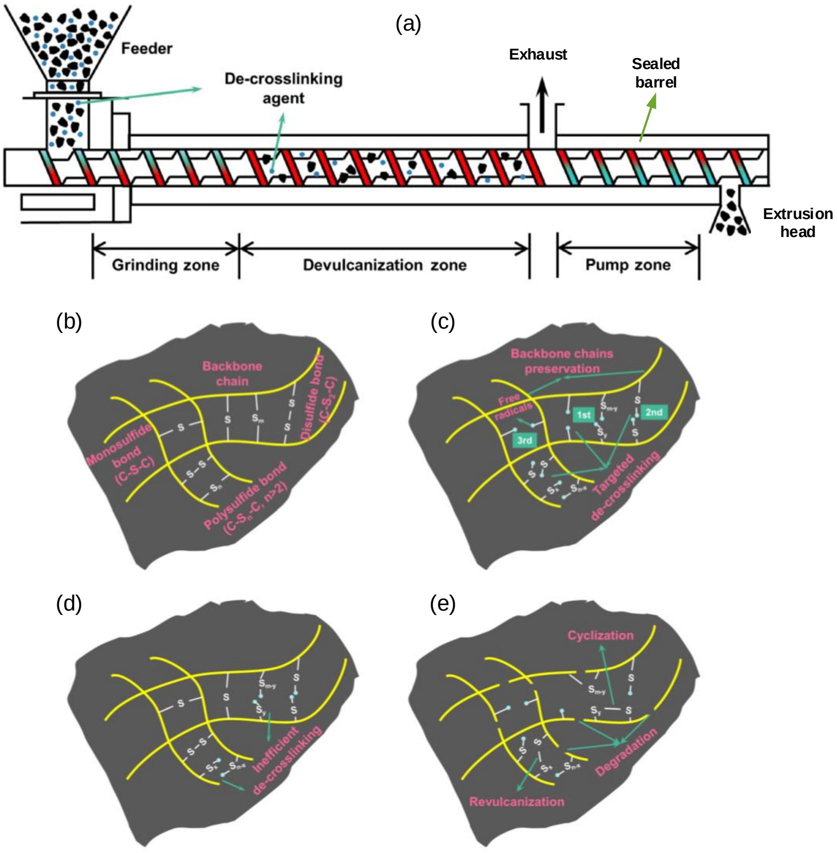


Figure 21 Illustration of: (a) diagram of CR devulcanization via extrusion, (b) crosslinked structure in CR, (c) ideal de-crosslinking, (d) inefficient de-crosslinking, (e) excessive de-crosslinking. (Jin Li et al., 2022)

Zhou et al. (2023) compared the rubberized asphalt prepared by extruded CR and untreated CR. The extrusion was conducted at 200 ℃ with a screw speed of 600 rpm.

The devulcanized CR was blended with asphalt at the dosages of 18%, 22%, 26%, and 30% to prepare modified asphalt. It was found that the devulcanized rubberized asphalt is remarkably better than conventional ones in terms of storage stability, high-temperature performance, fatigue resistance, and low-temperature performance (Q. Ma et al., 2021). The results show that the swelling process of devulcanized CR was more adequate and absorbs more light components during swelling, which was crucial to improve the performance and storage stability of the modified asphalt. An appearance comparison between the conventional rubberized asphalt and devulcanized rubberized asphalt is shown in Figure 22

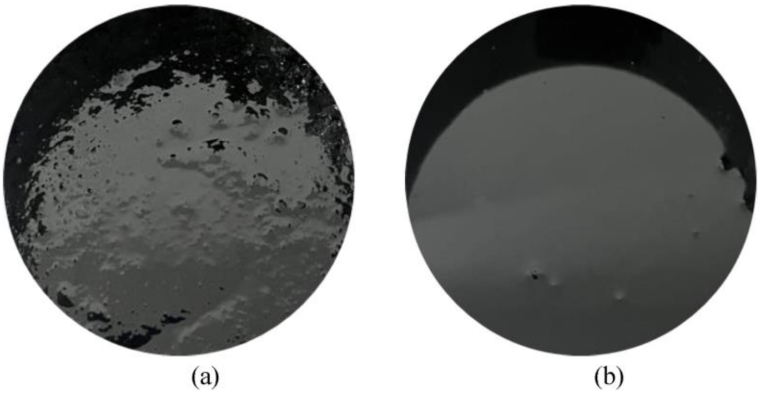
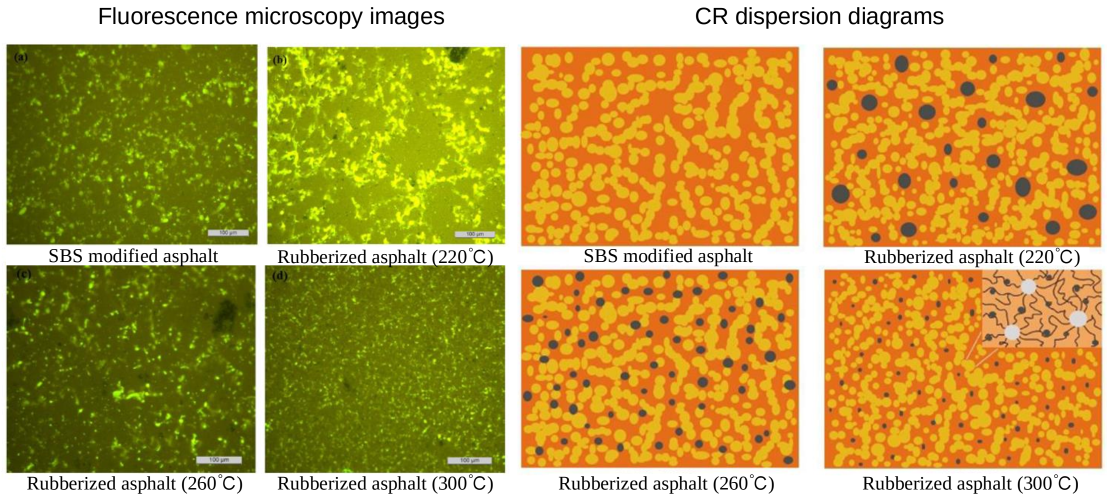


Figure 22 (a) conventional rubberized asphalt, (b) devulcanized rubberized asphalt.

The devulcanization degree of CR is affected by a series of factors like temperature, screw speed and even rotation directions. Temperature is usually considered as the main parameter (Phiri et al., 2022). Generally speaking, a high extrusion temperature will lead to more drastic devulcanization and even severe backbone degradation. On one hand, a higher devulcanization degree translates to better storage stability/lower construction viscosity and better fatigue/cracking resistance, but on the other hand, it may damage the high-temperature deformation resistance. Since the main issue associated with CR modifier is incompatibility, CR devulcanization usually employes a relatively higher extrusion temperature (up to 300℃).

Tur Rasool et al. (2017) investigated the effect of devulcanization degree on morphologies, physical properties and aging behavior of the modified asphalt. Three temperatures (220 ℃, 260 ℃, 300 ℃) were selected with a screw speed of 100 rpm. The resultant devulcanized CR was then blended with 5%SBS modified asphalt to prepare composite modified asphalt. They found out that all devulcanization degrees lead to good aging resistance, and the compatibility of higher devulcanization temperature is better. Also, by adding sulfur to the modified asphalt, more improvement can be achieved as sulfur can co-crosslink the devulcanized CR with SBS and asphalt, which makes the modified asphalts more homogeneous. To understand the modification mechanism of the devulcanized CR, Rasool et al. (2018) further conducted TGA, DSC and FM. It is indicated that temperature decides the size of the dispersed rubber particles. A higher degradation temperature leads to a smaller particle size. When the temperature is high enough, not only micro scale level rubber particle but nano-sized carbon black is observed, which is the sign of highly destruction of the rubber network. The extent of rubber dissolution in asphalt increases by up to 60% when the degradation temperature is raised up to 300℃. The FM images and corresponding CR distribution diagrams of different extrusion temperatures are shown in Figure 23. These different structures can lead to much different thermal and rheological behaviors of the modified asphalt.



SBS modified asphalt
Rubberized asphalt (220˚C)
SBS modified asphalt
Rubberized asphalt (220˚C)
Rubberized asphalt (260˚C)
Rubberized asphalt (300˚C)
Rubberized asphalt (260˚C)
Rubberized asphalt (300˚C)

Figure 23 FM images and CR dispersion diagrams of different modified asphalts. (Rasool et al., 2018)

G. Xu et al. (2022) also investigated the influence of extrusion temperatures on the devulcanization of CR, and they used Mooney viscosity of the extrudate to quantify the devulcanization degree. As the temperature increased from 240℃ to 260℃ and 280℃, Mooney viscosity decreased from 80 to 40 and 20. The molecular weight of the sol fraction within the CR also reduced. The resultant devulcanized CR are shown in Figure 24. Authors claim that as the devulcanization degrees of CR increased, the certain road performance of modified asphalt was improved, including low-temperature crack resistance, medium temperature fatigue.

