CHAPTER III

METHODOLOGY

3.1 INTRODUCTION

This chapter focuses primarily on the synthesis of polyurethanes for pure as well as with nanofillers (modified organoclay and MWCNTs) integrated in the PUs matrix to form nanocomposites. In the other half of the chapter, a brief and comprehensive description of analytical instruments which were employed in a comparative study of physicochemical properties of pure PUs and filler incorporated polymer-filler nanocomposites is discussed. Nanocomposites of PUs have heightened importance in wide scale applications during the last decade due to their improved properties over conventional composites. Due to the large consumption of PUs and the negative environmental impacts from petroleum based polyols, renewable resources as alternative materials are now of great interest to researchers. Castor oil, one of the major non-edible vegetable oils is an interesting renewable resource that contains a hydroxyl group (-OH) and unsaturated double bonds (C=C) in its organic chain, and is able to produce new polyurethane materials. The synthesis methodology encompass three different syntheses, which includes pure PUs with no fillers incorporated, PU/organoclay (Cloisite B30) nanocomposites and new PU/multi-walled carbon nanotube (MWCNT) nanocomposites which employs a mixture ratio of polypropylene glycol and castor oil as polyols.

The crystal structure was studied using X-ray diffraction (XRD). The XRD patterns were recorded using an X-ray diffractometer (*Rigaku* Mini Flex II, Japan) which employs graphite monochromator and CuKα radiation (λ = 0.15406 nm). The

morphology was examined using Scanning electron microscopy (SEM) on the JEOL 6300F (Japan) machine at an acceleration voltage of 5KV and field emission scanning electron microscopy (FESEM, *JEOL EVO-50, Japan*). Infrared absorption spectroscopy (IR) spectrum was measured at room temperature using a Fourier transform infrared (FTIR) spectrometer (*Nicolet* 5DX FT-IR, USA). Thermal stability was tested usingThermo-gravimetric analysis (TGA) on a thermal analyzer (*Mettler Toledo*, TGA/DSC1) at a rate of 10 ^{o}C min^{-1} and on a Differential Scanning Calorimetry (DSC) model of TA- Instrument DSC/Q 1000 (V9.6, Build 290). BET surface area of the composite was studied using gas adsorption studies (ASAP 2020, *Micromeritics*, USA). Atomic percentages of elements in neat COPUs, organoclay and MWCNTs were calculated using Energy Dispersive X-ray spectroscopy (EDX) attached within FE-SEM. The study of mechanical properties (tensile strength and elongation at break) were carried out using an Instron model 4505 universal testing machine at 25 ºC with a load cell of 5 KN, followed by ASTM D 638. Crosshead speed was set to 2 mm/min. Samples were cut into dumbbell shapes using ASTM D 638 (type V).

3.2 MATERIALS

Major building-blocks for the synthesis of renewable polyurethanes are:

3.2.1 Toluene Diisocyanate (TDI)

In this research, Toluene diisocyanate (TDI) was used for the preparation of PU samples. TDI used as received was supplied from SIGMA-Aldrich Company. Its physical properties are shown in Table 3.1. TDI is an aromatic diisocyanvate.

3.2.2 Polyols

Polyols are defined as chemical compounds that contain more than one hydroxyl group (diol). Polyols are separated into two categories, which are low molecular weight and high molecular weight polyols. High molecular weight polyols called oligo-polyols, are one of the main building blocks that represents the soft segment in the formation of polyurethane.

Table 3.1: Physical properties of TDI.

Constituent	**value**
Commercial name	Toluene Diisocyanate (TDI)
Molecular formula	$C_9H_6N_2O_2$
Molecular weight	174.2
Appearance	White or pale yellow solid
Density	1.214 g/cm^3, liquid
Melting point	21.8 °C (295 K)
Boiling point	251 °C (524 K)
Solubility in water	Reacts

In this research, a polyether polyol (Polypropylene Glycol, Molecular weight = 4000) was supplied by Sigma-Aldrich Company and was selected as the soft segment. The details are shown in Table 3.2.

Table 3.2: Properties of Polypropylene Glycol.

Constituent	**value**
Commercial name	P 4000
Appearance	Colorless liquid
Molecular weight	4000
OHV	28 mg KOH/g
Viscosity (25 ^oC)	1300 mPa.s
Functionality	1.7
Structure	CH_2-[O $-CH_2-CH(CH_3)]_m-CH_2CH_2$-OH | CH_2-[O $-CH_2-CH(CH_3)]_n-CH_2CH_2-OH$ | CH_2-[O $-CH_2-CH(CH_3)]_l-CH_2CH_2-OH$

3.2.3 Castor Oil

In this work, castor oil was used as an alternative to petrochemical based polyols and as a renewed resource that can potentially reduce cost in polyethane production. In this research, pure castor oil was purchased from Chengdu Organic Chemicals, China and polymerized directly without modifications. Table 3.3 shows the composition of castor oil, while Table 3.4 shows the properties of castor oil.