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LETTER TO THE EDITOR

Comments on the Paper: Kinetics Studies on Oxirane Cleavage of Epoxidized Soybean Oil by Methanol and Characterization of Polyols

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Dear Editor,

Recently a paper entitled “Kinetics Studies on Oxirane Cleavage of Epoxidized Soybean Oil by Methanol and Characterization of Polyols” was published in the *Journal of American Oil Chemists’ Society* (2008) 85:113–117 (DOI 10.1007/s11746-007-1187-5). The authors claimed they had achieved the synthesis of soy polyol from epoxidized soybean oil (ESO) by ring-opening with methanol WITHOUT A CATALYST. The authors also presented the oxirane cleavage kinetics and characterization of soy polyols by DSC and FTIR but no information on the polyol structures was provided.

The most important implication claimed in the paper by the authors would lead to the revision of ring-opening mechanisms of oxiranes. Ring-opening of internal oxiranes with methanol and other alcohols is usually catalyzed by protic acids and Lewis acids. No report has been published on the use of methanol as a ring-opener for oxirane without any catalyst at the temperatures the authors used in the paper!

We were skeptical about the findings since they contradict the well-established facts. We have examined the process by reproducing the experiments presented in the paper. In short, we could not corroborate the findings in the paper and the comments below are criticisms of the published paper.

We would like to point out some inconsistencies in the paper and show our results obtained by repeating the experimental procedures presented in the paper.

Inconsistencies in the Paper

1. Page 113, right column, line 7 from bottom: *The preparation of polyols from ESO with various reactants has been the subject of many studies [8, 9].* Reference 8 cited in this paper has nothing to do with fatty-based polyols.
2. Page 114, left column, line 2: *Other advantages of polyurethanes synthesized from soy-based polyols include a higher thermal stability and improved dielectric properties [1, 7].* Reference 7 is about polyols and does not have any relevance to thermal stability and dielectric properties of polyurethanes.
3. Page 114, Materials Section. The ESO utilized by the authors was not well characterized. Acid value, hydroxyl number (OH#) and Iodine value (IV) were missing. The acid value is critical, because the acid residue has a catalytic effect on ring-opening in the presence of methanol, especially those acids used in the epoxidation process. The infrared spectrum of pure ESO in Fig. 4 shows a relatively high concentration of hydroxyl groups at 3,500 cm^{-1}.
4. Hydrogen peroxide 30% and sulfuric acid 98% were listed in the materials section but nowhere in the paper were they used. They are usually chemicals used in epoxidation but the authors have used a commercially obtained ESO.
5. Page 114, left column, paragraph 3, Methods Section: “*ESO (40.0 g, 0.154 mol) was charged into a four-necked round-bottomed reaction flask equipped with a reflux condenser and was heated to the desired temperature in a constant-temperature water bath. Methanol, was prewarmed to the same temperature and then quickly added to the flask. Samples of the reaction mixture were taken at 30 min intervals during the*

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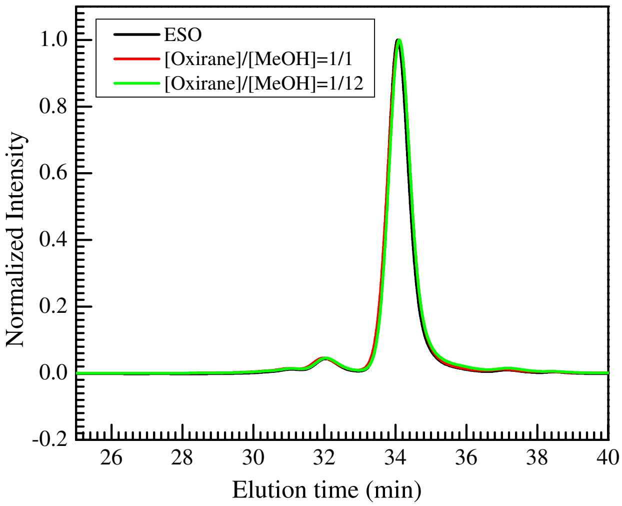

Fig. 1 GPC curves for ESO, and products at [Oxirane]/[MeOH] molar ratio of 1/1 and 1/12 (see text part above)

> *course of the experiment and analyzed for epoxy oxygen content (EOC) and hydroxyl content.*" Here, 0.154 mol should refer to epoxy rings, not ESO. Methanol's boiling point is 64.7 °C and it is not clear whether methanol can be preheated to 70 °C and then transferred into the ESO? Later in this section, the authors failed to explain how they treated the samples before epoxy oxygen content (EOC) and OH# measurements.

