The combination of clays with polymers having different characteristics opens a way to new composite materials showing novel properties. Electrorheological (ER) fluids show phase transition from a liquid to a solid-like state between the electrodes of a rheometer due to the interactions of polarized particles. Composite systems comprising biodegradable chitosan (CS) and natural bentonite (BNT) are important in ER applications. In this study, BNT/CS composites were synthesized by the in situ method. The structure and morphology of the synthesized composites were characterized using X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and scanning electron microscopy (SEM) techniques. Thermal stability was observed to increase with the presence of BNT clay. Conductivity of the composites was found the suitable range for ER measurements. According to ER results, BNT/CS composites were found to be sensitive to external electric field strength, exhibiting a typical shear thinning non-Newtonian viscoelastic behavior.