

Evaluation Of Thermal Analysis, Morphology And FT-IR Study Of Polypropylene Filled With Wollastonite And Silicon Rubber

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ABSTRACT

Some novel composites were prepared with polypropylene and silicon rubber with wollastonite as fibrous filler having aspect ratio 5:1 in different proportions. Subsequently, these composites were investigated with TGA and DSC for thermal analysis and morphology analysis with SEM to find out the compatibility of PP and Silicon rubber with untreated wollastonite composite on addition malicanhydride. The fibrous filler wollastonite particles were randomly dispersed in the PP matrix, lumps formation of silicon rubber and compatibility of silicon rubber and wollastonite in all compositions were observed. Fourier Transform Infrared Spectroscopy (FT-IR) non-destructive analytical technique was used to identify mainly organic materials. Composites were studied for the chemical bonds and molecular structure of a material. The methyl groups of polypropylene, -C=O- stretching vibration for carboxylic acid, Si-H stretching vibration were observed. The bond due to the asymmetric - Si-O-Si- stretching vibration occurred in $1072-987\text{cm}^{-1}$.

INTRODUCTION

Frequently, the properties of polymers are modified by incorporating fillers. The mineral fillers used in semi-crystalline polymers are usually talc and calcium carbonate and, to a lesser extent mica and wollastonite [1]. Generally; the addition of mineral fillers will have an embrittling effect on polymers and decrease the impact energy. In recent years, however, the fillers are more often used to fulfill a functional role, such as increasing the stiffness or improve the dimension stability of the polymer. Fillers (often different types of minerals) are traditionally used to lower the price of final product, while reinforcing agents (e.g. glass fibers) are used to improve mechanical properties, such as stiffness and strength [2]. Wollastonite reserves up to 200 million tons exist in China, the highest figure in the world [3, 4]. Incorporating minerals in the polymer matrix provides additional nucleation sites, thereby increasing the number of spherulites and reducing their size, with consequent increase in crystallinity. The reinforcement particles increase the modulus and yield stress, and influence the mobility of the molecular chains. The results of several investigations of micrometric reinforced polymer composites have convincingly shown that a higher tensile modulus is obtained relative to the unreinforced polymer [5-9]. Mineral fillers are added to polymers in commercial production primarily for cost reduction and stiffness improvement [10, 11]. But there are many applications in which less stiffness and more flexibility without scarifying the other properties of the blend is required. In presented work this has been achieved by incorporating silicon rubber in polypropylene and wollastonite at different proportions.

The factors affecting the properties of blended polymers are given below [12-18]

1. Particle size, size distribution and filler content.
2. Particle shape and surface structure.
3. Mechanical properties of the mineral (stiffness, strength, etc).
4. Compounding and molding methods used.
5. Bond strength between mineral and polymer. This will be influenced by the type of dispersion aid or coupling agent used.
6. Polymer properties, e.g. ductile polymers will behave differently than brittle ones when adding minerals to polymers.

To consider the characteristics of components, which influence the interfacial adhesion between the filler and polymer in the corresponding composites, the final performance of the composite material could be determined [19–21]. Although the PP wollastonite composites prove to have the weakest adhesion regarding the calculated adhesion parameters, they have somewhat higher values of notched impact strength with regard to the PP composites with Wollastonite as fillers used as was also observed by others [22, 23].

In this paper, some of these parameters were studied by adding wollastonite mineral as filler into polypropylene (PP). The silicon rubber was used to reduce stiffness and to improve the flexibility and whereas malicanhydride used as compatibilizer. More over, morphology, thermal properties and FT-IR observation of the compound were studied. A special interest was devoted to the measurement of degradation temperature and compatibility of wollastonite in SEM micrograph and FT-IR graphs. The proposed composites have great potential for their

application in the automotive and electrical/electronics industry such as under-bonnet and temperature sensitive components.

EXPERIMENTAL

Materials

Polypropylene, a commercially available polypropylene homo polymer, H 110 MA supplied by Reliance Industry Limited (India) having a melt index of 11.0 and a density of 0.903 g/cc, was used as matrix material. Mineral wollastonite ('S4', supplied by Wollkam Industries, India), a fibrous mineral, which gives only one-dimensional reinforcement, was used in the experiment without further treatment. Silicon rubber possesses excellent aging properties, resistance to oil, and oxidation by ultraviolet light and ozone and can retain its properties at very low as well as very high temperatures [24]. Silicon rubber of DOW CORNING make having K-740 translucent grade has been used in this experiment.

Compounding

Silicon rubber and malicanhydride were compounded on two roll mill to form lumps, which were subsequently cut into small chips with knife. Wollastonite and polypropylene were blended in a tumbler and silicon rubber chips were added to it. JSW Twin Screw compounding machine (α 30) with co-rotating general purpose screws was used for compounding the material. Volumetric feeder was used for dosing the twin screw extruder. Temperature of the twin screw extruder was set in the range of 100-180°C in nine zone of the extruder. The die temperature was set at 185°C. The zone sixth and eighth forming feed zone were decompression zones with natural vents. The strands were extruded through water for cooling the strands, dried by vacuum pump, and then granulated with cutter. The SR1, SR2, SR3 and SR4 compositions were made by compounding in twin screw extruder. Where as the SR1, SR2, SR3 and SR4 stands for PP+wollastonite-10%+silicon rubber 5%, PP+wollastonite-20%+silicon rubber 5%, PP+wollastonite-30%+silicon rubber 5% and PP+wollastonite-40%+silicon rubber 5%.

