

The Effect of Various Terminal Groups of Liquid Rubber on Thermal and Mechanical Properties of Rubber-modified Polybenzoxazine

Dwi N. Suwitaningsih, T. Kawauchi, and T. Takeichi
Department of Materials Science, Toyohashi University of Technology

1. Introduction

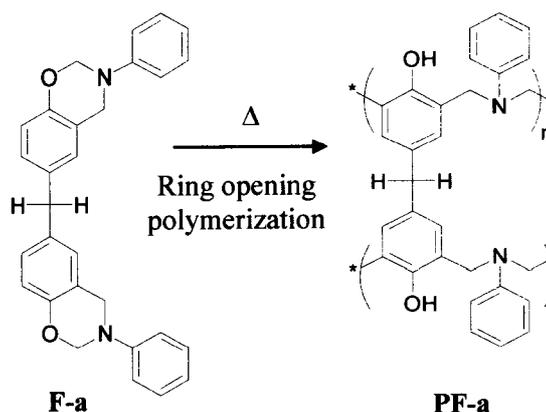
Phenolic resins are a major family of high temperature polymers. Its excellent characteristics such as high thermal stability, dimensional stability, good electrical properties [1] and flame retardance [2], have made them an important material for construction, automotive, electrical and appliance industries, as well as for electronics and aerospace.

Polybenzoxazine has been developed to overcome the shortcomings of traditional phenolic resins. It has all the advantage of phenolic resins but produces no by-product and undergoes ring polymerization through heat treatment without the need of catalyst and the generation of volatiles, thus having near zero shrinkage after curing [3,4] and maintaining the dimensional stability. [5] The structures of typical benzoxazine monomer bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropane (abbreviated as F-a) and polybenzoxazine (PF-a) are shown in scheme 1.

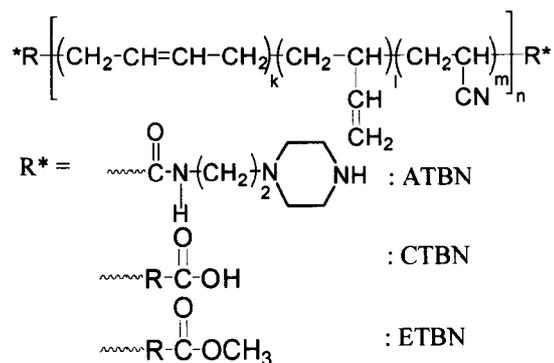
Polybenzoxazine shares the drawbacks of traditional phenolic resins such as brittleness and high temperature required for polymerization. To overcome this poly(butadiene-*co*-acrylonitrile) liquid rubber with three different terminal groups, ATBN (amine-terminated), CTBN (carboxylic-terminated) and ETBN (ester-terminated) were introduced individually in various wt. ratios to improve the toughness of polybenzoxazine and to investigate the effect of various terminal groups of liquid rubber on the polymerization of benzoxazine and thermomechanical properties they impose to the resulting hybrid. The structures are shown in scheme 2.

2. Experimental

The hybrid films were prepared by blending F-a and variety of liquid rubber in various ratios followed by curing. For PF-a hybrid containing 2.5 wt. % of ATBN, the procedure is as



Scheme 1. Chemical structures of F-a and PF-a.



Scheme 2. Chemical structures of liquid rubbers having amine, carboxylic and ester terminal groups.

follows; F-a (1.463 g, 3.365 mmol) was dissolved in THF (2 mL) and stirred at room temperature. ATBN (0.037 g) was dissolved in THF (3mL) and filtrated with cotton absorber. ATBN solution was introduced into F-a solution to afford transparent yellow solution. The mixture was then cast on a pre-treated glass plate and heated in an air oven at 50, 100, 150, 200, 240°C for 1h each to obtain films with thickness in the range of 80 to 100 μm . Similar procedure was carried out for PF-a/ ATBN with various ATBN content. PF-a/CTBN and PF-a/ETBN hybrids were prepared similarly.

