Response to Reviewer 1 Comments

Dear Reviewer:
Thank you for your comments concerning our manuscript entitled “Preparation and properties of acetoacetic ester-terminated polyether pre-synthesis modified phenolic foam”. Those comments are very helpful for revising and improving our paper, as well as the important guiding significance to our researches. We have studied comments carefully and try our best to improve the manuscript which we hope meet with approval. Revised portion are marked in red in the paper. The main corrections and the responds are as flowing:

**Point 1:** Some specific scientific terms used in the manuscript are different from the standard terms, e.g. “pre-synthesis modification”, “polyether diol N210”, “sulfuric acid ω=98%”, “acetoacetic ester-terminated polyether synthesis formula”, “glass water separator”, “potassium bromide abrasive sheet”, etc. This makes the text unclear and I would recommend thorough language and style professional editing of the manuscript.

**Response 1:** We have already polished the language by the MDPI platform when we submitted the manuscript. Considering your comments, we contacted the English editor of MDPI again and revised the manuscript. We have revised “polyether diol N-210”, “98% sulfuric acid”, “glass manifold”, “pressing potassium bromide troche”, etc. But sorry that we unable edit “pre-synthesis modification” and “acetoacetic ester-terminated polyether synthesis formula”.

The “pre-synthesis modification” is to name the procedure of the modified phenol reacted with paraformaldehyde to synthesize the phenolic resin which proposed after we summarize the synthesis method of phenolic resin. During the reaction of ethyl acetoacetate with the polyether diol, the polyether diol hydroxyl group are removed, and only remained the polyether skeleton and the acetoacetate in the final product. So it called “acetoacetic ester-terminated polyether synthesis formula”.

If you have any better suggestions, please let us know. Thank you very much.

**Point 2:** Abstract, line 20: “The effect of changing the added amount of acetoacetic ester-terminated polyether on the mechanical properties and microstructure of the modified phenolic foam was investigated.”

It would be useful to specify the range of modifier variation (e.g. from 10 to 20% of the phenol content).

**Response 2:** Thank you and we have added the range of modifier variation to the Abstract.

The effect of changing the added amount of acetoacetic ester-terminated polyether from 10 to 20% of the phenol content on the mechanical properties and microstructure of the modified phenolic foam was investigated.

**Point 3:** Introduction, lines 77-90: Although the choice of modifier and synthetic strategy are explained in the last paragraph of the introduction, the aim of the research is not clearly
presented. Please add a short paragraph stating the main goal of this investigation and how it will be achieved.

**Response 3:** We have added the main goal of the investigation and the methods to the Introduction.

Ge D et al. analyzed the effect of different molecular weight reactive polyether on the properties of phenolic foams, in which the modified phenolic resin and foam using the reactive polyether with a molecular weight of 1000 showed the best performance [30]. Therefore, we modified the phenolic resin by using an acetoacetic ester-terminated polyether with a molecular weight of about 1000 and cross-linked the obtained polyether resin with the base resin to prepare a modified phenolic foam. The polyether skeleton has low cohesive energy and easily rotates, which makes up for the disadvantage that the benzene ring is only connected by methylene groups in the phenolic resin structure and the density of the rigid group is too large to rotate, and using its unique flexible structure to toughen the phenolic foam. In the paper, the effects of the acetoacetic ester-terminated polyether on the properties (such as the resin molecular structure, foam strength, toughness, pulverization rate, and microstructure) of the phenolic foam were investigated.

**Point 4:** Lines 101-110: 2.2. Synthesis of Modified Phenolic Resin

Please state if the synthetic procedure is newly developed or provide reference(s) if it is adopted or modified from published work(s)? Please add information about the reaction yield and specify the isolation and purification procedure.

**Response 4:** The synthetic procedure for preparing acetoacetic ester-terminated polyether is involved in the patent published by Groegler G. in 1969 and still applied today [1-2]. The synthetic procedure of the polyether phenolic resin by reacting the modified phenol reacted with paraformaldehyde referred to the synthetic procedure of boron phenolic resin [3] and Xylok resin [4]. After the research group investigated and summarized the phenolic resin modification method, we named the method of the modified phenol reacted with paraformaldehyde to synthesize the phenolic resin as pre-synthesis modification method.

The final product phenolic foam needs to be measured for free formaldehyde emission （less than 1.5mg/L） and it can be applied after reaching the standard （according to the Chinese National Standard GB/T 20974-2014）. Since the free formaldehyde in a certain content range does not need to be removed, we did not calculate the yield of the resin. If the resin needs to calculate the yield, the formula is as follows.

\[ P = \frac{m - (0~0.1) \times m}{m_1 + m_2 + m_3} \times 100\% \]

\((m_1\) is the amount of the acetoacetic ester-terminated polyether, \(m_2\) is the amount of the phenol, \(m_3\) is the amount of the paraformaldehyde, \(m\) is the amount of the polyether phenolic resin.)

This paper mainly studies the properties of modified phenolic foams, in which acetoacetic ester-terminated polyether was selected as a modifier. The carbonyl of the keto-structure in the acetoacetic ester-terminated polyether was undergoing nucleophilic addition reaction under acidic conditions [5], forming an enol-like structure, and the final modifier were
reacted with phenol in the form of an enol structure during the experiment. Therefore, we believe that the keto and enol isomers of the acetoacetic ester-terminated polyether have no direct effect on the properties of the modified phenolic resin, so we have no separated and purified the modifier. The resin was only subjected to vacuum dewatering treatment during the synthesis procedure. So we unable provide the isolation and purification procedure, hope you can understand.