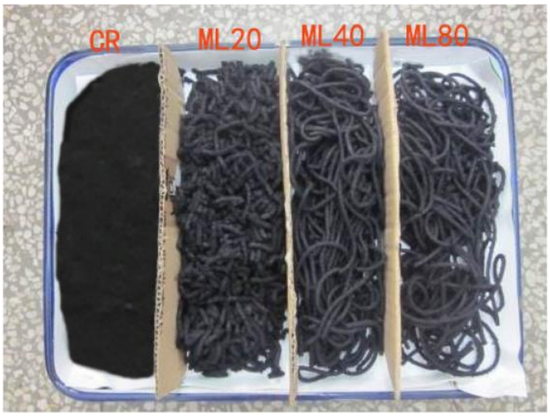


Figure 24 Devulcanized CR of different extrusion temperatures

At some point, when the devulcanization and degradation is so severe, CR may even become liquid and the resultant product is called liquid rubber. Wu et al. (2016)

once prepared extruded CR under 5 different temperatures (220℃, 240℃, 260℃, 280℃, and 300℃). The screw speed and barrel residence time is not mentioned, but it is inferred when the time is long enough, the extrudate starts to obtain fluidity. Waste oil was also added to further increase the fluidity of the extrudate. The extrudate (i.e. liquid rubber) showed a high sol content and similar properties to plain asphalt, such as low viscosity and balanced rheological properties. Liquid rubber could be used over 50% by weight as asphalt alternative, which endowed the asphalt with outstanding lower temperature property. Fini et al. (2016) have also reported a similar liquid rubber product as asphalt modifier, but they used vacuum pyrolysis instead of extrusion to achieve the devulcanization. Currently the vacuum pyrolysis of CR has been forbidden by most nations and areas due to environmental concerns.

Figure 25 Liquid rubber prepared by vacuum pyrolysis (Fini et al., 2016)

Though most articles utilized a relatively high extrusion temperature (up to 300℃) for CR, many scientists (Saiwari et al., 2014) from the reclaimed rubber field suggested that it might be beneficial to consider a lower extrusion temperature. This is because that low temperature ensures selective scission of crosslinked bonds (S-S) instead of main chain scission (C-C). Low temperature also intensifies the shearing force applied on the CR and thus reduce the energy cost needed for heating. The main problem associated with low temperature extrusion is the poor flowability and workability of CR, which can be resolved by the addition of plasticizers. Plasticizer is often composed of low molecular weight compounds with low viscosity, the common choices include treated distillate aromatic extract, naphthenic oil, waste engine oil, recycled cooking oil, heavy oils and etc (Formela et al., 2016b; K et al., 2014; Xu et al., 2014).

Li et al. (2019) used waste engine oil as a plasticizer in the extrusion and the devulcanized CR was added to asphalt for modification. It is concluded that addition of engine oil (25%~45%) effectively improves the devulcanization degree of CR, and reduce the extrusion temperatures to 150℃. An increase of oil content yields a better processing property and decreased stiffness of the modified asphalt, which results in better low-temperature cracking resistance. However, excessive engine oil adversely affects the storage stability due to an increase in flowability of asphalt, and worsens the rutting resistance at high temperature.

The bitumen itself can also be utilized as a plasticizer. Formela et al. (2016b) used a plain asphalt (penetration 160/220) and SBS modified asphalt (penetration 25-55) at variable content (2.5%, 5%, 10%, 20%) as plasticizers. The extrusion was conducted at a quite low temperature of 120℃. Correspondingly, a rather high screw speed of 600 rpm is utilized, which may cause extra shear to the CR. It was found that incorporation of asphalt during extrusion improves the processing through enhancement of physical and chemical interactions between CR and asphalt, it also prevents oxidation of CR. SBS-modified asphalt has a less aging resistance due to the C=C bonds presence in the structure of SBS copolymer and thus the plain asphalt is recommended. Using asphalt itself as an ingredient for extrusion can notably improve the compatibility between extrudate and the asphalt. Other references (Zhang et al., 2010, 2009; Z. Zhao et al., 2023b) also reported researches associated with mixing devulcanized CR directly with asphalt through extrusion. As the extrusion can process the product into different sizes and forms, it might be a potential pathway for the development of rollable pavement (Rollpave) (Naus et al., 2010).

8 Summary of formulas and extrusion parameters

A total of 51 articles are reviewed in this paper, and a summary of the mentioned equipment, extrusion parameters and formulas are presented in Table 5. Noted for extrusion temperature, some papers documented all temperature settings of the whole heating sequence from hopper to extrusion head. In these cases, only the temperature of the extrusion head is listed and it is marked as “head”. Also, many articles involve the comparison and optimization of multiple parameters or formulas. When a recommended parameter set or formula is provided, only recommendations are outlined in Table 5. Otherwise, all tested parameter sets or formulas will be presented.

Table 5 Summary of the reviewed articles in terms of extrusion parameters and formulas

No.	Topic	Source	Machine	Temperature (℃)	Screw speed (rpm)	Other parameters	Formula
1	Asphalt mastic	Tamrin (2023)	/	150	/	/	Sand:asphalt=3:1
2	PE-SBS	Wang (2022)	Twin-screw, Nanjing Keya Machinery, Nanjing, Jiangsu, China)	180	/	/	PE:SBS=8:1, 4:1, 2:1
3	PE-SBS	Cheng et al. (2020)	Twin-screw, SHJ-35, Nanjing, China	175~195	40	Feed speed:14 rpm	PE:SBS=4:6
4	PP-SBR	Vamegh et al. (2019)	Twin-screw, ZSK-25	160	80	/	PP:SBR=7:3
5	PP-SBR	Vamegh et al. (2020)	Twin-screw, ZSK-25	160	80	/	PP:SBR=7:3
6	Waste plastic mix	Celauro et al. (2021)	Twin-screw, Officine Meccaniche Conte, Fondi, Latina, Italy	270	120	Feed speed:6 rpm	Commercial product “Plasmix”, contains LDPE, HDPE, PP, PET, PS, metal and paper
7	Waste plastic mix	Banfield and Sanchez (2024)	/	200	/	/	Commercial, mostly HDPE
8	CR-HDPE	Wang et al. (2014)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	180	/	/	CR:HDPE=70:30, with 1%~5% LLDPE-g-MA
9	CR-PE	Peng et al. (2023)	Twin-screw, CTE-35 Kebelon Nanjing Machinery Co., LTD	160~170	360 ~ 420	Extrusion time: 5 min	CR:PE=85:15
10	CR-HDPE	Y. Ma et al. (2021a)	/	/	/	/	Commercial waste soaker hose, CR:HDPE=68:32
11	CR-HDPE	Ma et al. (2022)	/	/	/	/	Commercial waste soaker hose, CR:HDPE=68:32
12	CR-HDPE	Y. Ma et al. (2023)	/	/	/	/	Commercial waste soaker hose, CR:HDPE=68:32
13	CR-PE	Zhang et al.	Twin-screw, SJSZ-10A,	260	/	Extrusion	CR:PE=70:25, with 2%SBS, 2% EFAME,

		(2018)	Wuhan Yiyang Plastic Machinery, China			time: 30 min	2% naphthenic oil and 0.5% fluorocarbon surfactant
14	CR-PE	Liang et al. (2020a)	Twin-screw, SHJ-20, JieYa, Nanjing, China	180	100	/	CR:PE=2:1, 1:1
15	CR-LDPE	Wang et al. (2015)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	180	200	L/D:40	CR:LDPE: waste engine oil=70:30:15
16	CR-POE	Wang and Xie (2016)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	190	/	/	CR-POE=70:30 with 0%~6% Elvaloy
17	CR-PE	Liang et al. (2020c)	Twin-screw, SHJ-20, Nanjing, China	180	100	/	CR:PE:wax residue=80:20:10
18	Rapid-melting	Zhang et al. (2019b)	/	180 (head)	/	/	SBS: EVA: naphthenic oil: EVA-g-MAH: BHT=100:25:16:3:5.
19	Rapid-melting	Zhang et al.(2019a)	/	180 (head)	/	/	SBS: EVA: naphthenic oil: EVA-g-MAH: BHT=100:25:16:3:5.
20	Rapid-melting	L. Yu et al. (2022)	Twin-screw, SHJ-20, Nanjing, China	185 (head)	250	Feed speed:25 rpm, L/D:40	SBS, LDPE and LDPE (high fluidity), ratio unknown
21	Rapid-melting	Shi et al. (2020)	/	160	600	/	SBS:C9 resin:white oil:talcum powder= 79.5:15:5:0.5
22	Rapid-melting	H. Yu et al. (2022)	/	170	550	/	SBS:LDPE:C9 resin:aromantic oil:talcum powder=55:15:15:14.5:0.5
23	Rapid-melting	L. Chen et al. (2023)	/	180	42	/	SBS:terpene-styrene resin:DOP=64:34:2
24	Rapid-melting	C. Zhao et al. (2023)	Twin-screw, SHJ-20, Nanjing, China	180 (head)	15	/	CR:LDPE:LDPE (high fluidity) =1:1:1
25	Rapid-melting	T. Liu et al. (2022)	/	220	80	Feed speed:15 rpm	CR:LDPE=2:1
26	Rapid-melting	Z. Zhao et al. (2023a)	/	200	/	/	CR:asphalt (pene 60~80):calcium hydroxide=50:40:10
27	Rapid-melting	Z. Zhao et al.	/	200	/	/	de-CR:asphalt (pene 60~80):calcium

