Improved understanding on the reinforcement of low-temperature hydrogenated nitrile butadiene rubber composites by *in-situ* polymerization of unsaturated metal methacrylate: influences of salt cation

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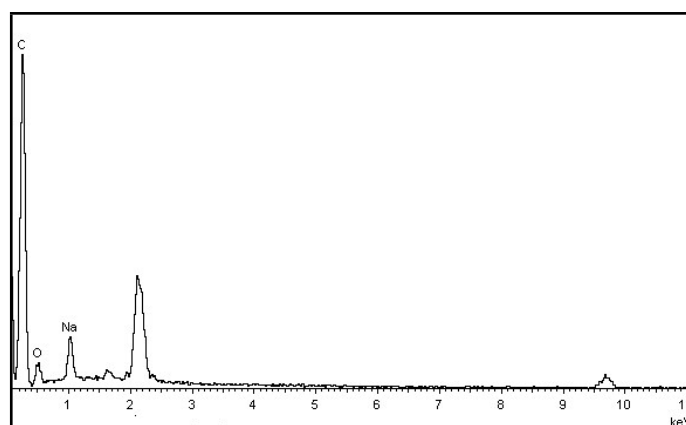
Fig. S1 EDS analysis of the composite from poly (NaMMA) in Fig. 2b.
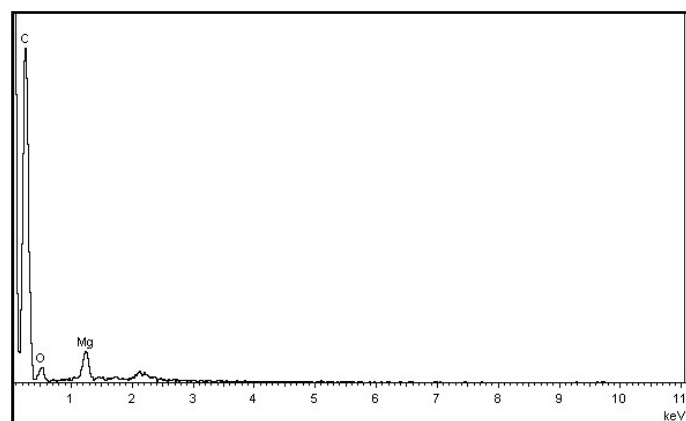

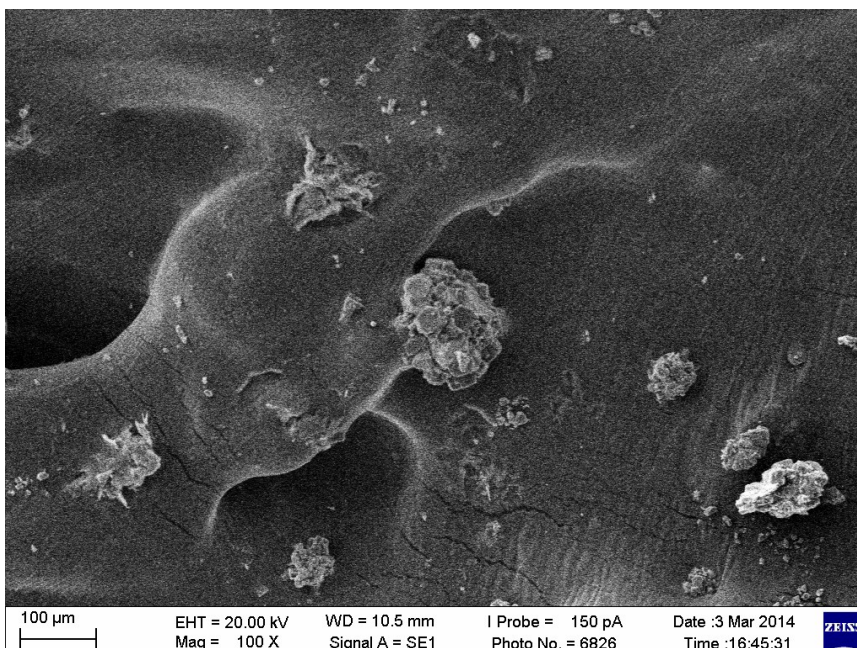**Fig. S2** EDS analysis of the composite from poly (MgMMA) in Fig. 2c.