**Point 5:** Line 120: Scheme 1 (this applies for Scheme 2 and entire section 3.3. Mechanism Analysis as well)

Chemical structures of acetoacetic ester-terminated PPG on Scheme 1 (as well as of resin on Scheme 2) is not convincing. It is well known that the molecule of ethyl acetoacetate (a β-ketoester) undergo dynamic process of intramolecular hydrogen bonding, i.e. keto-enol tautomerism is present:

(see the scheme from Thermo Fisher Scientific Inc. Application note AN52327_E 12/17M in the attached file)

The equilibrium is shifted to the keto-form and the content of enol isomer is estimated by different authors to be about 10% only. It is worth to mention that numerous research papers report on the keto-enol tautomerism of ethyl acetoacetate studied by different methods including NMR, FTIR and UV spectroscopy. It is misleading to present the keto and enol isomers of equal importance in studied reactions. In this context the chemical structures presentation and overall discussion should be reconsidered. If the authors have specific quantitative data on the keto-enol composition of the synthesized acetoacetic ester-terminated PPG it is worth to include it in the manuscript and discuss it in details.

**Response 5:** Thank you for your suggestion on the article. We strongly agree with your statement about the molecule of ethyl acetoacetate has keto-enol tautomeria. As you said, the keto and enol isomers of unequal importance in studied reactions. This is a question worthy of further discussion.

But as stated Response 4, the carbonyl of the keto-structure in the acetoacetic ester-terminated polyether was undergoing nucleophilic addition reaction under acidic conditions, forming an enol-like structure, and the final modifier were reacted with phenol in the form of an enol structure during the experiment. The acetoacetic ester-terminated polyether has been used in the polyurethane industry [1,6-8]. In the synthesis of polyether imide materials, the keto and enol content did not directly affect the preparation and properties of the final
product. Therefore, we believe that the keto and enol content will not affect the preparation and properties of the polyether phenolic resin, and we have no tested the keto and enol content of acetoacetic ester-terminated polyether in the experiment. So we unable provide the quantitative data on the keto-enol composition of the synthesized acetoacetic ester-terminated polyether. Although we also want to improve the level of the manuscript, the quantitative analysis of keto and enol requires a large number of experiments. The authors are facing the problem of master's paper, so we are sorry that we do not have enough time to conduct this research. Your suggestions are important to us. Because of your suggestions, we have found some shortcomings in my current work. We will improve the scientific research level according to your suggestions in the future work and get more achievements!


Point 6: Line 121: “The polyether phenolic resin is obtained by sealing the cooled resin for 24 hours.”

Unclear sentence - please rephrase.

Response 6: We have rephrased the sentence in the manuscript.

At this time, the resin polymerization reaction was not complete. In order to balance the reaction equation, the cooled resin was needed to seal for 24 hours to obtain the polyether phenolic resin.

Point 7: Line 122: Table 1 and further: Please specify the meaning of (phr)

Response 7: The “phr” means parts per hundreds in weight of resin.

Point 8: Lines 158-160: “The stretching vibration peaks of the —COOR group of the acetoacetic ester-terminated polyether are located at 1712.94 cm⁻¹. Moreover, the characteristic peaks of the C=O group of the modifier (acetoacetic ester-terminated polyether) are located at 1743.42 cm⁻¹ which in the resin are disappeared.”

The discussion on the FTIR spectra should be enhanced. As the C=O band is double, please specify the wavenumber of the second peak too. Please explain the reason why the peak at 1743.42 cm⁻¹ is disappearing.

Response 8: In the FTIR spectra, we have relabeled the peaks of C=O and COOR and corrected the description of the discussion on the FTIR spectra, the reason of the peak at 1743.42 cm⁻¹ disappearing was explained.
In the infrared spectrum of the acetoacetic ester-terminated polyether, the stretching vibration region of the C=O group and the —COOR group are located at 1743.42 cm\(^{-1}\) and 1719.47 cm\(^{-1}\). The stretching vibration peaks of the —COOR group of the polyether phenolic resin are located at 1712.94 cm\(^{-1}\). The C=O group of the ketone structure in acetoacetic ester-terminated polyether were undergoing a nucleophilic addition reaction under acidic conditions to form an enol-like structure. The characteristic peaks of the C=O group of the modifier (acetoacetic ester-terminated polyether) are located at 1743.42 cm\(^{-1}\) which in the resin are disappeared.

**Point 9:** Lines 164 and 179: Figures 2 and 3: The signals in the NMR spectra are marked with labels and numbers and further assigned in the text. It is advisable to include chemical structures with assigned labels and numbers on the spectra for clarity.

**Response 9:** Thank you very much for your valuable comments. We have put the chemical structures with assigned labels and numbers on the spectra.
**Figure 3.** The $^{13}$C NMR spectra of the basic phenolic resin and polyether phenolic resin (the amount of acetoacetic ester-terminated polyether is 16% of the amount of phenol).

**Point 10:** Line 393: Reference 17
“17. Joanna P. S.; Marcin B.; Boguslaw C.; Marek I. Effect…”
Please check the authors’ family names.

**Response 10:** We are very sorry for our incorrect writing of the authors’ family names of Reference 17, we have revised it.


Special thanks to you for your good comments and suggestions, and hope that the correction will meet your approval.