		(2023b)					hydroxide=80:10:10
28	Nano: PE-OMMT	Fang et al. (2013)	Twin-screw, SHJ-35, Nanjing, China	150 (head)	90	/	PE:OMMT=100:8~33
29	Nano: PVC-OMMT	Fang et al. (2014)	Twin-screw, SHJ-35, Nanjing, China	150 (head)	90	/	PVC:OMMT=100:5~25
30	Nano: SBS-kaolinite clay	Ouyang et al. (2005)	Two-rod mill	140	/	/	SBS: kaolinite clay=100:30
31	Nano: SBS-carbon black	Wang et al. (2003)	Two-rod mill	145	/	/	SBS:carbon black=100:50
32	Nano: SBS-CNTs	J. Chen et al. (2023)	/	/	/	/	/
33	Nano: SBS-CNTs	Wang et al. (2017)	/	180	/	/	SBS:CNTs=100:4.3
34	Nano: PP-GNP-carbon black	J. Liu et al. (2022)	/	/	/	/	Commercial, PP:GNP:carbon black=95:2.5:2.5
35	Nano: PE-CNTs	Xin et al. (2020)	/	/	/	/	Commercial, PE:CNTs=80:20
36	Nano: PE-CNTs	Liang et al. (2020b)	/	/	/	/	Commercial, PE:CNTs=80:20
37	Fiber: PE-PANCF	Zhang et al. (2016)	Twin-screw, SHJ-35, Nanjing, China	170	/	/	PE:PANCF=400:2~12, with the PANCF/asphalt ratio less than 0.1%
38	Grafting: PE-g-MAH	Ma et al. (2016)	/	175	250	L/D:28	PE:MAH:DCP=1000:7.5:5
39	Grafting: FPP-g-SMA	Malus et al. (2023)	/	210~230	40	/	Functionalized propylene (FPP) grafted with poly(styrene-co-maleic anhydride) (SMA), FPP:SMA=100:43,100:54
40	Grafting: PP degradation	X. Xu et al. (2022)	HAAKE rheometer	180	40	/	PP:DCP=1000:3
41	Grafting: PP-g-MAH/ESO	Xu et al. (2023)	HAAKE rheometer	180	40	/	PP:DCP:MAH:ESO=1000:3:15:5
42	Grafting: SBS-g-MAH, SIS-g-MAH, SEBS-g-	Vargas et al. (2015)	Twin-screw, HAAKE Rheocord Extruder 90	160	70	L/D:24	SBS:MAH=1000:4, SIS:MAH=1000:8, SEBS:MAH =1000:20

	MAH						
43	Grafting: SBS-g-MAH, SIS-g-MAH, SEBS-g-MAH	Vargas et al. (2015)	Twin-screw, HAAKE Rheocord Extruder 90	160	70	L/D:24	SBS:MAH=1000:4, SIS:MAH=1000:8, SEBS:MAH =1000:20
44	CR devulcanization	Zhou et al. (2023)	/	200	600	/	/
45	CR devulcanization	Tur Rasool et al. (2017)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	220, 260, 300	100	Feed speed:30 rpm, L/D:41	/
46	CR devulcanization	Rasool et al. (2018)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	220, 260, 300	100	Feed speed:30 rpm, L/D:41	/
47	CR devulcanization	G. Xu et al. (2022)	/	240~280	120	/	/
48	CR devulcanization	Wu et al. (2016)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	220,240,260, 280,300	100	Feed speed:30 rpm, L/D:41	CR and waste engine oil, ratio unknow
49	CR devulcanization (low-temperature)	Li et al. (2019)	Twin-screw, ZE 25A, Berstorff GmbH, Germany	150, 180, 210, 280	150	L/D:41	CR: waste engine oil=100:25~40
50	CR devulcanization (low-temperature)	Formela et al. (2016b)	Twin-screw, EHP 2x20, Zamak Mercator, Poland	120	600	L/D:40	CR: asphalt=100:2.5~20
51	Recrystallization of PP and PE	Junwei Li et al. (2022)	Twin-screw, Shanghai Xinshuo Precision Machinery Co., Ltd	165, 180, 200, 220	40	Extrusion time: 10 min	/

9 Discussion on the compound formula

Based on 38 articles which reported valid formulas, a summary of used materials and their functions are presented in Table 6. Based on used portions, they are divided into five categories, namely elastomer, plastic, plasticizer, nanomaterials and others. The average portions of these ingredients are summarized in Table 7, sorted by different applications. For better demonstration, a stacked bar is shown in Figure 26.

Table 6 Summary of components mentioned in this review

Type	Materials	Main functions
Elastomer	CR, SBS, SIS, SEBS, SBR	Provide strength and elasticity, carrier of nanomaterial
Plastic	PP, PE, POE, PET, PVC, PS, LDPE, HDPE	Provide strength, carrier of nanomaterial, partial replacement of elastomer for lower cost
Plasticizer	Waste engine oil, aromantic oil, white oil, naphthenic oil, EFAME, DOP, asphalt, wax residue,	Enhance workability and flowability of the extrudate, pre-swell the polymer, reduce extrusion temperature
Nanomaterial	OMMT, kaolinite clay, carbon black, CNTs, GNP, PANCF	Strengthening, anti-aging, reduce the density difference between polymer and asphalt, conductivity, etc.
Others		
Functionalized/reactive polymer	Elvaloy, LLDPE-g-MAH, EVA-g-MAH, PE-g-MAH, SBS-g-MAH, etc.	Compatibilizer between the original polymer and the asphalt matrix
Polymer with high melting index	High-fluidity LDPE, EVA	Plasticizer
Resin	C9, terpene-styrene	Enhance adhesion, partial replacement of elastomer
Agents	Fluorocarbon surfactant, calcium hydroxide, talcum powder, BHT	Anti-sticking, anti-aging
Grafting	MAH, ESO, DCP, Benzoil peroxide	Ingredients for grafting

Table 7 Average portion of different components for various applications

Type	Plastic compound	CR compound	Rapid-melting pellet	Nanomaterial compound	Grafting
Elastomer	34.5 (15.6*)	69 (6.5)	62.5 (13.8)	87.6 (7.2)	98.3 (0.4)
Plastic	65.5 (15.6)	27.8 (6.9)	13.3 (13.2)		

Plasticizer	/	2.6	14	/	/
Nanomaterial	/	/	/	12.4	/
Others	/	0.6	10.2	/	1.7
Total	100	100	100	100	100

