

Supporting Information

Orange is the New White: Rapid Curing of an Ethylene-Glycidyl Methacrylate Copolymer with a Ti-bisphenolate type Catalyst

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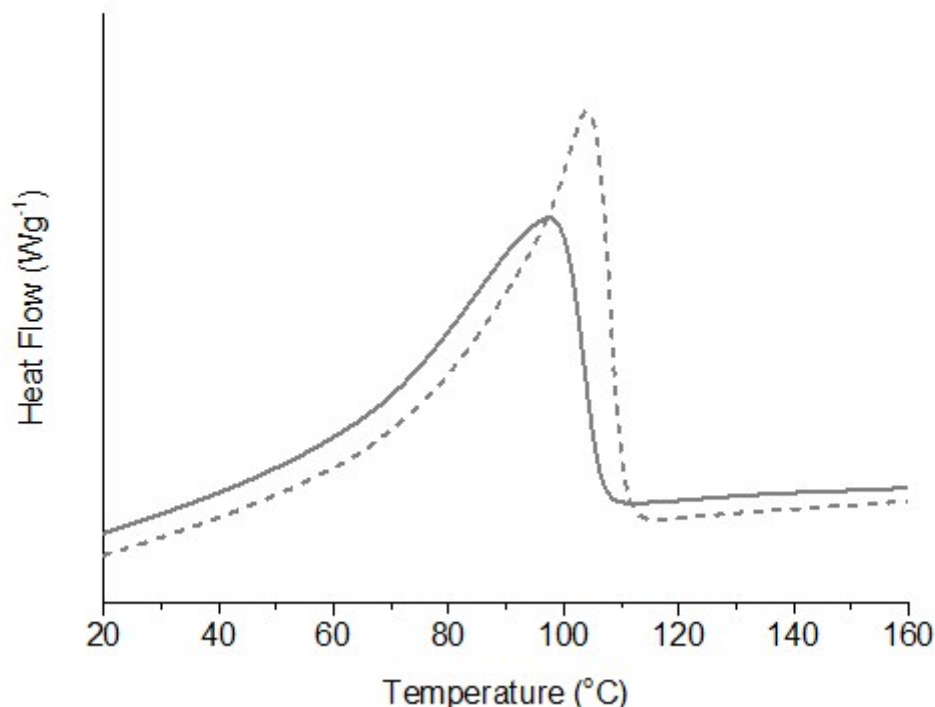


Fig. S1 DSC second heating thermograms of P(E-stat-GMA) crosslinked with BPP 3% (straight line) and BPP 3% + 0.5% Ti (dash line) for 5 min at 240°C.

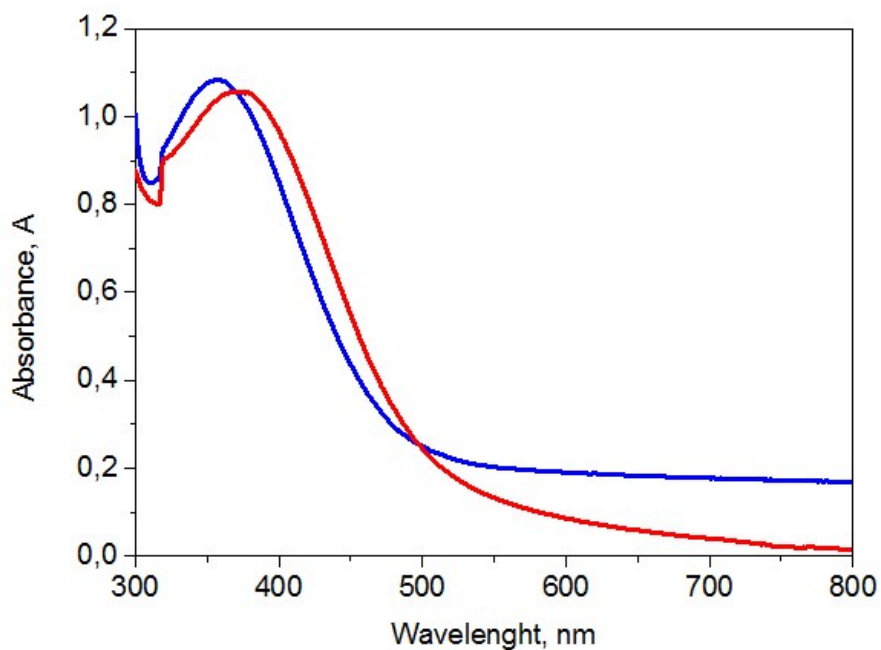


Fig. S2 UV-vis spectra of a 50 μm thick film of formulation **F2** containing P(*E-stat*-GMA), 3% BPP and 0.5% Ti(2-EtHexO)₄ melt-pressed at 150°C (blue), and a hexane solution of 4,4'-methylenebis(2-methylphenolate) bis titanium tri 2-ethylhexyloxide (red).

