The aim of this work is to prepare and characterize a series of bio-polyurethane foams (Bio-PUFs) based on renewably sourced polyols in order to increase their ecological potential, while maintaining their properties. Polyurethane foams (PUFs) were obtained using two sunflower based-polyols (SF-P1 and SF-P2) with different hydroxyl numbers synthesized through the acid-catalyzed ring-opening of epoxidized sunflower oil (ESFO) and subsequent partial reduction of the ethylenic linkages to give hydroxyl moieties. These SF-Ps were applied for replacement of petrochemical polyol Confort P0010 with a mass fraction of SF-P in the range of 40–100%. The resins were characterized by Fourier transform infrared (FTIR) spectroscopy. Their solution viscosity and thermal behavior were investigated. The obtained SF-Ps were reacted with diisocianates to yield PUFs at a fixed NCO index. Several experiments were conducted by varying the amounts of polyols, isocyanate, catalysts, and surfactants until acceptable foams were obtained. The structures of the obtained PUFs were confirmed by FTIR spectroscopy and scanning electron microscopy (SEM). The morphology, the apparent density, the thermal behavior (thermogravimetric analysis and differential scanning calorimetry), and the thermal conductivity of the PUFs were investigated. The study showed that it is possible to substitute petrochemical polyols by the addition of SF-P to achieve PUFs with desirable properties. It was found that the mixing of SF-Ps in formulations influences especially the thermal and morphological properties, and increases the end product renewable material content. The highest renewable material content showed SF-PUFs (reaching 76%) since the renewable material content in SF-P is high (~ 92%). As a result of the SF-Ps loading in the range of 40–100% the PUFs change from flexible to semi-flexible structures. Furthermore, they become denser and exhibit numerous cell shapes, such as semi-open cells and closed cells