3. Results and discussion

The effect of liquid rubber loading on F-a polymerization was studied using DSC after solvent removal at 60 °C for 12 hours. The result is summarized in Table 1. The onset of ring opening polymerization of F-a appears at 219 °C with its maximum centered at 247 °C. These values decrease to 203 and 239 °C respectively in the presence of 5 wt. % of ATBN and continue declining proportionally with ATBN content. Similarly, CTBN also lowers the ring opening polymerization temperature of F-a. In the presence of 5 wt. % of CTBN, the onset and the maximum temperatures decrease to 218 and 237 °C respectively. It was previously reported the carboxylic terminal group of CTBN may have acted as an acid catalyst for the ring opening polymerization [6] and thus lowering the cure temperature. As opposed to the ATBN and CTBN, no temperature shift is observed in the cure temperature of F-a in the presence of ETBN. Ester terminal group, having lower reactivity compared to amine and carboxylic counterpart, doesn't impose any effect on the ring opening polymerization. This phenomenon confirms that ATBN is the most effective modifier in lowering the ring opening polymerization temperature of F-a and the main chain of liquid rubber has little or no effect in the lowering of cure temperature of benzoxazine.

Table 1. DSC results of PF-a/ liquid rubber hybrids

Rubber content (%)	ATBN		CTBN		ETBN	
	Onset temperature (°C)	Max temperature (°C)	Onset temperature (°C)	Max temperature (°C)	Onset temperature (°C)	Max temperature (°C)
0	219	247	219	247	219	247
5	203	239	218	237	220	247
10	105	231	215	237	220	247
20	195	228	210	231	224	249
40	194	223	203	226	226	247
60	193	222	200	222	229	252
80	202	230	200	224	237	257

PF-a/ liquid rubber hybrids afford films ranging from orange to dark wine in color. PF-a/ATBN hybrids exhibit homogeneity and consistency for all weight ratios. PF-a/ CTBN hybrids show the same degree of consistency only at 5 wt. % content, above 10 wt. % voids and bubbles appear in some areas causing the surface to be uneven. We suspect that esterification may have

had occurred between the carboxylic terminal groups of CTBN and the phenolic moiety of polybenzoxazine, PF-a/ETBN hybrids exhibit poor compatibility as bubbles appear even at 10 wt. % ratio. The most likely reaction is the hydrolysis of ester under acidic condition, which takes place as soon as phenolic groups are generated by ring opening polymerization. From the visible inspection hybrid film comparison that terminal groups of liquid rubber, despite of their meager amount, show considerable difference in the extent of compatibility with polybenzoxazine matrix, assuming its significance in the structural formation of the hybrid.

Pristine PF-a gives a transparent film of orange color while PF-a/ATBN hybrid gives opaque films of dark wine color. From figure 1, it is apparent that the increase in ATBN content significantly improved the flexibility of the hybrid film. Another interesting phenomenon observed in this system is the change in film transparency at different content of ATBN. With the addition of ATBN from 2.5 to 20 wt. %, the hybrid films grow opaque whereas at higher content of ATBN the film gradually turns translucent.

Opaqueness exhibited by hybrid films is caused by phase separated morphology as revealed by SEM photographs. All hybrids containing up to 20 wt. % of rubber exhibited spherical rubber domains dispersed in continuous polybenzoxazine. We calculated the rubber domain size distribution of each hybrid films. For 10 wt. % rubber the hybrids exhibit substantial difference on the size distribution, ATBN maintains narrow distribution of rubber domain size of $1.2 \pm 0.3 \mu\text{m}$, CTBN exhibits larger domain size and wider distribution of $2.8 \pm 0.3 \mu\text{m}$, while ETBN shows the largest and the widest rubber domain size of $5.1 \pm 3.4 \mu\text{m}$ signifying poor compatibility between the dispersed and continuous phase hence the poor appearance shown in figure 2.

Tensile test revealed that PF-a/ATBN and CTBN hybrids exhibit improved toughness over pristine PF-a with the ATBN modified one giving the highest tensile and elongation at break (Figure 3). Provided that ATBN is the best modifier in accelerating the polymerization and the compatibility with F-a, extended observation on PF-a/ ATBN hybrids was carried out. It is revealed that the tensile strength of unmodified PF-a (81.8 MPa) increases to 87.1 and 83.2 MPa with the addition of 2.5 and 5 wt. % of ATBN respectively. The elongation at break of the unmodified PF-a increases from 3.1% to 3.8 to and 4.4% with the addition of 2.5 and 7.5 wt. % of ATBN respectively.

