Functionalization of NR with a bromine atom was developed and explored for its application in a silica-reinforced NR system. Two possible pathways were investigated: the direct addition of a bromine atom using N-bromosuccinimide (NBS) with FeCl₂ as a catalyst in the latex phase (NR–Br); and an indirect method using a ring opening of epoxidized natural rubber (ENR) with 2-bromopropionic acid (ENR–Br). The chemical structure, including determination of the bromine contents, was analyzed with proton nuclear magnetic resonance and Fourier transform infrared spectroscopy. The occurrence of bromine in NR–Br was confirmed using scanning electron microscopy with energy dispersive x-ray spectroscopy. Strong emission peaks for Br Kα at 1.5 eV was evidenced. Moreover, glass transition temperature of modified NRs increased after bromination. Two types of brominated NR, that is, NR–Br and ENR–Br containing 2 and 4 mol% of bromine function, respectively, were used in a range of 1–5 phr in the silica-reinforced NR system with silica loading of 10 and 30 phr. Both cure and mechanical properties of the rubber compounds were investigated. The incorporation of the bromine function in NR of both ENR–Br and NR–Br enhanced the cure reactivity of the NR–silica vulcanization system. The modified NRs may have a role as a coupling agent between the NR and the silica filler.