

Article

The Development of a Fully Renewable Lubricant: The Effect of Ethyl Cellulose on the Properties of a Polyhydroxyalkanoate (P34HB)-Based Grease

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Abstract: In the context of the ongoing evolution of the global economy and increasing environmental awareness, green sustainable development has emerged as a crucial pathway for future advancements in the lubrication industry. In this study, we prepared bio-based greases by employing a thickener system consisting of polyhydroxyalkanoate (P34HB) and ethyl cellulose, with castor oil serving as a base oil. The results indicate that ethyl cellulose significantly and effectively enhances the grease system's mechanical and colloidal stability. Notably, the addition of 5 wt% ethyl cellulose leads to superior mechanical and colloidal stability, while increasing concentrations gradually result in rheological properties similar to those of oleogels. Furthermore, the wear volume of grease containing 5 wt% ethyl cellulose was reduced by 39.20% compared to that of a reference P34HB grease, demonstrating its exceptional wear resistance. The present study provides a theoretical foundation and empirical evidence for the future development of biodegradable greases as substitutes for non-degradable materials, thereby expanding the range of environmentally friendly greases formulated with biomass-based thickeners.

Keywords: novel thickening agent; poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB); ethyl cellulose; renewable lubricant



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1. Introduction

In recent years, there has been a growing emphasis on the need for sustainable and environmentally friendly materials to address global ecological issues [1]. For instance, in the lubrication industry, using greases containing renewable, readily available, sustainable, and biodegradable constituents is a promising approach to promoting environmental conservation. This method has garnered increasing research interest in utilizing biopolymers (such as cellulose and its derivatives) and vegetable oils as viable sources for grease preparation. Cellulose and its derivatives are sustainable biomaterials obtained from renewable resources that find applications as thickeners in various substances and fields, including food, tissue [2], cosmetics, pharmaceuticals, paints, and coatings [3]. Of particular interest is the conversion of cellulose into valuable cellulose esters and ethers like ethyl cellulose, methyl cellulose, and hydroxyethyl cellulose, which has gained significant interest in the field of green and sustainable chemistry, resulting in advancements in environmental protection technologies [4]. Additionally, these materials demonstrate characteristics including increased strength and durability in composites, biodegradability [5], non-toxicity [6], and a relatively low cost [7]. Consequently, these materials have garnered considerable attention in recent decades for their utilization as additives or thickeners in lubricating greases [8]. For instance, the development of biodegradable greases involves the modification [9,10] of

thickeners such as cellulose, which significantly improves the rheological properties [11], mechanical stability [12], and lubricating characteristics [13] of greases.

Based on insights gleaned from our previous investigations, we have observed that both P34HB grease and specific cellulose-based oleogel systems suffer from deficiencies, particularly in terms of mechanical and colloidal stability. For instance, Sánchez et al. [12] examined various thickeners, including ethyl cellulose, methyl cellulose, cellulose acetate, and alpha cellulose, combined with castor oil as a base oil to prepare a series of bio-lubricating greases. However, these greases exhibited inferior mechanical stability and a higher propensity for leakage when compared to commercial counterparts. At present, various methods involving the combination of thickening agents (such as ethyl cellulose or methyl cellulose) are commonly employed in studies to enhance the mechanical stability or colloidal stability of bio-based greases [14–16]. The hydrophobic and hydrophilic nature of ethyl cellulose facilitates the formation of multiple hydrogen bonds and supramolecular systems, thereby promoting its potential for diverse applications in various scientific fields. For instance, Silva et al. [17] employed ethyl cellulose and coconut oil to prepare oleogels wherein potential hydrogen bond interactions between the two components led to the formation of a polymer network that encapsulated the oil phase while offering mechanical reinforcement. Notably, the formulation of a grease incorporating a blend of ethyl cellulose and methyl cellulose as thickeners results in mechanical stability comparable to that of commercially available greases. Yan et al. [18] demonstrated that the hydroxyl group of ethyl cellulose could engage in a non-covalent supramolecular system with effective plasticizers, thereby enhancing its overall property through robust interchain hydrogen bond interactions. In summary, this innovative research holds significant promise for addressing environmental concerns and reducing dependence on non-renewable energy sources, aligning perfectly with economic development strategies and sustainability principles.

This work investigates a pioneering effort in preparing a novel series of lubricating greases by employing a sustainable biomaterial (P34HB) and ethyl cellulose as thickeners for the first time, with castor oil serving as the fundamental base oil. The impact of thickener content on the colloidal stability, mechanical stability, rheological behavior, and tribological characteristics of the lubricating greases was compared with a reference P34HB grease. This research holds significant importance in regulating grease properties and developing environmentally friendly alternatives that demonstrate superior properties, thereby contributing substantially to sustainable economic and social advancement.

2. Materials and Methods

2.1. Materials

Refined castor oil (kinematic viscosity at 40 °C: 248.3 mm²/s) was purchased from Inner Mongolia Weiyu Biotechnology Co., Ltd. (Tongliao, China) as a biodegradable lubricating oil for greases. The following are different materials used as thickeners to prepare greases. P34HB powder (particle size of about 15 µm; industrial grade) (Mw: ~300,000 g/mol) was acquired from Tianjin Guoyun Biotechnology Materials Co., Ltd. (Tianjin, China). The P34HB powder was primarily polymerized through the polymerization of 3-hydroxybutyric acid (3HB) and 4-hydroxybutyric acid (4HB), with specific parameters provided by the manufacturer, as presented in Table 1. Ethyl cellulose powder (analytical grade) was purchased from Tianjin Zhonglian Chemical Reagent Co., Ltd. (Tianjin, China). Methyl cellulose powder (food grade) was sourced from Guangzhou Xinzhiwei Food Ingredient Mall. Bentonite powder (particle size of about 10 µm; industrial grade) was procured from Hebei Hongyao Mineral Products Processing Co., Ltd. (Shijiazhuang, China). Pre-made calcium stearate soap powder (industrial grade) was obtained from Huzhou Linghu Xinwang Chemical Co., Ltd. (Huzhou, China), and prefabricated 12 hydroxy-stearate lithium soap powder (industrial grade) was purchased from Qingdao Red Star Chemical Group Co., Ltd. (Qingdao, China). Lignin powder (industrial grade) was purchased from Chuangsheng Building Materials Chemical Co., Ltd. (Shanghai, China).

Table 1. Specific parameters of P34HB.

Properties	Unit	Property Parameter	Testing Standard
		P34HB	
Density	g/cm ³	1.2	[19]
Glass transition temperature	°C	2	[20]
Melting temperature	°C	155–165	[20]
Tensile strength	MPa	33	[21]
percentage of breaking elongation	%	10	[21]
Notched impact strength	KJ/m ²	3.7	[22]
Flexural strength	MPa	42	[23]
Flexural modulus	GPa	1.8	/
Thermal decomposition temperature	°C	286	[24]
Vicat softening temperature	°C	134	[25]

2.2. Preparation of Biopolymer-Based Lubricating Greases

Following the methodologies proposed by Sánchez et al. [26] and Martín-Alfonso et al. [27], crucial experimental parameters such as the reaction temperature, stirring rate, and duration were meticulously adjusted to prepare a series of lubricating greases. The final procedure for fabricating the lubricating grease was as follows: the mixture was prepared by heating the oil to approximately 160 °C, adding P34HB powder, and further heating it to 175 °C. During this period, the stirring speed was adjusted to 300–400 rpm, and the mixture was stirred for 10 min. Subsequently, the temperature was maintained at 175 °C with a stirring rate of 160 rpm for a reaction time of 1 h. A second thickening agent, such as ethyl cellulose, was then added and reacted under identical test conditions for an additional duration of 30 min. Finally, the mixture was poured into a steel pan and cooled at room temperature to obtain the desired complex P34HB-EC-based grease. The terminology of complex P34HB-EC-based greases varies according to the concentration of the thickener. For instance, a P34HB-EC-based grease containing 30 wt% P34HB and 5 wt% ethyl cellulose is designated as P30E5. The reference grease (P34HB grease) possessed a thickener content of 35 wt%. The process of preparing the reference grease was consistent with that of the composite P34HB-EC-based grease, except for the steps in which a second thickener was not required. Subsequently, the prepared grease was designated P35.