* Value in the bracket is standard deviation

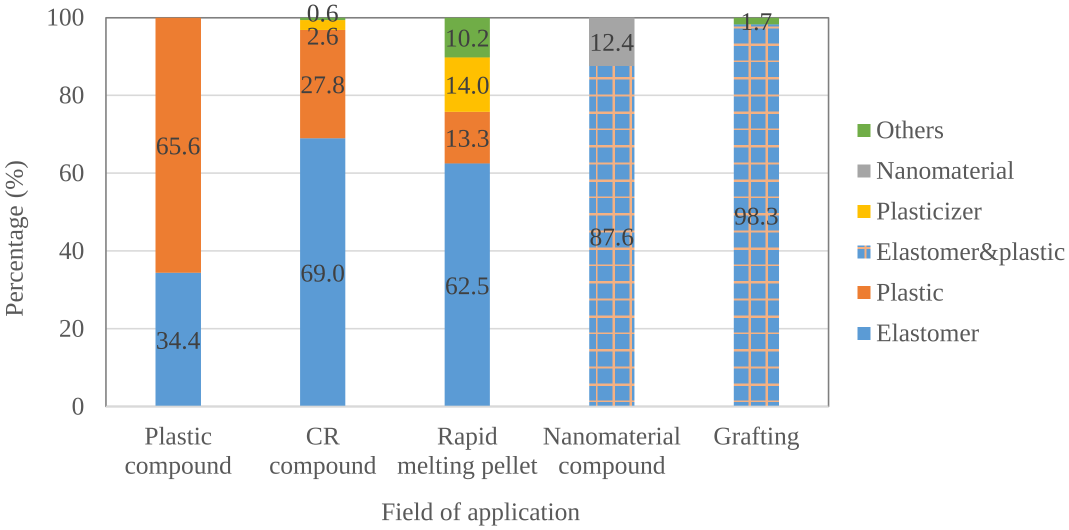


Figure 26 Average portion of different components for various applications

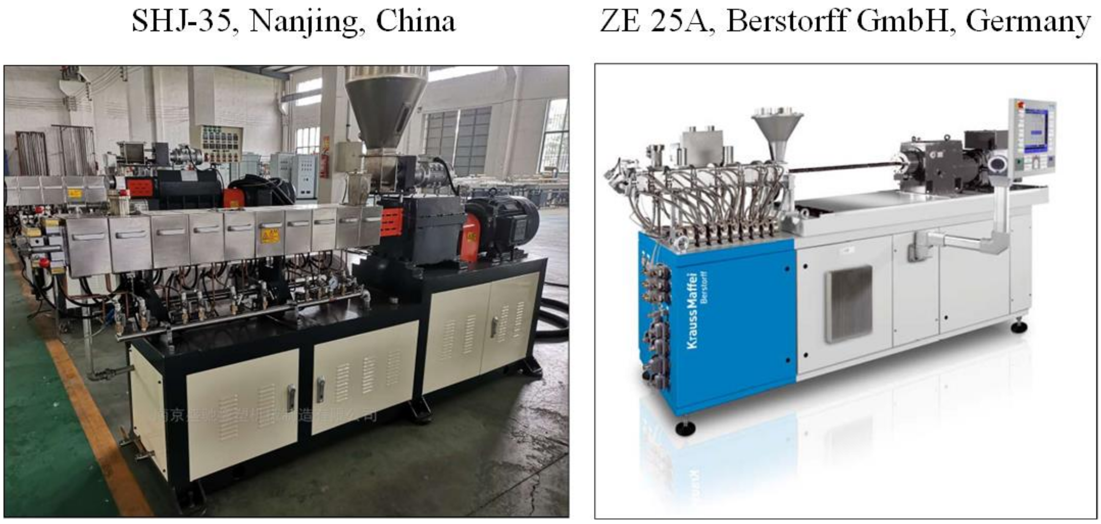
Based on Table 7 and Figure 26, plastic and elastomers are main ingredients for all types of applications. CR compound and rapid-melting pellets utilize more elastomers while plastic compound, as the name suggests, uses more fraction of plastics. A higher fraction of plastic leads to improved rutting resistance, but may also hinder the cracking resistance.

While plastic compounds are simple blend of plastic and elastomer, CR compound and rapid-melting pellet often include plasticizer. This choice is likely due to the inferior compatibility of elastomer with asphalt. Elastomers cannot fully dissolve into asphalt due to their unique crosslinked network, thus plasticizer is needed to facilitate the swelling of elastomers. Rapid-melting pellet, which requires a higher level of compatibility and workability, shows the highest plasticizer portion of 14%. It also shows the most diverse formula with a 10.2% portion of “other” ingredients, which are resin, functionalized/high-fluidity polymers, anti-aging agent and anti-sticking agent. Their functions are listed in Table 6. Compared with CR compound, fewer plastics are used in the rapid-melting pellet (13.3% vs 27.8%), it might be because the rapid-melting pellet is mainly utilized for Porous Asphalt Pavement (PAC) and requires excellent toughness for anti-raveling performance. The addition of stiff plastic might hinder this performance and thus the addition is limited.

For nanomaterial compound and grafting process, both elastomer and plastic are being used as carrying matrices, constituting the majority of the formula at percentages of 87.6% and 98.3%, respectively. The average nanomaterial portion is 12.4% and the average MAH portion is 1%, with the rest 0.7% being DOP and ESO. Based on multiple independent studies, the total addition of nanomaterial or MAH into the asphalt should be controlled within 1%~2% to avoid self-agglomeration or gelation.

10 Discussion on the extrusion parameters

Out of 29 articles that reported the used equipment, 25 of them used twin-screw extrusion, 2 used HAAKE rheometer and 2 used two-rod mill. The most mentioned twin-screw extrusion machines are the SHJ series (SHJ-20, SHJ-35) from Nanjing, China, with 8 published papers from three independent research groups (Shandong University, Changan University and Xi'an University of Technology). Type ZE 25A from Berstorff GmbH Germany was also reported in 7 published papers. They were all published by Shifeng Wang’s research group from Shanghai jiaotong university, with the main interest on the devulcanization of CR particles and its application as an asphalt modifier. The pictures of SHJ-35 and ZE 25A are shown in Figure 27.


SHJ-35, Nanjing, China

ZE 25A, Berstorff GmbH, Germany

Figure 27 Two most mentioned types of twin-screw extruder

Temperature is one of the most influential parameters for extrusion. From the feeder to extrusion head, the function of the screw can be categorized into five sections: conveying, melting, mixing, exhaust, and homogenizing compression, and each section can be customized with different temperatures to achieve specific functions. A typical example is shown in Figure 10. In the conveying section near the feeding hopper, the temperature should be a bit lower or close to material's melting temperature and gradually increase. The melting section requires a temperature slightly higher than the material's melting temperature to facilitate proper melting. In the mixing section, a higher temperature than the melting temperature is necessary to ensure fluidity and even distribution of the mixture. The exhaust section serves to remove small molecule volatiles and requires a temperature similar to that of the mixing section. In contrast, in the homogenization compression section, a lower temperature is needed to dense the material for smooth discharge at extrusion head.

Usually, raw material characteristics and thermal properties through tests like DSC and TGA are crucial for the determination of extrusion temperatures. When experimental conditions are limited or separation of raw material from waste is challenging, a melting index evaluation at different temperatures are recommended. For extrusion operations involving chemical reactions, operators must also be familiar with reaction conditions such as initiator type, concentration, and thermal decomposition half-life to set appropriate temperatures and extrusion residence times accordingly.

The average temperature selections regarding different applications are summarized in Figure 28 to give references for future related studies. For the purpose of conciseness, only the temperature of extrusion head (die) is analyzed. Generally, devulcanization of CR requires the highest extrusion temperature (245°C) as it needs the heat to break the strong chemical bonds within the crosslinked CR particles. Nevertheless, with the introduction of certain plasticizers, de-vulcanization at relatively lower temperatures (163°C) can be achieved. Grafting utilizes an intermediate temperature of 185°C, which is high enough to obtain fluidity for most polymers without causing serious degradation.

For compound extrusion, plastic compound requires the second-highest extrusion temperature of 199°C, followed by CR compound, rapid-melting pellet and nanomaterial compound. This might be explained from two aspects. Frist, PE is more chemical stable than elastomers (CR and SBS) and can endure a higher extrusion temperature without degradation, hence a higher extrusion temperature is preferred for better workability and efficiency. Second, most plastic compounds involve waste plastics which contains considerable portion of heavy fractions (e.g. PS, PET). Hence a higher extrusion temperature is necessary to meet the melting temperature of these heavy fractions. Most rapid-melting pellets use SBS as the main ingredient (6 out of 10 cases). Since SBS is prone to thermal degradation and has a lower softening point (around 100°C) (Masson et al., 2001) than CR and PE, the extrusion of rapid-melting pellet utilizes a lower extrusion temperature than both plastic compound and CR compound. Nanomaterial compound uses the lowest extrusion temperature of 157°C. This value is calculated based on limited data from three independent articles, and the possible explanation is that the compound extrusion involves nanomaterial manly aims for using the polymer as a carrier to achieve the efficient and evenly dispersion of nanomaterials. Therefore polymer with a high fluidity are preferred, leading to the choice of lower extrusion temperatures.

