

Polyolefin Elastomers: A Study on Crosslinking, Blends and Composites

Polymer properties can be enhanced via polymer modification, such as blending with other polymers, or chemical crosslinking. Extra new properties of polymeric materials are achieved by polymer composites preparation. All mentioned methods are used in the presented work.

Chapter 1 "Introduction" gives review about thermoplastic elastomers (TPE), polymer blends, conducting polymer composites crosslinking of polymers. Chapter 2 "Objective of the thesis and brief summary" introduce the main tasks and four author's articles, which are part of the thesis numbered in the "Content" as chapters 5 to 8. Conclusions, Contribution to science and practice and Scope for future studies are presented in Chapter 3 "Closing remarks". List of references used the introduction is as following chapter. List of publication with four publications (which are part of the thesis) placed at beginning of the thesis (page 9) is somewhat misleading. Because there is no other information on the page, a reader obtains impression it is the list of all authors publications. But that list is placed at total end of the thesis as last two pages.

Used thesis structure is more usual for professor thesis. For doctoral thesis I accept that as well if enclosed articles represent corresponding volume author's research work and results. However, articles with 7 – 8 authors bring me question, how big is Mr. Rajesh's portion. I expect the candidate will explain that during his presentation.

I have a few questions to applicant or comments of presented results:

- Stress/strain tests were performed at a crosshead speed of 10 mm min^{-1} (p. 21, 92, ...). What was specimen working part length or distance between clamps? That information is necessary for better image about strain rate. Readers generally are not familiar with tensile microsample dimensions.
- How tensile modulus was determined (Table 3, p. 36)? I am surprised with low accuracy for EOC (1 valid digit) and very high (4 valid digits) for PP.
- How Grafguard density of 2 g cm^{-3} (p. 41) has been obtained? In accordance with GrafTech Technical Data Sheet a specific volume of Grafguard particles before expansion is about $1.25 \text{ cm}^3 \text{ g}^{-1}$.
- You have found the percolation threshold around 16 vol. % (p. 46) which corresponds with theoretical value calculated for uniform spherical particles. Is that number OK also for flakes?
- I want to believe the thermal conductivity was measured carefully and correct way. However, using a simple presumption of volume contribution of both components to EOC/graphite composite conductivity calculation (graphite density: 2 g cm^{-3} , graphite conductivity: $80 \text{ W m}^{-1}\text{K}^{-1}$, EOC conductivity: $0.196 \text{ W m}^{-1}\text{K}^{-1}$), the conductivity of

12.6 W m⁻¹K⁻¹ for 30 wt% and 24.2 W m⁻¹K⁻¹ for 50 wt% is obtained. Your experimental values (Fig. 9, p. 62) are significantly lower. Can you explain a reason of that difference?

- Creep and dynamic mechanical properties presented in Paper 3 are mostly typical for thermoplastics with variable gel content. Significant changes of viscoelastic properties due network degradation at high temperature or high peroxide level I feel as more interesting, even I am not surprised with that. Polymers with hydrogen on tertiary C atom in backbone chain are sensitive to scission by peroxides or high energy radiation (free radicals). From that reason e.g. polypropylene cannot be crosslinked by that way.

Maybe I am surprised by possibility itself of peroxide crosslinking of EOC and network formation. Now you have the system with crosslinking and scission reactions running simultaneously which is interesting from crosslinking process point of view. From list of your journal publications (ref. No. 3, 4 and 7) I expect you (or your supervisor) are aware of that. Have you tried e.g. to estimate scission/crosslinking reaction rates ratio at curing temperature?

- If POEs are suggested as “good alternative for sealing applications” (p. 34, below the table), compression set (CS) is more important than “structural regularity and low toxicity”. Have you measured CS of uncrosslinked and crosslinked EOC?
- In Closing remarks (p. 24) you has mentioned increased creep resistance and improved elastic properties of crosslinked EOC at elevated temperatures and in Conclusions of Paper 3 (p. 71) you write that “crosslinking is absolutely necessary for majority of applications”. What do you think about real application possibilities of peroxide crosslinked EOC?
- Page 93 – “... CF-composites exhibits percolation jump at 10 wt.% (5 vol.%) ... MWCNT composites at 15 wt.% (8 vol.%). ...” However, in Fig. 4 (p. 109) I can see mentioned jumps starting at 5 wt.% or 10 wt.%, respectively, and around 15 wt.% already ending (for both). What is reason for your lower values?

Volumetric contents here and in Tab. 2 (p. 104) are probably inaccurate. Can you show their calculation? The use of whole numbers in Tab. 2 for a filler content in % means that the content uncertainty is ± 0.5 %. Otherwise at least in range up to 10 % I feel that as incorrect. I can accept that for wt. % because I suppose that composites have been made carefully and on weight basis. Than e.g. 5 wt. % I understand as 5.0 ± 0.05 wt. %. However, corresponding filler content in vol. % cannot be 2.0 vol. % for CF and 3.0 vol. % for MWCNT. Here 2 valid digits has to be used to express filler content more precisely and its accuracy as well.

The thesis is written clearly and results are given in logical order. The reader’s impression could be better if a few text errors would be corrected. Usually they are typical typing errors (p. 20: “... above their meting temperatures. ...”, p. 92: “... After CBC has aquired the temperature of 45 °C, hollow cyclinder ...”, ...), some of them looks more like grammatical errors (p. 15: “... their properties are mainly depend on ... Toughening of brittle polymers using an elastomer is a best example .. is often aimed for in specific applications [8] ...” ...),

however, understandability and meaning is not changed. Missing negative mark (p. 14 : “... The low T_g of the polymer (≈ 55 °C) ...”) is somewhat more serious. I am not going to comment the Abstrakt, I understand the Czech language is not easy for the applicant. However, correction of that with Czech language knowing person would be useful. Only question to discussion why for “expandable” graphite is used Czech term “rozvinutelný” instead of more frequent “expandovatelný”?

Conclusion

The author has obtained new results and he has demonstrated good orientation in the field of polymer material properties modification and knowledge of theoretical background for that. He has proved his capability of scientific work. The thesis fulfills all requirements and **I recommend** it to the defense.

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