2.3. Characterization Methods

The cone penetration, steel mesh oil separation, mechanical stability, drop point, and other physical and chemical properties of grease were determined according to relevant standards [28–31]. Furthermore, the microstructures of the lubricating greases were examined using a scanning electron microscope (SEM, JSM-7610F, JEOL, Tokyo, Japan). SEM pretreatment methods were categorized into the soaking method (compound P34HB-EC-based grease system) and the powder method (ethyl cellulose). In the soaking method, an appropriate amount of grease was applied to the copper grid, followed by 48 h of immersion in n-heptane. The solvent was gradually separated, and the sample was dried at room temperature before it is coated with gold for SEM characterization. As for the powder method, a small portion of vacuum-dried raw material was mixed with 7 mL of ethanol and subjected to ultrasound treatment for 5 min. This process was repeated three times after centrifugation. Finally, ethanol was added and shaken, and a drop of the mixture was placed on a copper grid for gold-coating and drying at room temperature before characterization testing. The lubricating grease underwent qualitative testing using Fourier infrared spectroscopy (FTIR, Tensor 27, Bruker, Bremen, Germany). Potassium bromide windows with a resolution of 4.0 cm^{−1} were utilized and scanned 32 times, maintaining a fixed path length of 100 µm while using air as the background. Infrared spectra were collected within the range of 4000 to 400 cm^{−1}.

2.4. Rheological Measurements

The rheological characteristics of the lubricating greases were methodically assessed utilizing an Anton Paar MCR302 rotational rheometer equipped with a PP25/TG plate-plate geometry (diameter: 24.958 mm; gap: 1 mm). The relationship between the apparent viscosity and shear rate of the greases was analyzed at a temperature of 25 °C, with the shear rate ranging from 0.01 s^{−1} to 100 s^{−1}. Oscillation mode tests were conducted at controlled temperatures of 25 °C and 80 °C with a constant angular frequency (ω) of 10 rad·s^{−1} through amplitude sweep tests. Subsequently, the grease was subjected to small-amplitude oscillatory shear (determined by an amplitude-scanning experiment) at a fixed strain (γ) of 0.0403% and an angular frequency (ω) ranging from 0.1 to 100 rad·s^{−1} within the linear viscoelastic region. The thixotropic behavior of the lubricating greases was examined under a fixed strain of 0.1% at a temperature of 25 °C.

2.5. Tribological Characterization

Friction tests were conducted using an Optimol-SRV long-stroke high-frequency reciprocating test machine (Germany Optimol Instrument Equipment Co., Ltd., München, Germany) under varying temperatures, loads, and frequencies. It was observed that the prepared complex P34HB-EC-based greases experienced lubrication failure under relatively light loads. The test temperatures were set at 60 °C and 80 °C, with a stroke of 1 mm. The frequencies tested included 1 Hz, 3 Hz, and 5 Hz. Additionally, two different loads of 10 N and 25 N were applied during the tests, which lasted 30 min. Subsequently, three-dimensional profilometry (Bruker Coutour GT-K, Tucson, AZ, USA) and scanning electron microscopy (EVO 10, Zeiss, Germany) were employed to characterize the worn surfaces of P30E5, P32E3, and P35 under the conditions of 5 Hz, 25 N, and 80 °C. Simultaneously, the wear scar of P30E5 was characterized using energy-dispersive X-ray spectroscopy (EDS, Xplore 15, Oxford Instruments, Oxford, UK) under the same conditions.

3. Results and Discussion

3.1. Physicochemical Properties of Complex P34HB-EC-Based Greases and P34HB-Based Grease

According to previous experiments, it was determined that greases containing 35 wt% P34HB achieved a stable state with a cured base oil. Consequently, the thickening agent's total concentration for this study was 35 wt%. The previous experiment attempted to enhance the mechanical and colloidal stability of lubricating grease through the compounding of methyl cellulose, yet no significant improvements were observed. Subsequent attempts with alternative thickeners also showed minimal enhancements in grease consistency or colloidal stability (as illustrated in Table 2). For instance, the incorporation of 5 wt% bentonite into the grease formulation resulted in non-saponification and the formation of a dense, yellow, solid mass. Therefore, ethyl cellulose and P34HB were chosen as thickeners with a fixed total content of 35 wt%. Various proportions of ethyl cellulose (0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, and 30 wt%) were investigated. The prepared greases are illustrated in Figure 1. The appearance of the complex P34HB-EC-based greases transitioned from a dark yellow hue to a lighter shade as the ethyl cellulose content increased.

Table 2. Supporting data from previous exploratory experiments.

Type	Unworked Penetration (0.1 mm)	Worked Penetration (0.1 mm)	Penetration Variation (0.1 mm)	Oil Separation (%)
P34HB (30 wt%)–Lignin (5 wt%)	317	424	107	11.58
P34HB (30 wt%)–Ethyl Cellulose (5 wt%)	277	363	86	2.60
P34HB (30 wt%)–Lithium Soap (5 wt%)	422	-	-	-
P34HB (30 wt%)–Calcium Soap (5 wt%)	224	354	129	18.28
P34HB (30 wt%)–Methyl Cellulose (5 wt%)	324	422	98	19.94

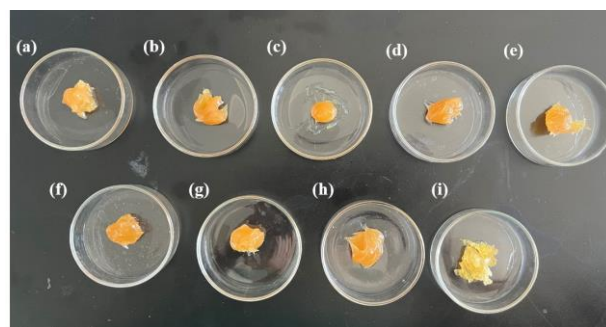


Figure 1. Images of complex P34HB-EC-based greases ((a) P35; (b) P32E3; (c) P30E5; (d) P28E7; (e) P25E10; (f) P20E15; (g) P15E20; (h) P10E25; and (i) P5E30).

The physicochemical properties of the complex P34HB-EC-based greases with varying ethyl cellulose contents (0 wt%, 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, and 30 wt%) were analyzed, as summarized in Table 3. It was observed that increasing the ethyl cellulose content resulted in a notable reduction in the worked penetration value of these greases, decreasing it from 110 to 44. This trend indicates that the incorporation of ethyl cellulose effectively enhances the mechanical stability properties of these greases. This enhancement is attributed to ethyl cellulose's capacity to elevate the grease system's viscosity, thereby contributing to the long-term physical stability of lubricating greases [26].

Table 3. Physicochemical properties of complex P34HB-EC-based greases with different thickener ratios.