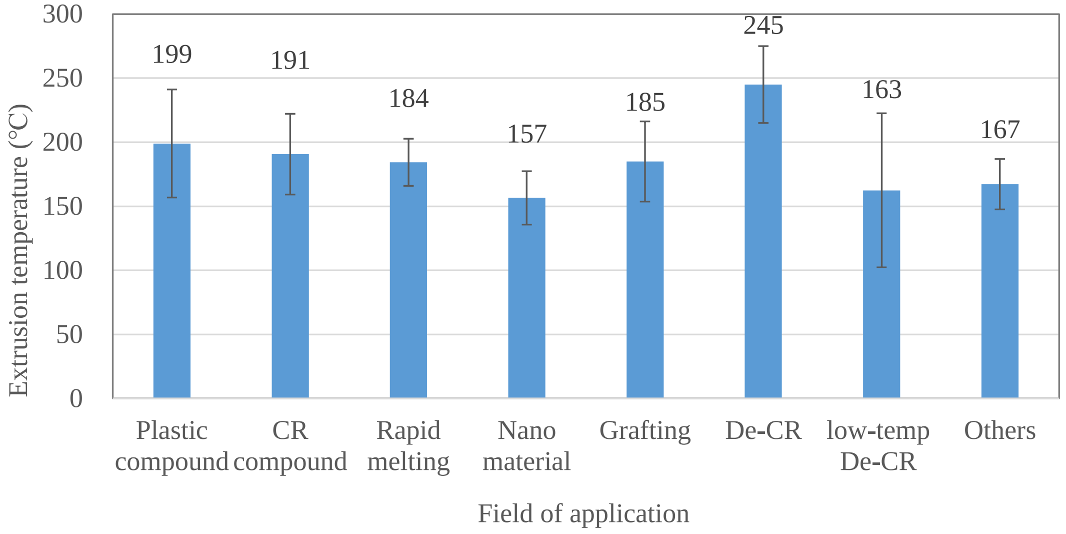


Figure 28 Average extrusion temperatures of different applications

The average screw speed regarding different applications is summarized in Figure 29. The screw speed plays a critical role in determining shear force and dispersion size during extrusion. Higher speeds result in greater shear force but may lead to thermal degradation and uneven mixing due to increased friction and lower residence time. Conversely, lower speeds reduce shear force but extend the residence time in extrusion process. Therefore, it is imperative to carefully consider basic extruder parameters and specific material characteristics when determining optimal rotational speed for successful extrusion processes. Unfortunately, only limited articles reported this parameter and thus the deviation is quite large. It is seen that CR devulcanization at low-temperature utilizes the highest average screw speed, which is reasonable because it needs high shearing force instead of heat to break the crosslinked chemical bonds. Formela et al. (2016b) even reported a shear speed of 600 rpm, with a relatively lower extrusion temperature of 120°C. Rapid-melting pellet reports the second-highest screw-speed, which matches its high plasticizer portion and good workability.

Besides temperature and screw speed, some other parameters including feed speed, extrusion time (barrel residency time) and L/D (length/diameter ratio of the barrel) are recorded. Typically, feed speed ranges from 6 to 30 rpm, extrusion time ranges from 5 to 30 min and L/D ranges from 24 to 41.

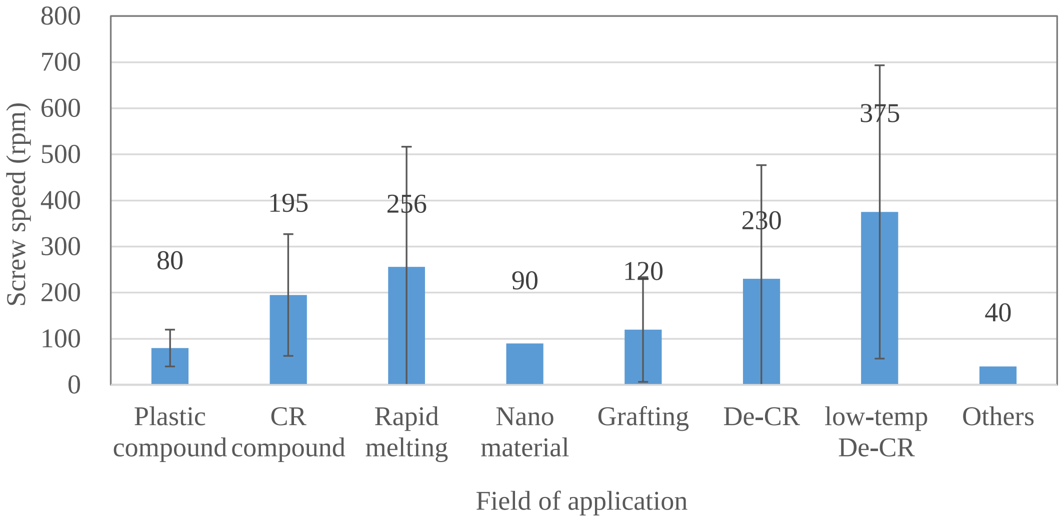


Figure 29 Average screw speed of different applications

11 Conclusions

Currently, there is a growing trend for asphalt suppliers to tailor the asphalt modifiers using screw extrusion. This paper aims to provide an overview of the application of screw extrusion process in the asphalt material field. Based on this overview, following conclusions and recommendations are drawn:

1) Screw extrusion has numerous merits, including multi-function, continuous production, solvent-free processing, centralized exhaust disposal and relatively lower cost. The most mentioned extruders for asphalt material are SHJ series from Nanjing and ZE 25A from Germany. Based on ingredients and processing purposes, the examined papers are categorized into six applications: i) Plastic compound; ii) CR compound; iii) Rapid-melting pellet; iv) Nanomaterial compound; v) Grafting; vi) Devulcanization of CR.
2) Plastic compound has an average plastic ratio of 65.6% with the rest being elastomers like SBS or CR. They are usually mixed for better stability within the asphalt. Without any elastomers, pure plastic compounds extruded from heterogeneous waste plastics were also reported. Since waste plastics are usually heterogeneous and contains heavy ones like PS or PET, plastic compound demonstrates a relatively higher average extrusion temperature of 199℃.
3) CR compound has an average CR ratio of 69% with the rest being mostly plastics. CR is usually lightly devulcanized and sometimes a small fraction of plasticizer is also included to improve compatibility. Plasticizer can also improve the low-temp/fatigue performance with an acceptable negative influence on the rutting resistance of the mixture. It is generally accepted that CR compound can improve rutting resistance of the asphalt. Also, the carbon black and anti-aging agents provided by the CR particle can enhance the aging resistance.
4) Rapid-melting pellets, which focuses on the mixing efficient and workability, demonstrates the highest average plasticizer portion of 14%. It also contains diverse ingredients like resin, functionalized/high-fluidity polymers, anti-aging

agent and anti-sticking agent. The main gradient of rapid melting pellet is elastomer (mostly SBS). Compared with CR compound, fewer plastics are used in the rapid-melting pellet (13.3% vs 27.8%), it might be because the rapid-melting pellet is mainly utilized for Porous Asphalt Pavement (PAC) and requires excellent toughness for anti-raveling performance.

5) For nanomaterial compound and grafting process, both elastomer and plastic are being used as carrying matrices, constituting the majority of the formula at percentages of 87.6% and 98.3%, respectively. The average nanomaterial portion is 12.4% and the average MAH monomer portion is 1%. Based on multiple independent studies, the total addition of nanomaterial or MAH into the asphalt should be controlled within 1%~2% to avoid self-agglomeration or gelation.
6) CR devulcanization requires the highest average extrusion temperature of 245℃. Through this process, the size of the dispersed CR particle becomes much smaller, renders the blend more homegroups. This process mainly benefits the performance of rubberized asphalt in terms of three aspects: improved storage stability, enhanced mechanical properties and increased aging resistance. But in some cases, excessive breakage of chemical bonds may hinder high-temperature resistance. The optimal devulcanization degree is case-specific and should be determined carefully.
7) Future research recommendations that may worth more attention:
    - Researches on the effects of extrusion parameter (temperature, screw speed, rotation direction, barrel residence time) to optimize the process for asphalt modifiers;
    - Compound extrusion with more kinds of recycled polymers and nanomaterial such as LDHs or lignin fiber;
    - Using coextrusion to create asphalt modifiers with different layer structures to achieve multi-functions.

Acknowledgements

The authors gratefully acknowledge the financial supports from the National key R&D program of China (2022YFB2602603), Hong Kong scholars program (XJ2022040), National Natural Science Foundation of China (52008353), Sichuan Youth Science and Technology Innovation Research Team (2021JDTD0023，2022JDTD0015)

References

Banfield, S., Sanchez, X., 2024. Laboratory Investigation into the Partial Replacement of Aggregates with Recycled High-Density Polyethylene in a Dense Graded Asphalt Mix. Transp. Res. Rec. 2678, 286–295. https://doi.org/10.1177/03611981231170620

Brodin, M., Vallejos, M., Opedal, M.T., Area, M.C., Chinga-Carrasco, G., 2017.