Fig. S3 SEM image of uncured rubber compounding with AlMMA.
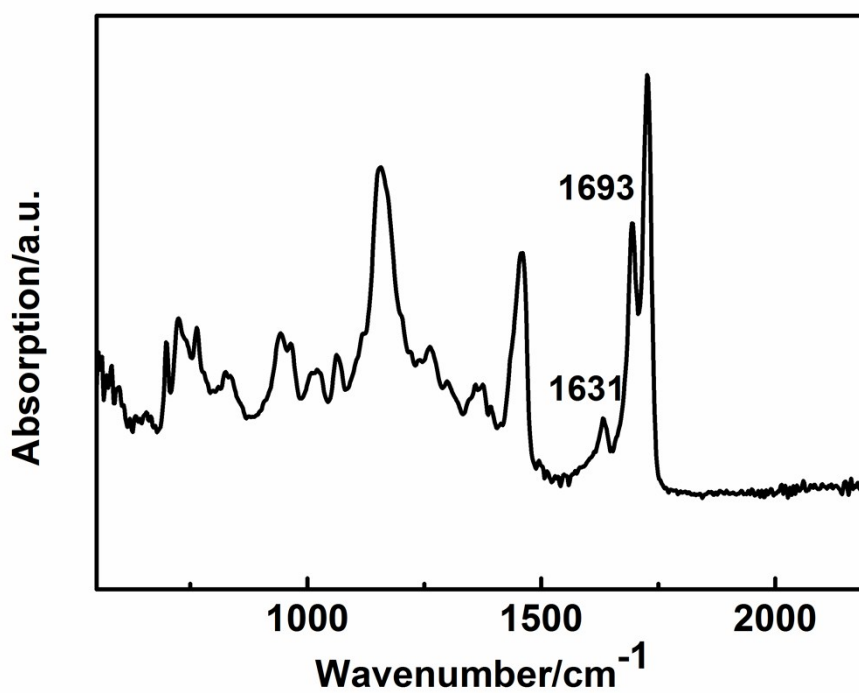

Fig. S4 FTIR spectrum of uncured rubber compounding with AlMMA.

Discussion about the ionic and covalent crosslinks in the composites with different UMMs

Crosslink densities of rubber and its composites are always necessary information to investigate their network structures. We adopted equilibrium swelling measurement to examine the total density of rubber and its composites. On the other hand, the ionic crosslinks were destroyed by the special solvents and the covalent crosslinks were obtained by the same swelling tests. Then ionic crosslink density can be checked by calculating the differences between them. The detailed methods see the past literature (*J. Appl. Polym. Sci.*, 2000, 77, 2740.). Fig. S5 shows the covalent, ionic and total crosslink density of the HNBR vulcanizates. Pure rubber has the maximum covalent crosslink density among them. Enough amounts of vulcanizing agent (DCP) is used to construct covalent crosslink networks in the pure rubber. In contrast, a part of DCP is initialized to develop *in-situ* polymerization of UMM, so there are fewer covalent crosslink densities in the composites with UMM. Interestingly, the composite with NaMMA has almost the same covalent crosslink density as that with MgMMA. But the composite with AlMMA has more covalent crosslinks than them. We believe that more DCP has joined the polymerization of UMM, which leads to less covalent bonds to produce networks. On the other aspect, the composite with NaMMA has the most ionic crosslink density than the others. In our TEM observations, more poly (NaMMA) particles are seen, which brings more ionic pairs or bonds in the composite. The composite with AlMMA has lower ionic crosslink density because a tiny amount of poly (AlMMA) is generated and not able to provide enough ionic bonds. What is more, there are fewest total crosslink densities for the composite with AlMMA. Unreacted methacrylic acid (MMA) is polymerized to produce poly (MMA), which is linear chain structures and cannot provide enough crosslinks to improve the total crosslink density.
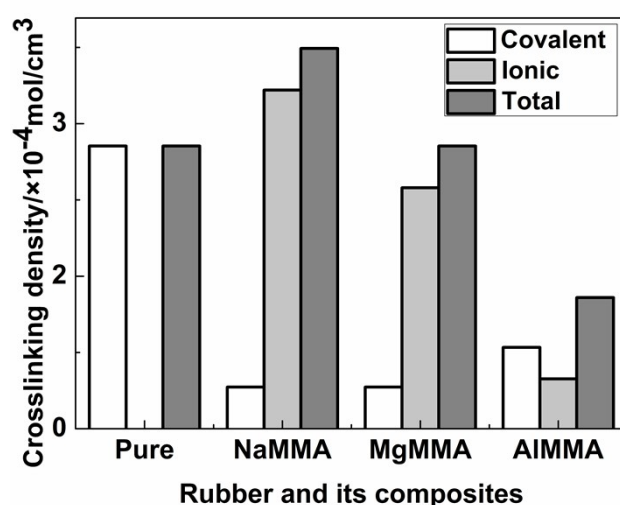