Type	Thickening Agent Concentration (wt%)		Unworked Penetration (0.1 mm)	Worked Penetration (Roller Test, 25 °C, 2 h, 0.1 mm)	Penetration Variation (0.1 mm)	Abbreviation
	P34HB	Ethyl Cellulose				
1	35	0	318	428	110	P35
2	30	5	277	363	86	P30E5
3	25	10	237	300	63	P25E10
4	20	15	200	245	45	P20E15
5	15	20	150	194	44	P15E20
6	10	25	115	Too hard, causing the drum to operate abnormally		P10E25
7	5	30	95			P5E30

An analysis of the experimental results reveals that when the ethyl cellulose content surpasses 10 wt%, the consistency of a composite P34HB-EC-based grease gradually escalates, potentially impeding subsequent experiments. Therefore, an ethyl cellulose content within or below 10 wt% was selected. Complex P34HB-EC-based greases with ethyl cellulose contents of 0 wt%, 3 wt%, 5 wt%, 7 wt%, and 10 wt% were prepared, as depicted in Figure 2. With an increased ethyl cellulose content, these greases exhibited a distinctive semi-fluid state with specific viscosity. The fundamental physicochemical properties of the complex P34HB-EC-based greases were examined, as outlined in Table 4. As the ethyl cellulose content increased, the working penetration value of the grease decreased from 110 to 63, indicating a significant improvement in the mechanical stability of these greases. However, the mechanical stability of the complex P34HB-EC-based grease studied is marginally inferior to that of the oleogel or lithium-based grease prepared by Sanchez et al. [12]. The cone penetration rate of these types of greases was also reduced from 13.61% to a range between 2 and 5%. This suggests that ethyl cellulose effectively enhanced the colloidal stability of these greases within a specific range by potentially reducing oil separation by increasing grease system viscosity [12]. However, when the ethyl cellulose content was 3 wt%, its mechanical property did not improve, indicating that adding a small amount of ethyl cellulose does not enhance the mechanical stability of a complex P34HB-EC-based grease. This disparity in the binding capacity of base oils is attributed to variations in the microstructural composition of these greases. Notably, the

complex P34HB-EC-based grease (with 5 wt% ethyl cellulose and 30 wt% P34HB) provided better mechanical stability and colloidal stability. Through an analysis of Tables 3 and 4, it can be inferred that the dropping points of P20E15, P15E20, P10E25, and P5E30 exhibit a gradual decrease, while the oil separation rate of the steel mesh demonstrates a progressive increase. This phenomenon may be due to the increased sensitivity of the ability of the oil to bind the base oil to temperature changes after the oil reaches a certain threshold of ethyl cellulose concentration.

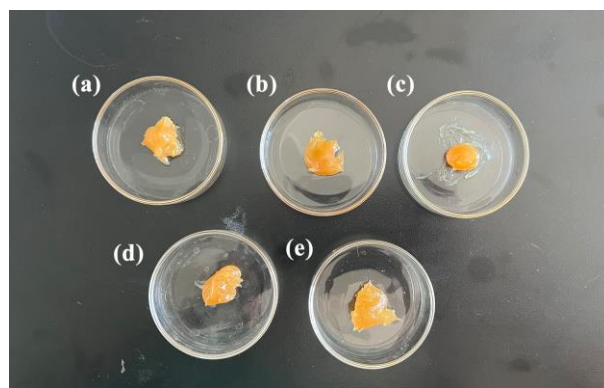


Figure 2. Photographs of complex P34HB-EC-based greases with different thickener ratios ((a) P35; (b) P32E3; (c) P30E5; (d) P28E7; and (e) P25E10).

Table 4. Physicochemical properties of complex P34HB-EC-based greases in a small range of ethyl cellulose content.

Type	Thickening Agent Concentration (wt%)		Unworked Penetration (0.1 mm)	Worked Penetration (Roller Test, 25 °C, 2 h, 0.1 mm)	Penetration Variation (0.1 mm)	Dropping Point (°C)	Oil Separation (%)	Abbreviation
	P34HB	Ethyl Cellulose						
1	35	0	318	428	110	144	13.61	P35
2	32	3	294	408	114	142	4.28	P32E3
3	30	5	277	363	86	147	2.60	P30E5
4	28	7	258	348	90	142	2.67	P28E7
5	25	10	237	300	63	145	5.76	P25E10

3.2. Structural Characterization of Complex P34HB-EC-Based Greases and P34HB-Based Grease

As depicted in Figure 3, the raw material ethyl cellulose manifests as adhesive block-like aggregates. With an escalation in ethyl cellulose content, the microstructure of a complex P34HB-EC-based grease undergoes a transition from larger-sized flakes to flakes exhibiting varying stacking degrees and sizes. The irregular stacking degree trend in the flake microstructures of these greases, in comparison to pure P35, is as follows: P30E5 > P28E7 > P32E3 (Appendix A Figures A1 and A2). This suggests that the addition of ethyl cellulose enhances the stability of the network microstructure of the grease, corroborating the cone penetration rate test results. As the ethyl cellulose content reaches 10 wt%, the microstructure of the composite P34HB-EC-based grease gradually transforms from a relatively irregularly stacked lamellar aggregate to a larger lamellar structure. It is observed that increasing the ethyl cellulose content induces a structural transformation within the grease. This suggests that the microstructure gradually transitions to a different form as the ethyl cellulose content increases. The observed phenomenon is attributed to the polarity of castor oil, facilitating an effective interaction with the ethyl cellulose network [32]. In summary, the microstructure of complex P34HB-EC-based grease evolves with variations in ethyl cellulose content.

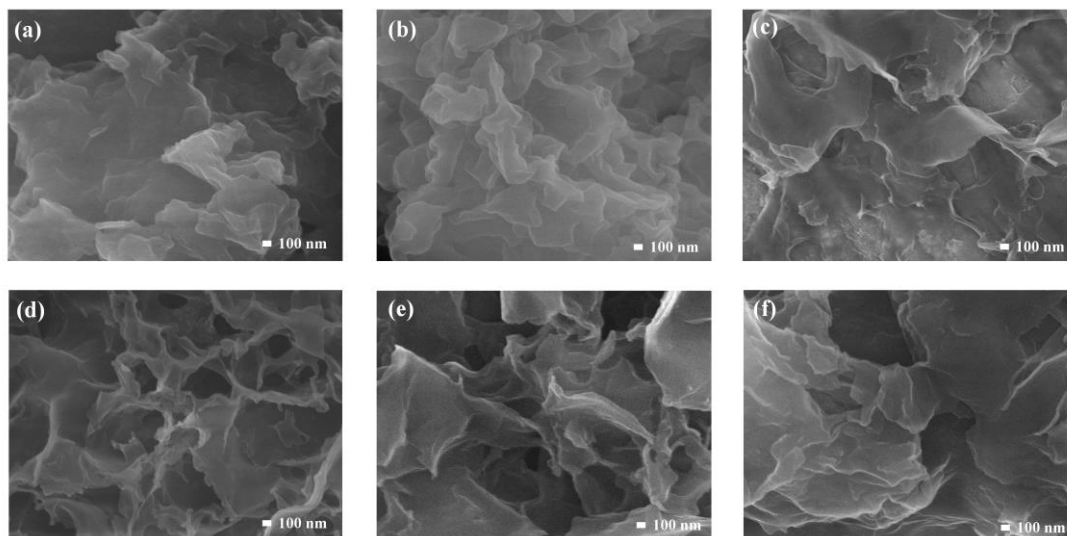


Figure 3. Microscopic morphology of greases with different thickener ratios magnified 30,000 times ((a) P35; (b) Ethyl cellulose; (c) P32E3; (d) P30E5; (e) P28E7; and (f) P25E10).