Lignocellulosics as sustainable resources for production of bioplastics – A review. J. Clean. Prod. 162, 646–664. https://doi.org/10.1016/j.jclepro.2017.05.209

Celauro, C., Teresi, R., Graziano, F., La Mantia, F.P., Protopapa, A., 2021. Preliminary Evaluation of Plasmix Compound from Plastics Packaging Waste for Reuse in Bituminous Pavements. Sustainability 13, 2258. https://doi.org/10.3390/su13042258

Chen, J., Huang, Z., Wang, H., Yang, Z., Zhang, T., 2023. Investigating the Rheological Properties of Styrene-Butadiene-Styrene-Based High-Viscosity Modified Asphalt Using Carbon Nanotubes. Sustainability 15, 71. https://doi.org/10.3390/su15010071

Chen, L., Zhang, Z., Wang, Z., Liu, H., Zhang, D., Sun, J., 2023. Using SBS/terpene-styrene resin blends as a novel high-viscosity asphalt modifier. J. Appl. Polym. Sci. 140, e53355. https://doi.org/10.1002/app.53355

Cheng, Y., Han, H., Fang, C., Li, H., Huang, Z., Su, J., 2020. Preparation and properties of nano-CaCO3/waste polyethylene/styrene-butadiene-styrene block polymer-modified asphalt. Polym. Compos. 41, 614–623. https://doi.org/10.1002/pc.25392

Du, Z., Jiang, C., Yuan, J., Xiao, F., Wang, J., 2020. Low temperature performance characteristics of polyethylene modified asphalts – A review. Constr. Build. Mater. 264, 120704. https://doi.org/10.1016/j.conbuildmat.2020.120704

Fang, C., Liu, X., Yu, R., Liu, P., Lei, W., 2014. Preparation and Properties of Asphalt Modified with a Composite Composed of Waste Package Poly(vinyl chloride) and Organic Montmorillonite. J. Mater. Sci. Technol. 30, 1304–1310. https://doi.org/10.1016/j.jmst.2014.11.001

Fang, C., Yu, R., Li, Y., Zhang, Mengya, Hu, J., Zhang, Min, 2013. Preparation and characterization of an asphalt-modifying agent with waste packaging polyethylene and organic montmorillonite. Polym. Test. 32, 953–960. https://doi.org/10.1016/j.polymertesting.2013.04.006

Fang, C., Zhang, Y., Yu, R., Liu, X., Hu, J., Zhang, M., 2015. Effect of organic montmorillonite on the hot storage stability of asphalt modified by waste packaging polyethylene. J. Vinyl Addit. Technol. 21, 89–93. https://doi.org/10.1002/vnl.21376

Fini, E.H., Hosseinnezhad, S., Oldham, D.J., Sharma, B.K., 2016. Investigating the effectiveness of liquid rubber as a modifier for asphalt binder. Road Mater. Pavement Des. 17, 825–840. https://doi.org/10.1080/14680629.2015.1124800

Formela, K., Cysewska, M., Haponiuk, J.T., 2016a. Thermomechanical reclaiming of ground tire rubber via extrusion at low temperature: Efficiency and limits. J. Vinyl Addit. Technol. 22, 213–221. https://doi.org/10.1002/vnl.21426

Formela, K., Klein, M., Colom, X., Saeb, M.R., 2016b. Investigating the combined impact of plasticizer and shear force on the efficiency of low temperature reclaiming of ground tire rubber (GTR). Polym. Degrad. Stab. 125, 1–11.

https://doi.org/10.1016/j.polymdegradstab.2015.12.022

Gaspar-Cunha, A., Covas, J.A., Sikora, J., 2022. Optimization of Polymer Processing: A Review (Part I—Extrusion). Materials 15, 384. https://doi.org/10.3390/ma15010384

Grigoryeva, O.P., Fainleib, A.M., Tolstov, A.L., Starostenko, O.M., Lievana, E., Karger-Kocsis, J., 2005. Thermoplastic elastomers based on recycled high-density polyethylene, ethylene–propylene–diene monomer rubber, and ground tire rubber. J. Appl. Polym. Sci. 95, 659–671. https://doi.org/10.1002/app.21177

Hyvärinen, M., Jabeen, R., Kärki, T., 2020. The Modelling of Extrusion Processes for Polymers—A Review. Polymers 12, 1306. https://doi.org/10.3390/polym12061306

Jiang, X., Zhu, H., Yan, Z., Zhang, F., Ye, F., Li, P., Zhang, X., Dai, Z., Bai, Y., Huang, B., 2023. A state-of-art review on development and progress of backfill grouting materials for shield tunneling. Dev. Built Environ. 16, 100250. https://doi.org/10.1016/j.dibe.2023.100250

Jun, L., Yuxia, Z., Yuzhen, Z., 2008. The research of GMA-g-LDPE modified Qinhuangdao bitumen. Constr. Build. Mater. 22, 1067–1073. https://doi.org/10.1016/j.conbuildmat.2007.03.007

K, F., M, C., K, J., 2014. Effect of addition of reclaimed rubber on curing characteristics and mechanical properties of styrene-butadiene rubber. Przemysl Chem. 93, 666–671.

Kang, Y., Wang, F., Chen, Z., 2010. Reaction of asphalt and maleic anhydride: Kinetics and mechanism. Chem. Eng. J. 164, 230–237. https://doi.org/10.1016/j.cej.2010.08.020

Li, C., Zhang, Yong, Zhang, Yinxi, 2003. Melt grafting of maleic anhydride onto low-density polyethylene/polypropylene blends. Polym. Test. 22, 191–195. https://doi.org/10.1016/S0142-9418(02)00079-X

Li, Junwei, Jia, S., Yang, D., Li, X., Li, D., Ye, X., Guan, P., Zhao, Y., 2022. Reutilization of crystalline waste plastics for modified asphalt using twin-screw extrusion: Polyethylene and polypropylene as typical subjects. J. Appl. Polym. Sci. 139, e52690. https://doi.org/10.1002/app.52690

Li, J., Jia, W., Yuan, W., 2014. Effect of Polyethylene Grafted with Maleic Anhydride on Asphalt Properties. J. Perform. Constr. Facil. 28, 04014012. https://doi.org/10.1061/(ASCE)CF.1943-5509.0000516

Li, Jin, Xiao, X., Chen, Z., Xiao, F., Amirkhanian, S.N., 2022. Internal de-crosslinking of scrap tire crumb rubber to improve compatibility of rubberized asphalt. Sustain. Mater. Technol. 32, e00417. https://doi.org/10.1016/j.susmat.2022.e00417

Li, Y., Cao, D., Zhang, Y., Jia, X., 2021. Performance of a dry-method-epoxy modifier and a modified epoxy-asphalt mixture. Constr. Build. Mater. 266, 120229. https://doi.org/10.1016/j.conbuildmat.2020.120229

Li, Y., Shen, A., Lyu, Z., Wang, S., Formela, K., Zhang, G., 2019. Ground tire rubber thermo-mechanically devulcanized in the presence of waste engine oil as asphalt modifier. Constr. Build. Mater. 222, 588–600. https://doi.org/10.1016/j.conbuildmat.2019.06.162

Liang, M., Ren, S., Sun, C., Zhang, J., Jiang, H., Yao, Z., 2020a. Extruded Tire Crumb-Rubber Recycled Polyethylene Melt Blend as Asphalt Composite Additive for Enhancing the Performance of Binder. J. Mater. Civ. Eng. 32, 04019373. https://doi.org/10.1061/(ASCE)MT.1943-5533.0003044

Liang, M., Su, L., Li, P., Shi, J., Yao, Z., Zhang, J., Jiang, H., Luo, W., 2020b. Investigating the Rheological Properties of Carbon Nanotubes/Polymer Composites Modified Asphalt. Materials 13, 4077. https://doi.org/10.3390/ma13184077

Liang, M., Sun, C., Yao, Z., Jiang, H., Zhang, J., Ren, S., 2020c. Utilization of wax residue as compatibilizer for asphalt with ground tire rubber/recycled polyethylene blends. Constr. Build. Mater. 230, 116966. https://doi.org/10.1016/j.conbuildmat.2019.116966

Liang, M., Xin, X., Fan, W., Zhang, J., Jiang, H., Yao, Z., 2021. Comparison of rheological properties and compatibility of asphalt modified with various polyethylene. Int. J. Pavement Eng. 22, 11–20. https://doi.org/10.1080/10298436.2019.1575968

Lievana, E., Karger-Kocsis, J., 2004. Use of Ground Tyre Rubber (GTR) in Thermoplastic Polyolefin Elastomer Compositions. Prog. Rubber Plast. Recycl. Technol. 20, 1–10. https://doi.org/10.1177/147776060402000101

Liu, J., Hao, P., Sun, B., Li, Y., Wang, Y., 2022. Rheological Properties and Mechanism of Asphalt Modified with Polypropylene and Graphene and Carbon Black Composites. J. Mater. Civ. Eng. 34, 04022343. https://doi.org/10.1061/(ASCE)MT.1943-5533.0004513

Liu, T., Li, X., Li, R., Pei, J., Zhao, X., 2022. Performance of Dry Mixed Rubber–Plastic Composite Modified Asphalt Mixture. J. Mater. Civ. Eng. 34, 04022243. https://doi.org/10.1061/(ASCE)MT.1943-5533.0004407

Lu, D., Jiang, X., Tan, Z., Yin, B., Leng, Z., Zhong, J., 2023. Enhancing sustainability in pavement Engineering: A-state-of-the-art review of cement asphalt emulsion mixtures. Clean. Mater. 9, 100204. https://doi.org/10.1016/j.clema.2023.100204

Ma, C., Xin, X., Zhang, N., Wang, J., Wang, C., Liang, M., Zhang, Y., Yao, Z., 2023. Encapsulation for Sensing Element and Its Application in Asphalt Road Monitoring. Coatings 13, 390. https://doi.org/10.3390/coatings13020390