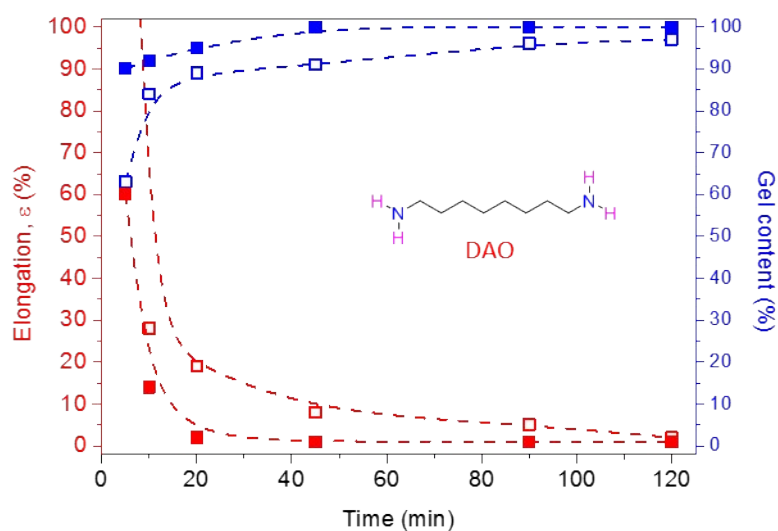


Fig. S3 Hot set elongation (red), and gel content (blue) of P(E-stat-GMA) crosslinked with DAO 1 wt% (hollow squares) and DAO 1% + 0.5% Ti (full squares) at 220 °C for 5 to 120 min.

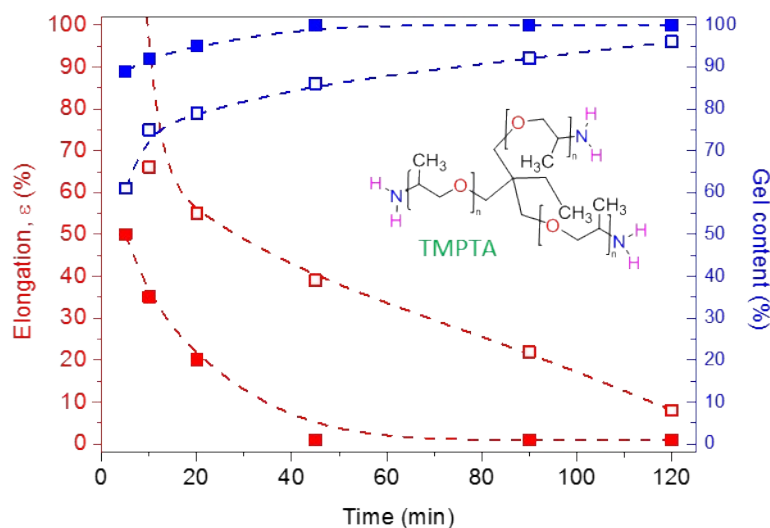


Fig. S4: Hot set elongation (red), and gel content (blue) of P(E-stat-GMA) crosslinked with TMPTA 2 wt% (hollow squares) and TMPTA 1% + 0.5% Ti (full squares) at 220 °C for 5 to 120 min.

NMR Characterisation: Solid-state NMR ^{13}C NMR spectra are shown in Figure 8. It should be emphasised that the spectrum of both the unreacted and cross-linked P(E-stat-GMA), respectively, is heavily dominated by two peaks from methylene groups in the polymer backbone. This two-peak feature appears due to the presence of conformational γ -gauche effect of the polyethylene and the chemical resolution allows for fractional quantification of the two conformations ^{1,2}. At the same time, the large methylene NMR peaks partly impede, from a spectral resolution point of view, the interpretation of small-intensity peaks in the 20-50 ppm range.

Detailed information of smaller peaks could still be obtained, which is here shown in the magnified part of the ^{13}C solid-state NMR spectra (10-80 ppm) before and after crosslinking. The assignment of these peaks of the P(E-*stat*-GMA) material are described in the Experimental section and not further discussed here. Peaks at 38.1, 27.9, 23.7, and 14.8 ppm originates from local chain branches along the polyethylene backbone. The solid-state NMR experiments also allows a direct observation of the cross-linkage reaction. The carbon peaks marked by red colour correspond to the three carbons in and near the epoxy ring, which all are expected to have a significant downfield change in chemical shift subsequently to cross-linkage. The corresponding peaks after reaction are clearly smaller but no new distinct peaks have appeared. This absence of narrow peaks is most likely due to inhomogeneous crosslinking where differently rigid structures along the polymer leads to less motional averaging and hence signal broadening. This downfield shift and signal broadening effect is most possibly observed as the new broad peaks around 60 to 85 ppm for the crosslinked sample. Analogously, the α and β carbons are affected by the rigid structure as well, generating signal broadening. Additional experiments with higher temperature may increase spectral resolution of crosslinked PE as mobility increases. In addition, it should be noted that the new peak at 17.2 ppm originates from the two methyl groups in the BPP molecular group.

1. W. L. Earl and D. L. Vanderhart, *Macromolecules*, 1979, **12**, 762-767.
2. J. L. Koenig, *Spectroscopy of Polymers (Second Edition)*, ELSEVIER SCIENCE & TECHNOLOGY, 1999.