A comparative analysis of the infrared spectra of P34HB, ethyl cellulose, castor oil, and P30E5 is depicted in Figure 4a. In the spectrum of P30E5, the O-H stretching vibration peak near 3479 cm^{-1} experiences a shift and broadening, with no new absorption peaks observed. This suggests the presence of intermolecular forces (such as hydrogen bonds or van der Waals forces) in complex P34HB-EC-based greases prepared with P34HB, ethyl cellulose, and castor oil [33,34]. As illustrated in Figure 4b, the spectrum of P35 exhibits prominent peaks near 3437 cm^{-1} , 1746 cm^{-1} , 1056 cm^{-1} , and 1640 cm^{-1} , representing the stretching vibration peaks of free O-H, C=O, and C-O-C and the bending vibration peak of O-H, respectively [35]. Compared to P35, the infrared spectra of greases with varying ethyl cellulose contents exhibit noticeable shifts from 3437 cm^{-1} to a range between 3466 and 3523 cm^{-1} in their O-H stretching vibration peaks. This phenomenon suggests an electron density rearrangement effect within the grease molecules [36]. Simultaneously, the absorption peak of the OH stretching vibration in the associated state of a carboxylic acid is observed within the range of $3200\text{--}2500\text{ cm}^{-1}$. For instance, a series of continuous minor peaks within the range of $2700\text{--}2500\text{ cm}^{-1}$ was observed, corresponding to characteristic absorption peaks associated with the stretching vibration of the carboxylic acid hydroxyl group. A comparative analysis of the infrared spectra for P30E5 and P35 reveals a significant broadening of the peaks within the range of $2700\text{--}2500\text{ cm}^{-1}$. The incorporation of ethyl cellulose indicates the formation of novel hydrogen bond states in these greases. As the ethyl cellulose content increases, the peak of the O-H stretching vibration in the complex P34HB-EC-based grease shifts from 3523 cm^{-1} to lower frequencies, with no significant change in the position of the C=O stretching vibration peak. These observations indicate the formation of more hydrogen bonds and a reduced force constant in the bound state between ethyl cellulose and P34HB, which are responsible for the formation of connection points in the microstructure [18,37]. In summary, the microstructure of complex P34HB-EC-based greases remains solidified due to hydrogen bonding, impeding base oil flow. The hydrogen bond state formed by these greases changes with an increasing ethyl cellulose content, indicating that ethyl cellulose also plays a crucial role in restricting the flow of the base oil within the microstructure.

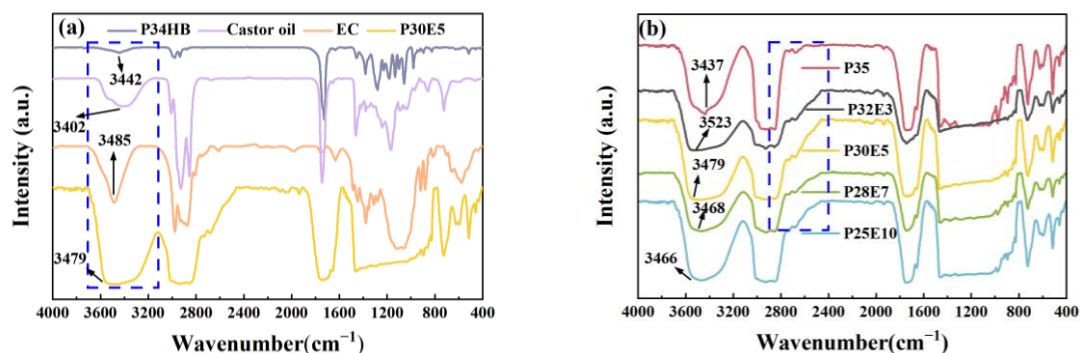


Figure 4. Infrared spectra of complex P34HB-EC-based grease with different thickener ratios (a) and its raw materials (b). (The blue boxes in a and b represent the absorption peaks of OH tensile vibration in different states).

3.3. Rheological Properties of Complex P34HB-EC-Based Greases and P34HB-Based Grease

The experimental results presented in Figure 5 demonstrate the strain scanning and frequency scanning experiments conducted on the complex P34HB-EC-based greases. It is widely recognized that the energy storage modulus (G') and the loss modulus (G'') represent a grease's elastic and viscous potential energy. The point at which $G' = G''$ signifies the structural transformation or flow point, indicating a transition to a fluid state in which $G' < G''$. Therefore, the shear stress at this transition point reflects the structural strength of the grease [38]. At a temperature of 25 °C, an increase in ethyl cellulose content results in a decrease in the gap between G'' and G' for this grease system, indicating that the structural characteristics of the grease are influenced by the ethyl cellulose content. Moreover, with an increasing temperature, significant variations in flow points are observed between two temperatures for P35, P32E3, P30E5, P28E7, and P25E10 which correspond to 206.8 Pa, 210.1 Pa, 330.9 Pa, 356.0 Pa, and 2427.2 Pa, respectively. These findings demonstrate that the intermolecular distance of the thickener in the microstructure is significantly increased by temperature and shearing, leading to a weakening of intermolecular forces and resulting in a pronounced alteration in structural strength. The temperature sensitivity of these greases then exhibited a gradual increase with the augmentation of the ethyl cellulose content, providing empirical evidence for predicting the drop point and oil separation trend on steel mesh when the ethyl cellulose content exceeds 10 wt%. This phenomenon is attributed to the hydrogen bonding ability of composite P34HB-EC-based grease at different temperatures, including an increased instability in the polymer network due to hydrogen bond breakage at elevated temperatures [39]. The frequency-dependent behavior of the SAOS function for the complex P34HB-EC-based greases with varying thickener contents at 25 °C is depicted in Figure 5d. The composite P34HB-EC-based grease system always maintains a $G' > G''$ state in the linear viscoelastic region, indicating that the greases' storage and loss moduli are influenced by frequency. Notably, the linear viscoelastic curve of P35 displays a plateau region in which both G'' and G' gradually increase with frequency, resembling a phenomenon observed in commercial greases based on mineral oil and metal soap. Extensive research has shown that typical storage modulus (G') values of standard lithium greases (NLGI 1-3) [40–42] range from 10^4 to 10^5 Pa, depending on their composition and processing conditions, and approximate loss modulus (G'') values are also available. With an increased ethyl cellulose content, the early moduli, G' and G'' , of the complex P34HB-EC-based greases initially stabilize before exhibiting a significant upward trend. The observed phenomenon indicates substantial alterations in internal structure during the shearing process. Moreover, the progressive increase in the composite modulus (G' and G'') values of these greases gradually resembles the rheological behavior reported by Davidovich-Pinhas et al. [43] in oil gels, particularly as the ethyl cellulose content rises. This phenomenon is commonly observed in polymer systems with pronounced entanglement and shows characteristics demonstrated by previously studied oleogels [44]. Consequently, it suggests a transition toward a gel-like structure in complex P34HB-EC-based greases

with an increasing ethyl cellulose content. Additionally, a higher thickener content leads to elevated values of G' and G'' , indicating a progressive enhancement of the microstructural network within these greases. This observation highlights ethyl cellulose's crucial role in influencing both the rheological behavior and structural properties of these greases.