Ma, D., Zhao, D., Zhao, J., Du, S., Pang, J., Wang, W., Fan, C., 2016. Functionalization of reclaimed polyethylene with maleic anhydride and its application in improving the high temperature stability of asphalt mixtures. Constr. Build. Mater. 113, 596–602. https://doi.org/10.1016/j.conbuildmat.2016.03.096

Ma, Q., Guo, Z., Guo, P., Yang, F., Li, H., 2021. Research on the Viscosity-Temperature Properties and Thermal Stability of Stabilized Rubber Powder Modified Asphalt. Sustainability 13, 13536. https://doi.org/10.3390/su132413536

Ma, Y., Wang, S., Zhang, M., Jiang, X., Polaczyk, P., Huang, B., 2023. Weather aging effects on modified asphalt with rubber-polyethylene composites. Sci. Total Environ. 865, 161089. https://doi.org/10.1016/j.scitotenv.2022.161089

Ma, Y., Wang, S., Zhou, H., Hu, W., Polaczyk, P., Huang, B., 2022. Recycled polyethylene and crumb rubber composites modified asphalt with improved aging resistance and thermal stability. J. Clean. Prod. 334, 130102. https://doi.org/10.1016/j.jclepro.2021.130102

Ma, Y., Wang, S., Zhou, H., Hu, W., Polaczyk, P., Huang, B., 2021a. Potential Alternative to Styrene–Butadiene–Styrene for Asphalt Modification Using Recycled Rubber–Plastic Blends. J. Mater. Civ. Eng. 33, 04021341. https://doi.org/10.1061/(ASCE)MT.1943-5533.0003946

Ma, Y., Zhou, H., Jiang, X., Polaczyk, P., Xiao, R., Zhang, M., Huang, B., 2021b. The utilization of waste plastics in asphalt pavements: A review. Clean. Mater. 2, 100031. https://doi.org/10.1016/j.clema.2021.100031

Malus, M., Bojda, J., Sienkiewicz, M., Bouyahyi, M., Yang, L., Javier Navarro, F., Soliman, M., Duchateau, R., Jasinska-Walc, L., 2023. Structurally well-defined functionalized polyolefins and graft copolymers thereof as bitumen modifiers. Constr. Build. Mater. 390, 131630. https://doi.org/10.1016/j.conbuildmat.2023.131630

Masson, J.-F., Pelletier, L., Collins, P., 2001. Rapid FTIR method for quantification of styrene-butadiene type copolymers in bitumen. J. Appl. Polym. Sci. 79, 1034–1041. https://doi.org/10.1002/1097-4628(20010207)79:6<1034::AID-APP60>3.0.CO;2-4

Moad, G., 1999. The synthesis of polyolefin graft copolymers by reactive extrusion. Prog. Polym. Sci. 24, 81–142. https://doi.org/10.1016/S0079-6700(98)00017-3

Ngoc, U.N., Schnitzer, H., 2010. Environmental understanding of agro-based industrial systems and sustainable development. Int. J. Environ. Sustain. Dev. 9, 149–180. https://doi.org/10.1504/IJESD.2010.029968

Noor, A., Rehman, M.A.U., 2022. A mini-review on the use of plastic waste as a modifier of the bituminous mix for flexible pavement. Clean. Mater. 4, 100059. https://doi.org/10.1016/j.clema.2022.100059

Ouyang, C., Wang, S., Zhang, Yong, Zhang, Yinxi, 2005. Preparation and properties of styrene–butadiene–styrene copolymer/kaolinite clay compound and asphalt modified with the compound. Polym. Degrad. Stab. 87, 309–317. https://doi.org/10.1016/j.polymdegradstab.2004.08.014

Peng, W., Li, P., Gong, W., Tian, S., Wang, Z., Liu, S., Liu, Z., 2023. Preparation and mechanism of rubber-plastic alloy crumb rubber modified asphalt with low viscosity and stabilized performance. Constr. Build. Mater. 388, 131687.

https://doi.org/10.1016/j.conbuildmat.2023.131687

Phiri, M.M., Phiri, M.J., Formela, K., Wang, S., Hlangothi, S.P., 2022. Grafting and reactive extrusion technologies for compatibilization of ground tyre rubber composites: Compounding, properties, and applications. J. Clean. Prod. 369, 133084. https://doi.org/10.1016/j.jclepro.2022.133084

Rasool, R. tur, Song, P., Wang, S., 2018. Thermal analysis on the interactions among asphalt modified with SBS and different degraded tire rubber. Constr. Build. Mater. 182, 134–143. https://doi.org/10.1016/j.conbuildmat.2018.06.104

Saiwari, S., Dierkes, W.K., Noordermeer, J.W.M., 2014. COMPARATIVE INVESTIGATION OF THE DEVULCANIZATION PARAMETERS OF TIRE RUBBERS. Rubber Chem. Technol. 87, 31–42. https://doi.org/10.5254/rct.13.87933

Salehi, S., Arashpour, M., Kodikara, J., Guppy, R., 2022. Comparative life cycle assessment of reprocessed plastics and commercial polymer modified asphalts. J. Clean. Prod. 337, 130464. https://doi.org/10.1016/j.jclepro.2022.130464

Shi, J., Zhao, P., Fan, W., Yang, Z., Lin, Y., Ouyang, J., 2020. Facile preparation and application performance evaluation of SBS/C9 petroleum resin blends as modifier for high viscosity asphalt. Constr. Build. Mater. 262, 120073. https://doi.org/10.1016/j.conbuildmat.2020.120073

Su, L., Liang, M., Wang, J., Xin, X., Jiao, Y., Wang, C., Zhang, Y., Yao, Z., 2023. Robust orientation-3D conductive network enabled high-performance flexible sensor for traffic monitoring: Role of surface functionalization on self-assembled microspheres arrays. Chem. Eng. J. 468, 143564. https://doi.org/10.1016/j.cej.2023.143564

Tamrin, Ritonga, A.H., Aritonang, B., 2023. The enhancement of mechanical, physical, and thermal properties of modified asphalt mixture with lignin from mahogany sawdust in the presence of diphenylmethane 4,4′-diisocyanate. Int. J. Adhes. Adhes. 125, 103431. https://doi.org/10.1016/j.ijadhadh.2023.103431

tur Rasool, R., Wang, S., Zhang, Y., Li, Y., Zhang, G., 2017. Improving the aging resistance of SBS modified asphalt with the addition of highly reclaimed rubber. Constr. Build. Mater. 145, 126–134. https://doi.org/10.1016/j.conbuildmat.2017.03.242

Vamegh, M., Ameri, M., Chavoshian Naeni, S.F., 2020. Experimental investigation of effect of PP/SBR polymer blends on the moisture resistance and rutting performance of asphalt mixtures. Constr. Build. Mater. 253, 119197. https://doi.org/10.1016/j.conbuildmat.2020.119197

Vamegh, M., Ameri, M., Chavoshian Naeni, S.F., 2019. Performance evaluation of fatigue resistance of asphalt mixtures modified by SBR/PP polymer blends and SBS. Constr. Build. Mater. 209, 202–214. https://doi.org/10.1016/j.conbuildmat.2019.03.111

Vargas, M. de los A., Sanchez-Solis, A., Vargas, M.A., Manero, O., 2023. Evaluation of rheological behavior of asphalt mixtures modified with triblock polymers grafted maleic anhydride and montmorillonite clay. J. Appl. Polym. Sci. 140, e53825. https://doi.org/10.1002/app.53825

Vargas, M.A., Sánchez, A., Guthausen, G., Manero, O., 2015. Viscoelastic behaviour of asphalt modified by grafted tri-block copolymers: predictions of fractional rheological models. Int. J. Pavement Eng. 16, 730–744. https://doi.org/10.1080/10298436.2014.953501

Vargas, María A., Vargas, Miguel A., Sánchez-Sólis, A., Manero, O., 2013. Asphalt/polyethylene blends: Rheological properties, microstructure and viscosity modeling. Constr. Build. Mater. 45, 243–250. https://doi.org/10.1016/j.conbuildmat.2013.03.064

Wang, P., Dong, Z., Liu, Z., 2017. Influence of Carbon Nanotubes on Morphology of Asphalts Modified with Styrene–Butadiene–Styrene. Transp. Res. Rec. 2632, 130–139. https://doi.org/10.3141/2632-14

Wang, S., Wang, Q., Wu, X., Zhang, Y., 2015. Asphalt modified by thermoplastic elastomer based on recycled rubber. Constr. Build. Mater. 93, 678–684. https://doi.org/10.1016/j.conbuildmat.2015.06.047

Wang, S., Xie, Y., 2016. Crumb Tire Rubber Polyolefin Elastomer Modified Asphalt with Hot Storage Stability. Prog. Rubber Plast. Recycl. Technol. 32, 25–38. https://doi.org/10.1177/147776061603200102

