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Citation for published version (APA):

Kierkels, J. T. A., Leblanc, T., Goossens, J. G. P., Govaert, L. E., & Meijer, H. E. H. (2005). *Influence of network density on the strain hardening of PMMA copolymers*. Poster session presented at Mate Poster Award 2005 : 10th Annual Poster Contest.

Document status and date:

Published: 01/01/2005

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
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Influence of network density on the strain hardening of PMMA copolymers

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Introduction

The intrinsic toughness of glassy polymers depends on the post-yield behavior, on strain softening and strain hardening. Dependent on the loading condition, the macroscopic response to deformation might be brittle, e.g. for poly(methyl methacrylate) (PMMA) and polystyrene (PS) (Fig. 1). Polycarbonate (PC) is ductile, since it necks in tensile testing. Commercial PMMA always contains some copolymer to reduce unzipping and facilitate processing, e.g. ethyl acrylate (EA). Network density and strain hardening can be influenced by addition of EA.

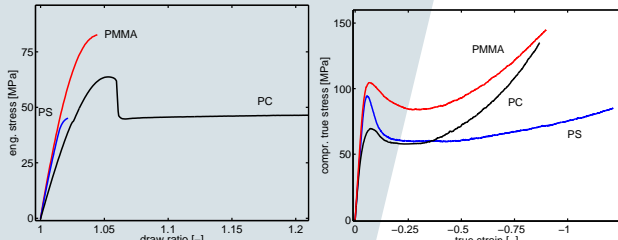


Fig. 1): The deformation behavior of PS, PMMA, and PC in a) tension can be predicted from the intrinsic properties as measured in b) compression. All tests are performed at $\dot{\epsilon} = 10^{-2} \text{ s}^{-1}$

Materials and methods

PMMA-co-PEA containing 0.5 to 25 wt % EA was provided by Arkema. Dynamic mechanical thermal analysis (DMTA) was used to determine the network density. Uniaxial compression was performed at various temperatures to yield the strain hardening modulus.

Results

By DMTA (Fig. 2), the network density can be calculated from the rubbery modulus G_N^0 by $\nu_e = N_A G_N^0 / RT$ where R is the molar gas constant, T is the absolute temperature, and N_A is the Avogadro number.¹ The network density decreases upon addition of EA, see Table 1.

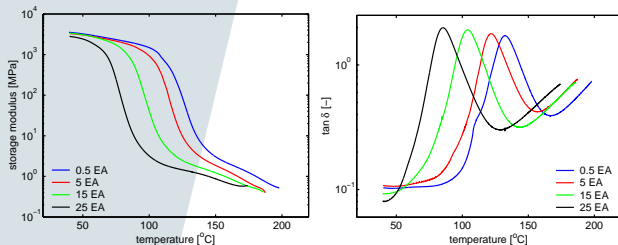


Fig. 2): DMTA results; a) dynamic modulus E' and b) $\tan \delta$ as a function of temperature. T_g and network density increase with decreasing copolymer content.

Table 1: Properties of PMMA-co-PEA copolymers

	M_n	PDI	T_g	ν_e	G_R	G_R
	[kg/mol]	[-]	[°C]	$\cdot 10^{26}$	(20°C)	($T_g - 35$)
	SEC	SEC	DMTA	[chains/m ³]	[MPa] compr.	[MPa] compr.
EA 0.5	42.5	2.07	132.1	0.85	44	9
EA 5	38.5	2.18	121.8	0.83	39	9
EA 15	58.9	2.33	102.7	0.81	31	11
EA 25	52.3	3.34	86.1	0.79	21	12

Uniaxial compression tests at room temperature show that G_R decreases with increasing EA content, see Fig. 3 and Table 1. Fig. 4a shows that G_R decreases with temperature for all 4 copolymers investigated. The thermal mobility of the chains is dependent on the distance in temperature below T_g . Shifting the G_R curves onto a $(T - T_g)$ - axis results into a master curve (Fig. 4b).²

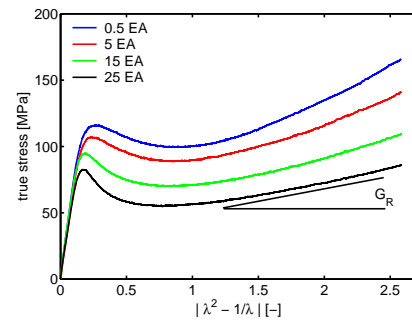


Fig. 3): Compressive behavior of PMMA-co-PEA at room temperature at $\dot{\epsilon} = 10^{-2} \text{ s}^{-1}$.

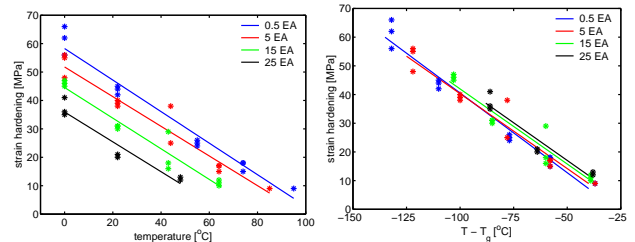


Fig. 4): Strain hardening as a function of a) temperature and b) shifted temperature $(T - T_g)$.

Conclusions

Increasing the EA content in PMMA increases the chain mobility and thereby reduces the network density and strain hardening modulus. All copolymers seem to behave identical at a certain temperature below their respective T_g s, since a universal master curve can be constructed. For optimal toughness, the EA content should be low, since high network density and strain hardening are essential for stable deformation.

References:

- [1] TRELOAR, L.R.G.: *The Physics of Rubber Elasticity*, 3rd edn., Clarendon Press (Oxford, UK 1975)
- [2] V MELICK, H.G.H., GOVAERT, L.E., MEIJER, H.E.H.: *Pol* 44 (p2493, 2003)