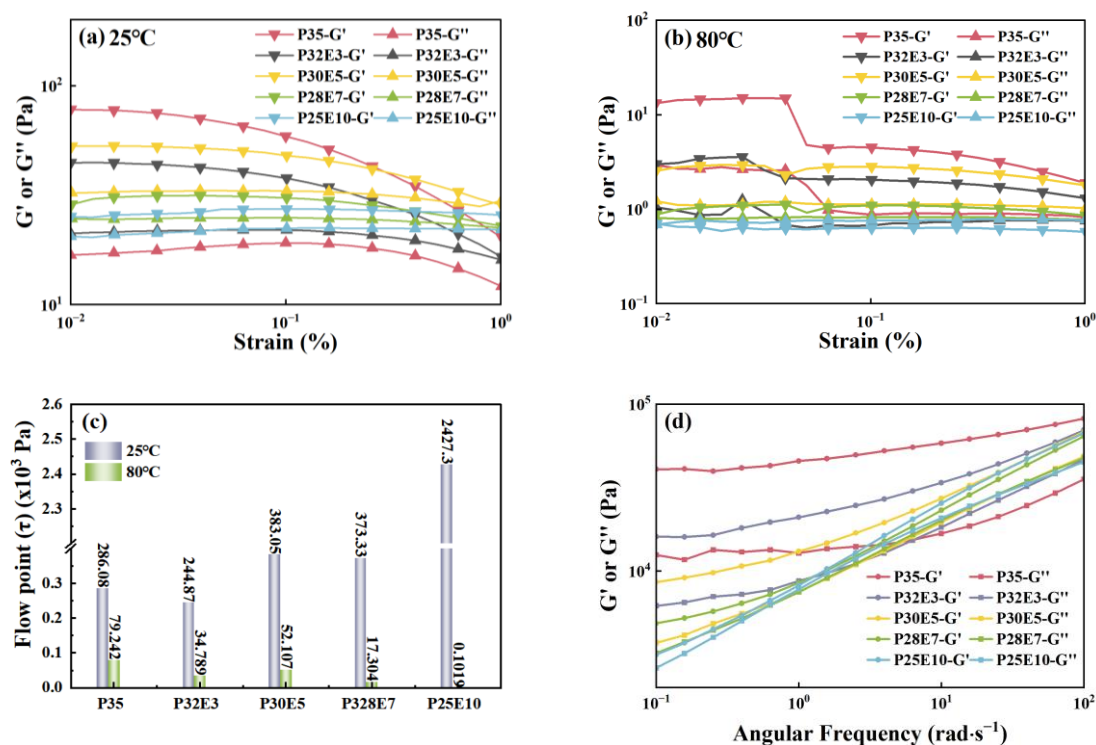


Figure 5. Modulus and shear stress variation curves of complex P34HB-EC-based grease at different temperatures ((a), 25 °C; (b), 80 °C), and flow Shear stress value at flow point (c); (d) Frequency scanning curve of complex P34HB-EC-based grease with different thickening agent additives.

To further investigate the thixotropic property of complex P34HB-EC-based greases, the thixotropic loop method was employed to characterize differences in thixotropic behavior. Figure 6 illustrates the thixotropic loops and corresponding area bar charts for these greases with different thickener ratios. It is evident that the complex P34HB-EC-based grease systems prepared using various concentrations of ethyl cellulose and P34HB as thickeners show distinct areas within their respective thixotropic loops. It is worth noting that at high shear rates, the microstructure of P35 undergoes irreversible damage. The results indicate that P35 exhibits a limited affinity for base oil binding, inadequate mechanical stability, and diminished recovery capability. However, the composite P34HB-EC grease's microstructure reorganizes into a stable spatial network structure with disorderly thixotropic loop changes and macroscopic thixotropic areas upon external force recovery. As shown in Figure 6b, the calculated thixotropic values for the P35, P32E3, P30E5, P28E7, and P25E10 greases are $75,142.8 \text{ Pa}\cdot\text{s}^{-1}$, $67,557.8 \text{ Pa}\cdot\text{s}^{-1}$, $292,870.1 \text{ Pa}\cdot\text{s}^{-1}$, $237,375.5 \text{ Pa}\cdot\text{s}^{-1}$, and $453,645.7 \text{ Pa}\cdot\text{s}^{-1}$, respectively. This indicates that as the ethyl cellulose content decreases, the lubricating grease's thixotropic property improves, aligning with the results of the structural strength test. The reason behind this phenomenon lies in the fact that greases with lower ethyl cellulose contents exhibit reduced structural strength and possess larger cavity volumes within their microstructures. Consequently, these greases demonstrate enhanced recovery capabilities after experiencing damage, thereby leading to an improvement in their thixotropic property [45].

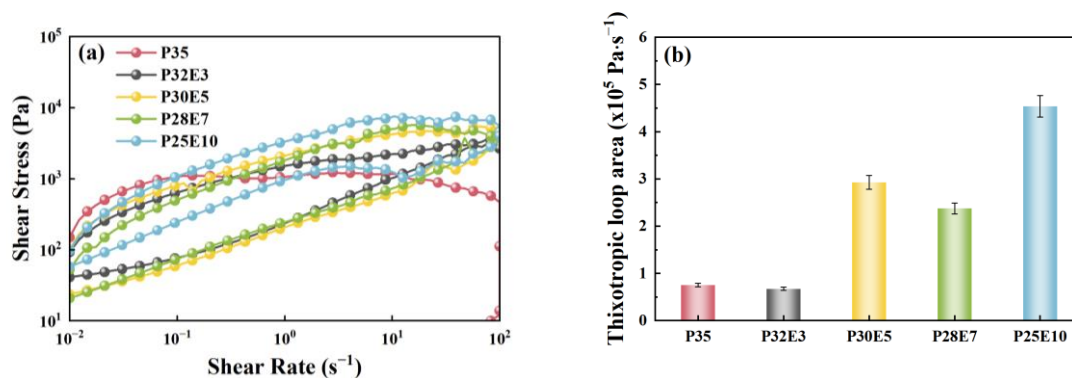


Figure 6. Thixotropic loops (a) and their area histograms (b) for complex P34HB-EC-based greases with different thickener ratios.

3.4. Tribological Characteristics of Complex P34HB-EC-Based Greases and P34HB-Based Grease

The tribological properties of the prepared greases were systematically evaluated through tribological tests conducted on an Optimol-SRV long-stroke high-frequency reciprocating test machine. As shown in Figures 7 and 8, the friction coefficient curves of P28E7 and P25E10 fluctuate significantly, which results in lubrication failure. This phenomenon indicates that the microstructures of the greases with higher thickener contents are easily destroyed at the test temperature, resulting in softening, loss, and increased friction, which corresponds to the results of the amplitude scanning test. Moreover, the viscosity increment of the grease caused by gelation contributes to an elevation in its coefficient of friction [46]. Figure 7a–c depicts the friction coefficient curves of complex P34HB-EC-based greases under conditions of 25 N and 80 °C at frequencies ranging from 1 Hz to 3 Hz and 5 Hz. The friction coefficient of P30E5 is comparable to that of the reference grease (P35), while P32E3 exhibits a slightly higher friction coefficient than P35. These results suggest that the inclusion of 5 wt% ethyl cellulose in the P34HB-EC-based grease improves its tribological properties, making it comparable to P35. When the frequency exceeds 1 Hz, consistently lower friction coefficients are observed for the P30E5 sample compared to P32E3 and P35 (refer to Figure 7d). The findings indicate that the tribological properties of complex P34HB-EC-based grease demonstrate superior characteristics when incorporating a 5 wt% ethyl cellulose content. In summary, the tribological properties of composite P34HB-EC-based greases are slightly improved within a specific ethyl cellulose content range. These findings suggest that the addition of 5 wt% ethyl cellulose enhances tribological characteristics, rendering them comparable to those exhibited by the reference (P35).