Wang, S., Yuan, C., Jiaxi, D., 2014. Crumb tire rubber and polyethylene mutually stabilized in asphalt by screw extrusion. J. Appl. Polym. Sci. 131. https://doi.org/10.1002/app.41189

Wang, S., Zhang, Yong, Zhang, Yinxi, 2003. SBS/Carbon Black Compounds Give Asphalts with Improved High-Temperature Storage Stability. Polym. Polym. Compos. 11, 477–485. https://doi.org/10.1177/096739110301100606

Wang, T., 2022. Study and Application of Compatibility of Waste Polyethylene-Modified Asphalt. J. Mater. Civ. Eng. 34, 04022203. https://doi.org/10.1061/(ASCE)MT.1943-5533.0004315

Wu, S., Montalvo, L., 2021. Repurposing waste plastics into cleaner asphalt pavement materials: A critical literature review. J. Clean. Prod. 280, 124355. https://doi.org/10.1016/j.jclepro.2020.124355

Wu, X., Wang, S., Dong, R., 2016. Lightly pyrolyzed tire rubber used as potential asphalt alternative. Constr. Build. Mater. 112, 623–628. https://doi.org/10.1016/j.conbuildmat.2016.02.208

Xin, X., Luan, X., Su, L., Ma, C., Liang, M., Ding, X., Yao, Z., 2022a. The Innovative Self-Sensing Strain Sensor for Asphalt Pavement Structure: Substitutability and Synergy Effects of Graphene Platelets With Carbon Nanotubes in Epoxy Composites. Front. Mater. 9.

Xin, X., Qiu, Z., Luan, X., Ding, X., Liang, M., Yao, Z., Li, Y., 2022b. Novel Conductive Polymer Composites for Asphalt Pavement Structure in Situ Strain Monitoring: Influence of CB/CNT and GNP/CNT Nano/Micro Hybrid Fillers on Strain Sensing Behavior. IEEE Sens. J. 22, 3945–3956.

https://doi.org/10.1109/JSEN.2022.3140934

Xin, X., Yao, Z., Shi, J., Liang, M., Jiang, H., Zhang, J., Zhang, X., Yao, K., 2020. Rheological properties, microstructure and aging resistance of asphalt modified with CNTs/PE composites. Constr. Build. Mater. 262, 120100. https://doi.org/10.1016/j.conbuildmat.2020.120100

Xu, G., Kong, P., Yu, Y., Yang, J., Zhu, M., Chen, X., 2022. Rheological properties of rubber modified asphalt as function of waste tire rubber reclaiming degree. J. Clean. Prod. 332, 130113. https://doi.org/10.1016/j.jclepro.2021.130113

Xu, J.-Y., Mei-Shen, Wang, X.-Q., Chen, C.-H., Xin, Z.-X., 2014. The Effect of Reclaim Softener on Properties of Reclaimed Rubber. J. Macromol. Sci. Part B 53, 1182–1192. https://doi.org/10.1080/00222348.2013.832618

Xu, X., Chu, Y., Chen, R., Wu, Q., Chen, X., Zou, F., Peng, C., 2022. Thermo-mechanochemical recycling of waste polypropylene into degradation products as modifiers for cleaner production and properties enhancement of bitumen. J. Clean. Prod. 379, 134792. https://doi.org/10.1016/j.jclepro.2022.134792

Xu, X., Chu, Y., Luo, Y., Peng, Y., Yang, N., Yan, J., Chen, X., Zou, F., Sreeram, A., 2023. Thermal-and-mechanochemical recycling of waste polypropylene into maleated-epoxided degradation products as warm-mix asphalt modifier: Performance improvement and production mechanism analysis. J. Clean. Prod. 426, 139222. https://doi.org/10.1016/j.jclepro.2023.139222

Yan, C., Xi, J., Ai, C., Leng, Z., 2024. Investigating the unique entropy-elasticity of polymer modified asphalt. Clean. Mater. 11, 100216. https://doi.org/10.1016/j.clema.2023.100216

Yan, X., Wu, D., Hu, K., Zhang, W., Xing, J., Cui, L., Shi, S., Yang, J., Yang, C., 2023. The Modification Mechanism, Evaluation Method, and Construction Technology of Direct-to-Plant SBS Modifiers in Asphalt Mixture: A Review. Polymers 15, 2768. https://doi.org/10.3390/polym15132768

Yu, H., Jin, Y., Liang, X., Dong, F., 2022. Preparation of Waste-LDPE/SBS Composite High-Viscosity Modifier and Its Effect on the Rheological Properties and Microstructure of Asphalt. Polymers 14, 3848. https://doi.org/10.3390/polym14183848

Yu, L., Lyu, L., Li, R., Du, Y., Pei, J., 2022. Microscopic Mechanism of Direct-Input Waste Plastic Modified Asphalt. J. Transp. Eng. Part B Pavements 148, 04022003. https://doi.org/10.1061/JPEODX.0000347

Zhang, F., Li, J., Yaseen, M., Han, M., Yin, Y., Yang, S., 2018. Preparation Methods and Performance of Modified Asphalt Using Rubber–Plastic Alloy and Its Compounds. J. Mater. Civ. Eng. 30, 04018163. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002356

Zhang, L., Shan, M., Xing, C., Cui, Y., Wang, P., Liu, M., 2023. Mechanism of physical hardening on the fracture characteristics of polymer-modified asphalt binder. Constr. Build. Mater. 409, 134091. https://doi.org/10.1016/j.conbuildmat.2023.134091

Zhang, M., Fang, C., Zhou, S., Cheng, Y., Hu, J., 2016. Modification of asphalt by dispersing waste polyethylene and carbon fibers in it. New Carbon Mater. 31, 424–430. https://doi.org/10.1016/S1872-5805(16)60022-7

Zhang, S.L., Xin, Z.X., Zhang, Z.X., Kim, J.K., 2009. Characterization of the properties of thermoplastic elastomers containing waste rubber tire powder. Waste Manag., First international conference on environmental management, engineering, planning and economics 29, 1480–1485. https://doi.org/10.1016/j.wasman.2008.10.004

Zhang, S.L., Zhang, Z.X., Xin, Z.X., Pal, K., Kim, J.K., 2010. Prediction of mechanical properties of polypropylene/waste ground rubber tire powder treated by bitumen composites via uniform design and artificial neural networks. Mater. Des., Design of Nanomaterials and Nanostructures 31, 1900–1905. https://doi.org/10.1016/j.matdes.2009.10.057

Zhang, W., Jia, Z., Wang, F., 2019a. Effect and prediction of aromatic oil on swelling degree of direct-to-plant SBS modifier in bitumen. Pet. Sci. Technol. 37, 1033–1040. https://doi.org/10.1080/10916466.2019.1570255

Zhang, W., Jia, Z., Zhang, Y., Hu, K., Ding, L., Wang, F., 2019b. The Effect of Direct-to-Plant Styrene-Butadiene-Styrene Block Copolymer Components on Bitumen Modification. Polymers 11, 140. https://doi.org/10.3390/polym11010140

Zhao, C., Li, R., Kuang, D., Li, X., Pei, J., 2023. Preparation of direct injection waste PE/rubber powder composite modified granules and performance for recycling asphalt. Constr. Build. Mater. 367, 130124. https://doi.org/10.1016/j.conbuildmat.2022.130124

Zhao, Z., Wu, S., Xie, J., Yang, C., Yang, X., Chen, S., Liu, Q., 2023a. Recycle of waste tire rubber powder in a novel asphalt rubber pellets for asphalt performance enhancement. Constr. Build. Mater. 399, 132572. https://doi.org/10.1016/j.conbuildmat.2023.132572

Zhao, Z., Wu, S., Xie, J., Yang, C., Yang, X., Wang, F., Liu, Q., 2023b. Utilization of high contents desulfurized crumb rubber in developing an asphalt rubber pellets modified asphalt. Constr. Build. Mater. 402, 133043. https://doi.org/10.1016/j.conbuildmat.2023.133043

Zhou, Y., Xu, G., Leng, Z., Kong, P., Wang, H., Yang, J., Qiu, W., Xu, Z., Chen, X., 2023. Investigation on storage stability and rheological properties of environment-friendly devulcanized rubber modified asphalt. Phys. Chem. Earth Parts ABC 129, 103332. https://doi.org/10.1016/j.pce.2022.103332

Zhu, J., Birgisson, B., Kringos, N., 2014. Polymer modification of bitumen: Advances and challenges. Eur. Polym. J. 54, 18–38. https://doi.org/10.1016/j.eurpolymj.2014.02.005

Zou, F., Xu, X., Chen, R., Lan, J., Li, G., Tan, Z., Xu, J., Jiang, X., Leng, Z., 2024. A novel foaming additive derived from waste polyethylene terephthalate (PET) for low-carbon warm mix asphalt. Resour. Conserv. Recycl. 202, 107377.

https://doi.org/10.1016/j.resconrec.2023.107377