Fig.S5 Covalent, ionic and total crosslink density of the HNBR vulcanizates

Discussion about the low temperature properties of rubber composites with poly (UMMs)
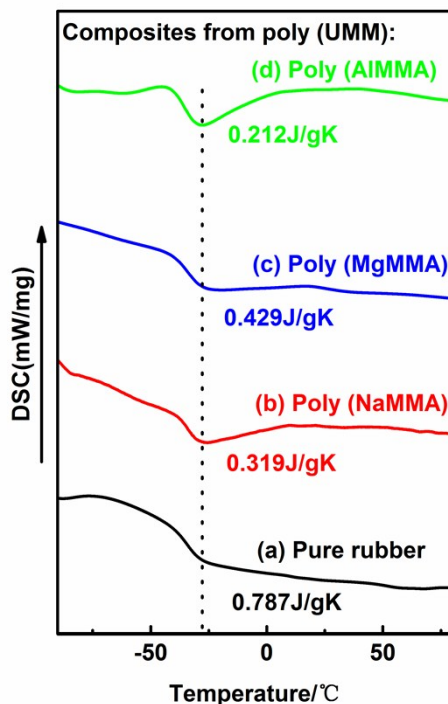
Fig. S6 DSC curves of pure rubber and its corresponding composites

Rubber composites always serve at their rubbery states for the most applications. So their low-temperature property should be evaluated by the glassy transition temperature (Tg). Fig. S6 shows DSC curves of LTG-HNBR and its composites from different poly (UMMs). It is delightedly seen that the values of Tg (~-30℃) stay unchanged for all composites. The confinements of ion crosslink suppress the mobility of rubber segments, but the grafting poly (UMMs) serve as plasticizers for the bulk, making the temperature of Tg barely shift. Thus it is stressed that electrostatic interactions of in-situ poly (UMMs) play positive roles in the modification of low-temperature-grade rubber. Moreover, there is less enthalpy in DSC curves for the composite than the pure rubber owing to the complex interactions of constituent pairs, for example, rubber and poly (UMMs) nano-particles or grafting poly (UMMs), particles and multi-sized aggregations.

Table S1 Valence numbers of salt cations, measured TA, $tan\delta_{max}$ and T_{max} of the composites by DMA.

Composites from poly (UMMs)	valence numbers of salt cations	$\tan\delta_{max}$		T_{max}/°C		TA/°C	
		$\tan\delta_{max,1}$	$\tan\delta_{max,2}$	$T_{max,1}$	$T_{max,2}$	TA_1	TA_2
Pure rubber	/	1.75	/	-14.3	/	52.4	/
Poly (NaMMA)	1	0.66	/	-11.9	/	29.2	/
Poly (MgMMA)	2	1.03	/	-14.1	/	37.5	/
Poly (AlMMA)	3	1.49	0.27	-12.2	130	45.3	24.5

Table S2 Fitting parameters of eqn. 3 to simulate the relaxation plots

Composite	δ_e/MPa	δ_1/MPa	δ_2/MPa	δ_3/MPa	τ_1/s	τ_2/s	τ_3/s
Pure rubber	0.61	0.1	0.08	0.03	3.1	37.0	404.0
NaMMA	3.84	0.4	0.4	0.7	289.5	36.4	4.6
MgMMA	2.43	0.1	0.2	0.6	116.7	265.9	4.64
AlMMA	1.17	1	0.2	0.1	1.67	19.3	240.2

Note: the relaxation equation: $\delta(t) = \delta_1 \exp\left(-t/\tau_1\right) + \delta_2 \exp\left(-t/\tau_2\right) + \delta_3 \exp\left(-t/\tau_3\right) + \delta_e$