To further explore the differences in the tribological properties of complex P34HB-EC-based greases with varying thickening agent concentrations, experiments were carried out under a constant load of 10 N. As illustrated in Figure 8, it is evident that the P35 exhibits inferior tribological characteristics across all tested frequencies, indicating lubrication failure. In all test conditions, the friction coefficient of P30E5 either matches or surpasses that of P35, suggesting excellent anti-friction properties for P30E5. These findings are generally consistent with those obtained under the 25 N test conditions. We found through previous studies [46] that cellulose acetate butyrate-based oleogels with high viscosity and yield stress are only suitable for low-friction applications. Furthermore, under low load conditions, the prepared grease (P30E5) exhibits similar frictional properties to those observed in a pure oleogel dispersion with a high thickening agent content (7 wt% CAB), as reported in this study. In conclusion, the behavior of complex P34HB-EC-based greases in response to load and temperature conditions exhibits distinct variations, thereby highlighting the superior tribological characteristics of P30E5 under light load and temperature conditions.

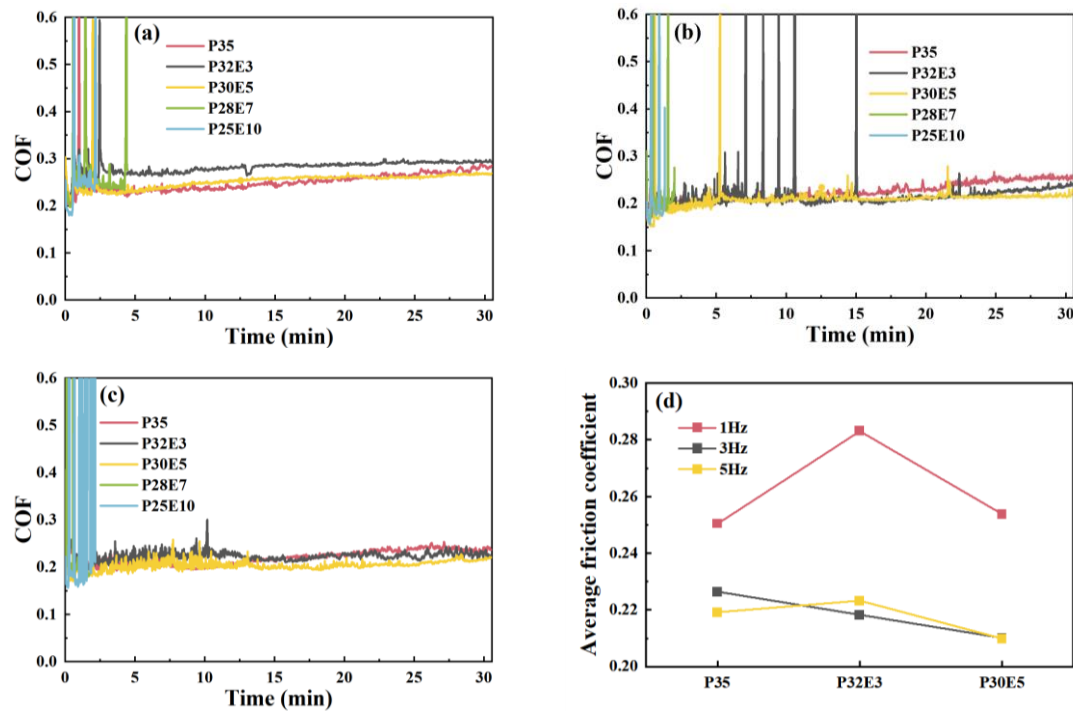


Figure 7. Friction coefficient curves ((a) 1 Hz; (b) 3 Hz; and (c) 5 Hz) and average friction coefficients (d) of complex P34HB-EC-based greases at different frequencies at 25 N and 80 °C.

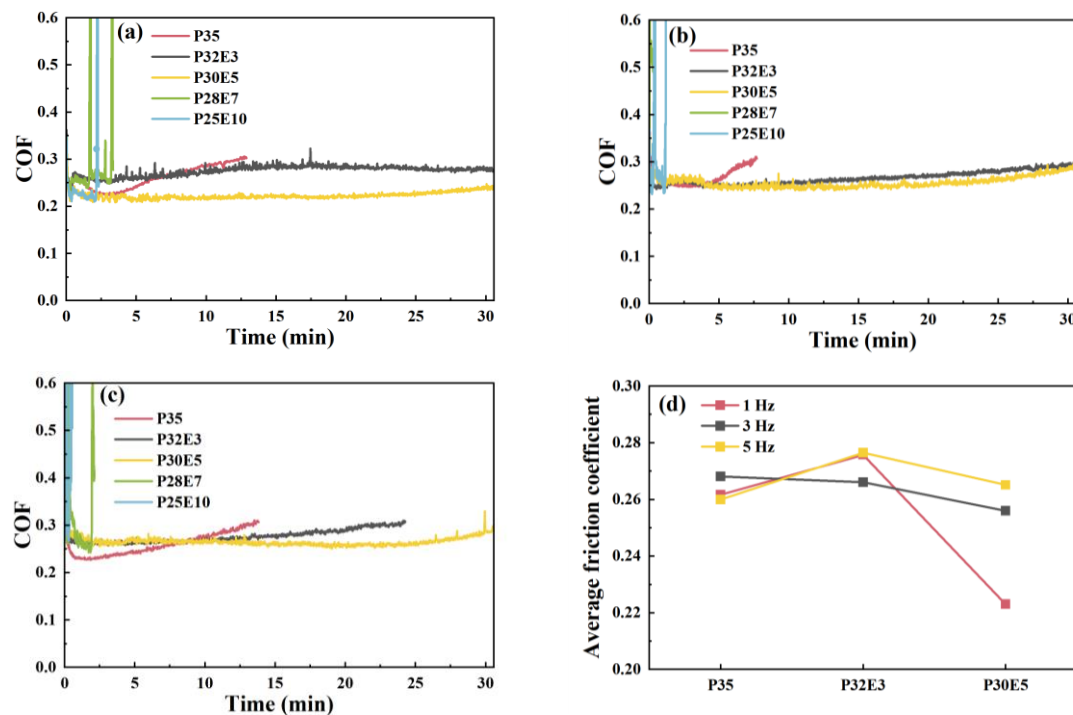


Figure 8. Coefficient of friction curves ((a) 1 Hz; (b) 3 Hz; and (c) 5 Hz) and the average coefficient of friction (d) of complex P34HB-EC-based greases at different frequencies at 10 N and 60 °C.

The anti-wear characteristic of the composite P34HB-EC-based grease system was further compared and analyzed, as depicted in Figure 9. Compared to P35 (Figure 9a), the wear volumes of P30E5 and P32E3 were reduced by 39.20% and 28.14%, respectively, indicating that the addition of ethyl cellulose effectively mitigates wear in P34HB grease. This is attributed to ethyl cellulose increasing the viscosity of the grease system, thereby enhancing

the thickness of the lubricating film and reducing wear [47]. Longitudinal two-dimensional plots of surface scratch depth (Figure 9b–e) and three-dimensional contour maps illustrate the worn surface characteristics of steel blocks treated with different compound P34HB-EC base greases. It is evident that all three greases have similar wear widths, while P30E5 demonstrates a relatively shallow wear depth with a slight furrow, followed by P32E3 and then P35, consistent with their respective wear volumes. In summary, P30E5 shows superior friction reduction and anti-wear properties compared to P35 under lighter loads and temperatures. However, further enhancement of the tribological characteristics of composite P34HB-EC-based greases is still warranted when compared to conventional greases available on the market.