Our Results from Repeating the Experiments in the Paper

In order to check whether ESO can really be simply ring-opened by methanol without any catalyst, we tried to repeat two of the reactions performed by the authors in the paper: at [methanol]/[epoxy ring] molar ratio of 1/1 and 12/1 (weight ratios are 1/7.15 and 1.68/1, respectively). The ESO used here is Epoxol 7–4, from American Chemical Service, Inc., having an epoxy oxygen content = 7.0%, OH# = 6.46 mg KOH/g, acid number = 0.12 mg KOH/g, and IV = 0.6. Methanol used is of 99.9% pure HPLC grade from Fisher. ESO and methanol at the specific ratio were mixed and heated at 60–62.5 °C for 3 h, then medium vacuum was applied at 65 °C for 45 min to remove unreacted methanol, after which the liquids were submitted to EOC, GPC, and FTIR tests.

The results for ESO, product from 1/1, and product from 1/12 showed EOC 7.0, 7.032, and 7.030%, respectively, which indicates that no epoxy groups were consumed upon heating at 60–62.5 °C for 3 h.

Figure 1 depicts the GPC for ESO, product from 1/1 and product from 1/12, again. We found that no ring-opening happened in the two ESO–methanol mixtures upon heating at 60–62.5 °C for 3 h.

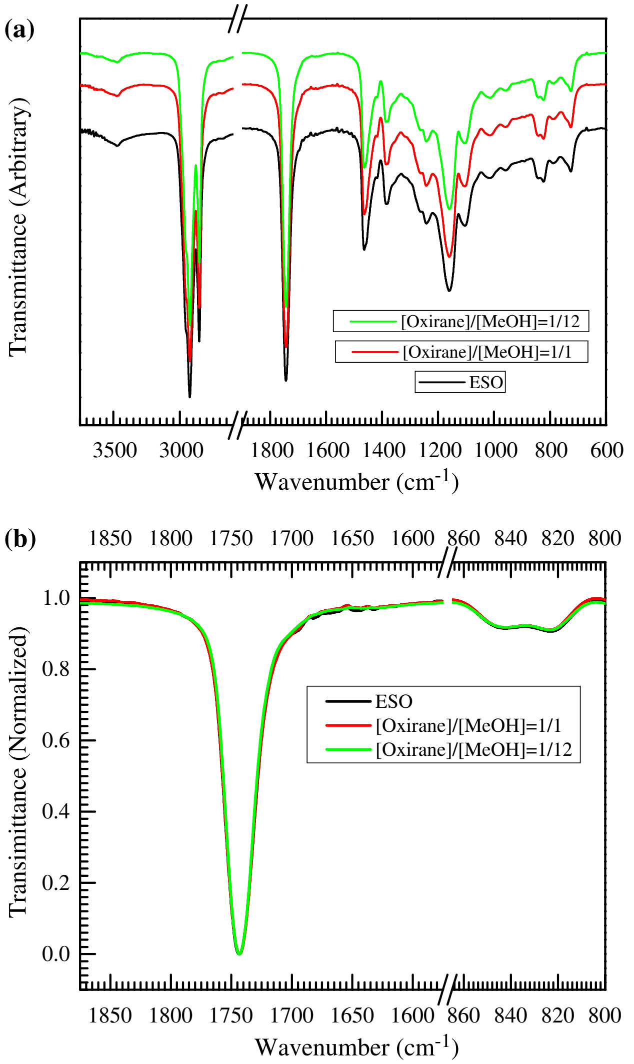

Fig. 2 FTIR spectra (**a**) and expanded FTIR spectra for carbonyl and epoxy groups (**b**) for ESO, products from [Oxirane]/[MeOH] molar ratio of 1/1 and 1/12

Figure 2 shows the FTIR results from ESO, product from 1/1 and product from 1/12. The results also suggest no ring-opening happened during the 3-h heating with methanol.

Conclusion

From the discussion and results above, we believe that ring-opening of ESO by methanol without any catalyst cannot happen. We consider the observed ring-opening in the systems presented in the paper to be due to impurity either in the ESO or in the methanol.