Natural rubber (NR) is one of the most important agriculture products of Thailand, which is an important material with unique and special characteristics used in wide range of applications such as mechanical properties, excellent strength, and elasticity. However, it is inferior in oil resistance due to the presence of hydrogen and carbon in its structure. This inherent drawback of NR has limited its application in industry. In order to expand the use of NR, this research is interested to improve the oil resistance of NR without loss of outstanding properties by grafting NR with acrylonitrile (AN) monomer to form the nano-matrix structure. The influences of the initial monomer concentration and initial initiator concentration were investigated. These effects on structure, mechanical properties and oil resistance properties were studied by Fourier transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy, tensile machine, and swelling in toluene, respectively. It was found that the tensile strength and oil resistance properties of graft copolymerization of AN onto NR increased with increasing the percentage grafting efficiency of acrylonitrile monomer.