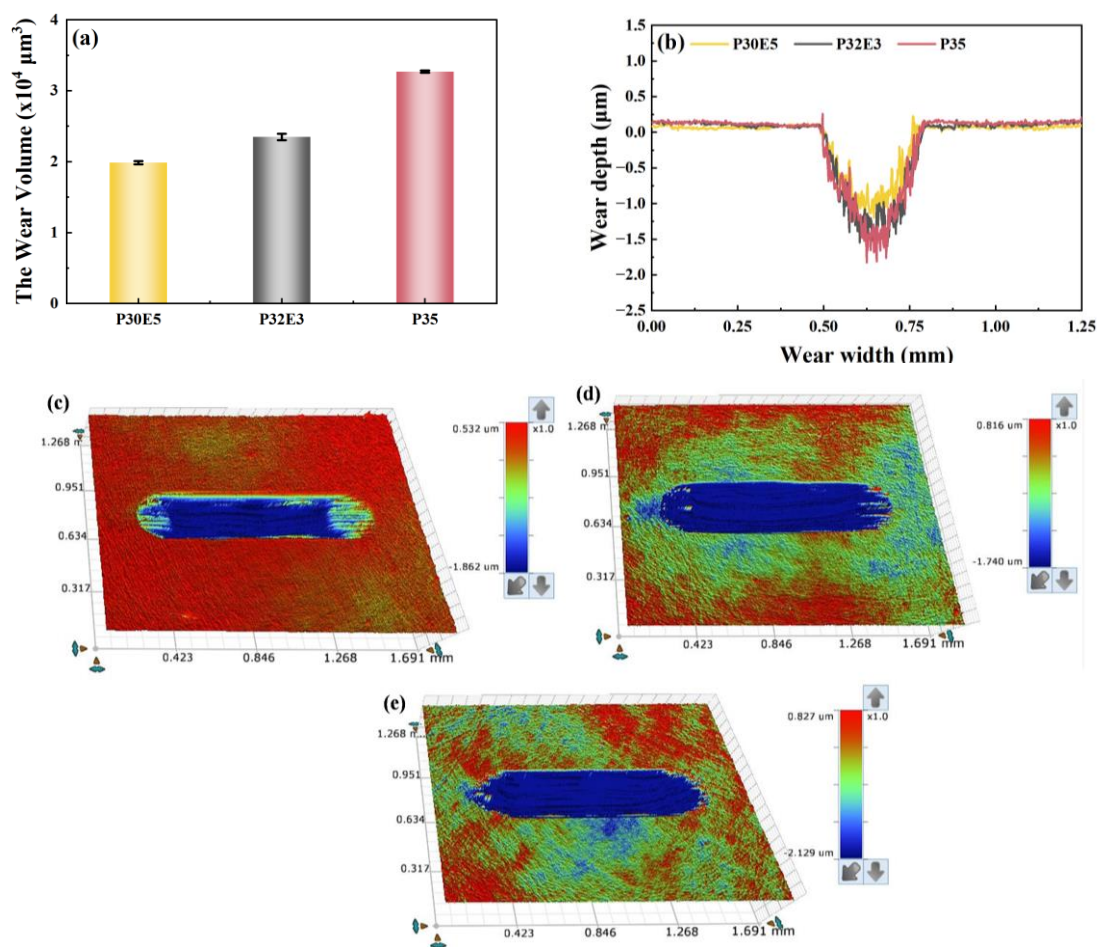


Figure 9. Wear volume (a), depth of abrasion (b), and three-dimensional contours ((c) P30E5; (d) P32E3; and (e) P35) of complex P34HB-EC-based greases under test conditions of 25 N, 5 Hz, and 80 °C.

The surface wear characteristics of the complex P34HB-EC-based greases were investigated using SEM and EDS, as depicted in Figure 10a–c. Based on an analysis of the wear surfaces magnified 100 times, it can be observed that the addition of ethyl cellulose effectively reduces the width of the scratches as the content of ethyl cellulose increases. When magnified 500 times, the worn surface of pure P35 exhibits larger black precipitates and deeper furrows in its scratches. However, P32E3 exhibits narrower wear marks and slightly shallower furrows compared to P35, indicating that the inclusion of trace amounts of ethyl cellulose in compound P34HB-EC-based grease effectively mitigates wear. As the ethyl cellulose content increases to 5 wt%, the scratches in the complex P34HB-EC-based grease gradually narrow, and the furrows gradually become shallower compared to P35. This indicates that adding a certain amount of ethyl cellulose effectively reduces wear, which

is consistent with the wear volume results. An elemental analysis of the wear surfaces of P30E5, P32E3, and P35 after friction under the conditions of 25 N, 5 Hz, and 80 °C is presented in Figure 10d–f. The presence of ethyl cellulose in composite P34HB-EC-based grease was found to exclude other elements involved in the friction reaction, suggesting that the friction process primarily generates a lubricating film comprising elements such as C, O, Fe, N, and others. The increased content of element C in P30E5 indicated an enhanced adsorption of carbon-containing organic matter on the friction pair surface, underscoring the beneficial anti-wear role played by P30E5.

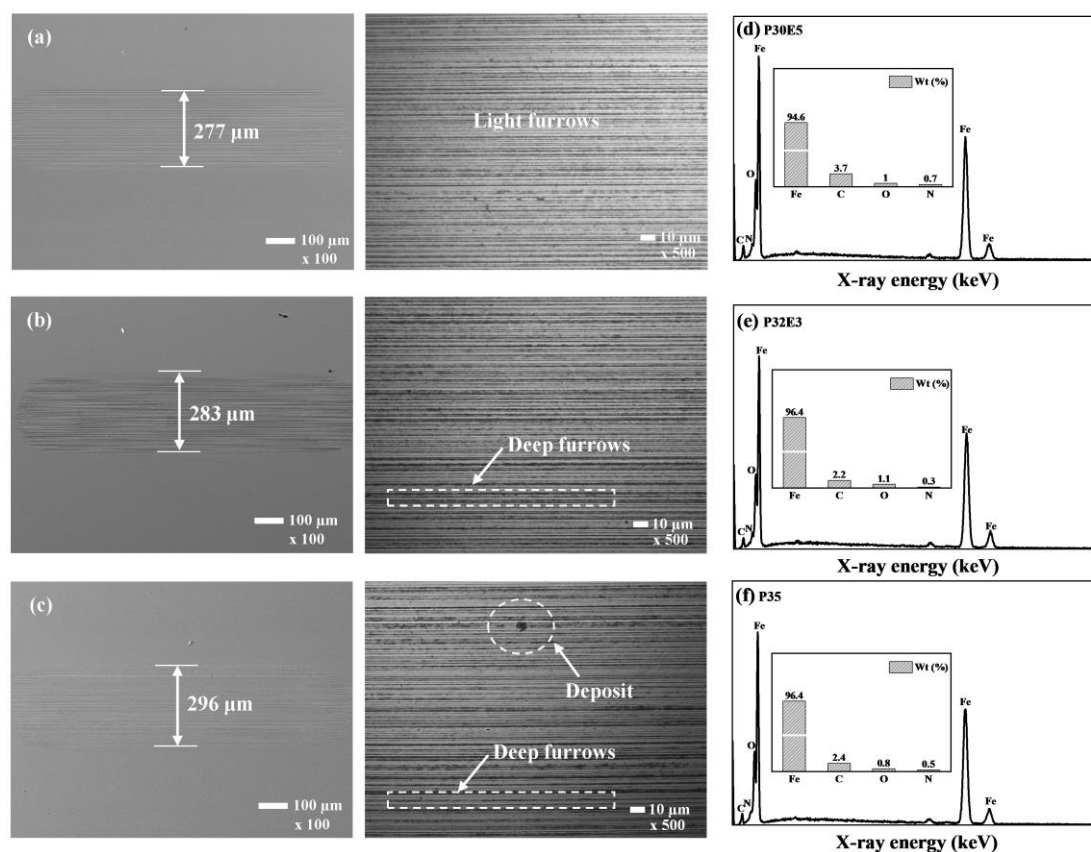


Figure 10. SEM ((a) P30E5; (b) P32E3; and (c) P35) and EDS analyses of wear surfaces of greases-lubricated steel blocks under 25 N, 5 Hz, and 80 °C test conditions ((d) P30E5; (e) P32E3; and (f) P35).