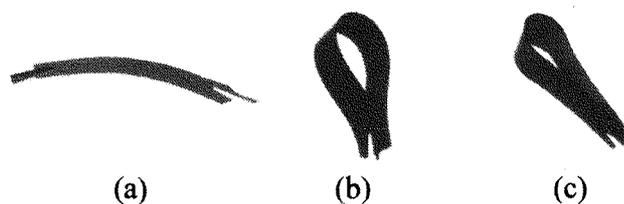


Figure 1. Photographs of PF-a/ ATBN hybrid films at 0% (a), 20% (b) and 80% (c) wt. ratio.

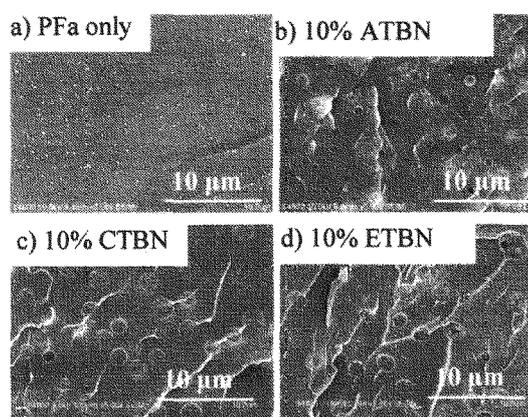


Figure 2. SEM photographs of pristine PFa (a) and PFa hybrids having 10% content of ATBN (b), CTBN (c), and ETBN (d).

The comparison of DMA profile of PF-a/ liquid rubber hybrids cured at 180°C revealed that the variety in terminal groups impose very little influence to the Tg. PF-a/ ATBN hybrid shows Tg at 175.2 whereas the CTBN at 172.3 °C. Extended observation on PF-a/ ATBN hybrids cured at 240°C revealed that with the addition of 10% and 20 wt. % of ATBN, Tg of the pristine PF-a increases from 189 °C to 191 and 228 °C respectively. It is plausible that the ATBN backbone may have crosslinked with itself through the reaction amongst the *cis*-1,4-butadiene groups of ATBN at elevated temperature, rendering additional crosslink in addition to the network formation afforded by PF-a and improving Tg of the hybrid. The thermal crosslinking of *cis*-1,4-polybutadiene is described elsewhere.[7, 8]

The thermal stability of PF-a and PF-a/ liquid rubber hybrids was evaluated using TGA under N₂ atmosphere. Generally the hybrids exhibit higher decomposition temperature than pristine PF-a, though the modification doesn't seem to increase the thermal flame retardance of the hybrids.

4. References

1. S. B. Shen and H. Ishida, *J. Appl. Polym. Sci.*, **61** 1596 (1996).
2. H. Y. Low and H. Ishida, *J. Polym. Sci. B: Polym. Phys.*, **36**, 1935, (1998).
3. G. Reiss, et al. in *Advances in Polymer Synthesis*, B. M. Culbertson and J. E McGrath, Eds. Plenum, New York, (1985).
4. H. Ishida and H. Y. Low, *Macromolecules*, **30**, 1099 (1997).
5. T. Takeichi and T. Agag, *High Perform. Polym.*, **18**, 777 (2006).
6. J. Jang and D. Seo, *J. Appl. Polym. Sci.*, **67**, 1 (1998).
7. G. Janowska and L. Ślusarski, *J. Thermal Anal. and Calor.*, **65**, 205 (2001).
8. X. Zeng, and T. Ko, *J. Appl. Polym. Sci.*, **67**, 2131 (1996).

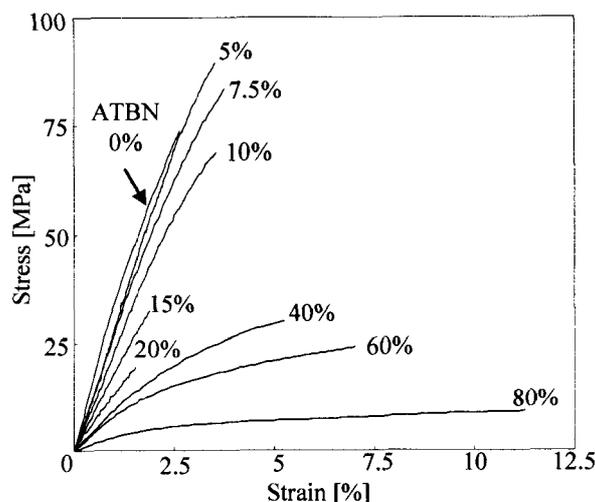


Figure 3. Tensile test of PF-a/ ATBN hybrids.