4. Conclusions

This study introduces a novel approach to optimizing environmentally friendly greases, offering a fresh perspective for the future development of biodegradable greases in the sustainable lubrication industry. The primary objective is to formulate a fully renewable and sustainable composite P34HB-EC-based grease by adjusting the concentration ratio of ethyl cellulose to P34HB and investigating its mechanical, rheological, and tribological characteristics. The findings are as follows:

(1) An analysis of physical and chemical properties revealed that the incorporation of ethyl cellulose significantly enhanced both the mechanical stability and colloidal stability of the compound P34HB-EC grease. Remarkably, the lubricating grease containing 5 wt% ethyl cellulose demonstrated superior colloidal stability.

(2) The incorporation of ethyl cellulose significantly influences the structural formation of complex P34HB-EC-based greases. On one hand, by incorporating varying amounts of ethyl cellulose and P34HB into a lubricating grease to form different hydrogen bond states (such as associated hydroxyl groups), the flow binding ability of the base oil is altered.

This phenomenon leads to a transformation in the microstructure of the thickener from large-sized sheets to stacked structures of varying degrees and sizes. On the other hand, an increase in the ethyl cellulose content gradually reduces the gap between the storage modulus (G') and loss modulus (G'') of complex P34HB-EC-based grease, resulting in a structure that has gel-like properties.

(3) Furthermore, the lubricating grease containing 5 wt% ethyl cellulose demonstrates comparable tribological characteristics to the reference P34HB grease. It is hypothesized that a lubricating film composed mainly of C, O, Fe, and N elements is formed in P34HB-EC-based grease and traditional P34HB-based grease during friction processes.

Therefore, the preparative utilization of the environmentally friendly thickener ethyl cellulose and P34HB represents an exceptionally effective and promising strategy that can substantially augment the mechanical stability of grease while ensuring absolute dependence on sustainable resources. Nevertheless, additional refinement is necessary with respect to the grease's composition and tribological characteristics to determine the appropriateness of ethyl cellulose–P34HB-based greases for industrial implementations. Moreover, the quantification of hydrogen bonding strength remains a formidable challenge with current experimental conditions and methodologies. Consequently, we envision that our future investigations will delve deeper into comprehending the underlying mechanism of hydrogen bonding exhibited by these lubricants through the utilization of advanced techniques such as molecular dynamics models or chemometrics models.

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Data Availability Statement: All data generated during this study are included in this article, and the datasets are available from the corresponding author upon reasonable request.

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

Appendix A

The micromorphologies of grease with varying ratios of thickening agents were meticulously analyzed and compared using scanning electron microscope images at magnifications of 10,000, 30,000, and 50,000.

The microstructures of greases with varying ethyl cellulose content exhibit distinct winding degrees, as evidenced in Appendix A Figure A1. Through electron microscopy analyses of adhesives Figures A1f and A2f, when the ethyl cellulose content reaches 10 wt%, the microstructure of the composite P34HB-EC-based grease was determined to consist of distinctly irregularly aggregated lamellar assemblies. The microstructure of this grease gradually forms larger chunks and cohesive layers, with a significant increase in the volume of interlamellar voids. This indicates that an increase in ethyl cellulose content induces a structural transformation in the grease. It is noteworthy that the microstructure of P25E10 exhibits adherence to both small and large sheet structures, with the small-size sheet structure on its surface resembling that of ethyl cellulose (see Figure A1). Furthermore, a cellulose-strip-like structure can be observed in the lower right corner of Figure A1. This phenomenon suggests that ethyl cellulose can modulate the microstructure of grease.

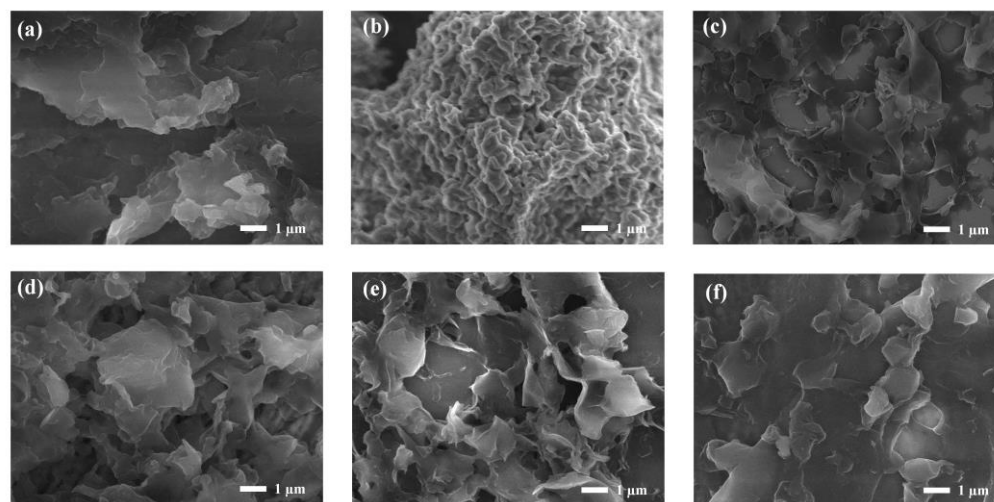


Figure A1. Microscopic morphology of greases with different thickener ratios magnified 10,000 times ((a) P35; (b) Ethyl cellulose; (c) P32E3; (d) P30E5; (e) P28E7; and (f) P25E10).

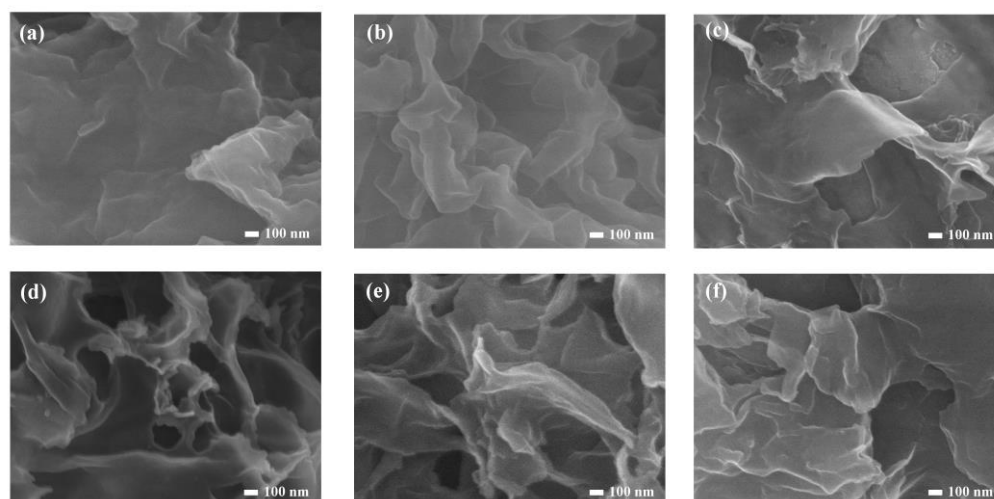


Figure A2. Microscopic morphology of greases with different thickener ratios magnified 50,000 times ((a) P35; (b) Ethyl cellulose; (c) P32E3; (d) P30E5; (e) P28E7; and (f) P25E10).

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