Scanning electron microscopy

Scanning electron microscope (SEM) JEOL JSM-840A was used for the morphology observation. The samples were fractured in before they were covered with gold and examined microscopically, at an acceleration voltage of 15 kV. Properties of the polymer composites also depend on structural characteristics at a higher super molecular level, especially on their phase morphology. For this reason, SEM observations were used for studying the morphology of the composites.

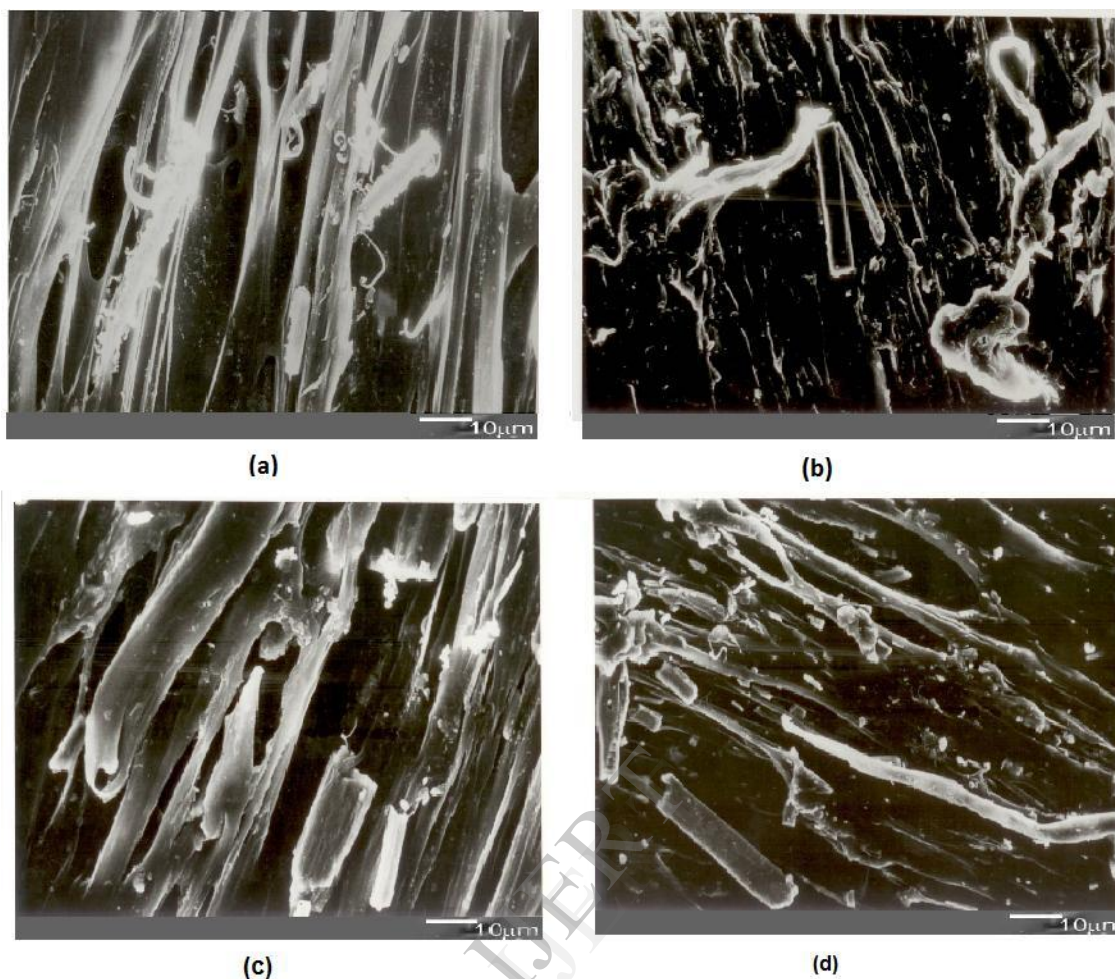


Fig 1. SEM micrographs of fractured samples of the PP/wollastonite/silicon rubber composites at 15V a) SR1, b) SR2 d c) SR3 and d) SR4.

Thermal Analysis:

The composites was studied to measure physical and mass changes in materials associated with transition and thermal degradation endotherms, exotherms, weight loss on heating or cooling and more. Thermogravimetric analyzer (TGA) of PerkinElmer (Italy Make) was used for the Thermogravimetric analysis. Samples of approximately 8 to 15mg were tested in the TGA to determine the % of filler contents and other impurities in the samples.

As shown in Fig-2, the samples SR1 containing 10 % wollastonite, similarly samples SR2,SR3,SR4, contain 20,30,40% wollastonite respectively. TGA curves of PP/wollastonite /silicon rubber are shown in Fig 2. With the addition of wollastonite (10 to 40%), an increase in decomposition temperature compared to neat PP was observed. The increase in

decomposition temperature is attributed to the hindered diffusion (i.e., barrier effect) of volatile decomposition products caused by the dispersed wollastonite particles in the PP matrix [25]. The derivative peak temperature (DTP) of neat PP was 435.7°C, while the composite showed an increase in the derivative peak temperatures in the range of 29 to 33 °C. This increase was probably due to the physico-chemical adsorption of the volatile products on the wollastonite [26], The TGA thermographs of the composites of PP + Wollastonite +silicon rubber 5% are shown in Fig-2. The addition of wollastonite and silicon rubber (10 to 40 %) increased the decomposition temperature of composite. At the maximum weight loss level, the addition of 10–40 % of wollastonite increased the decomposition of composite by 40°C.

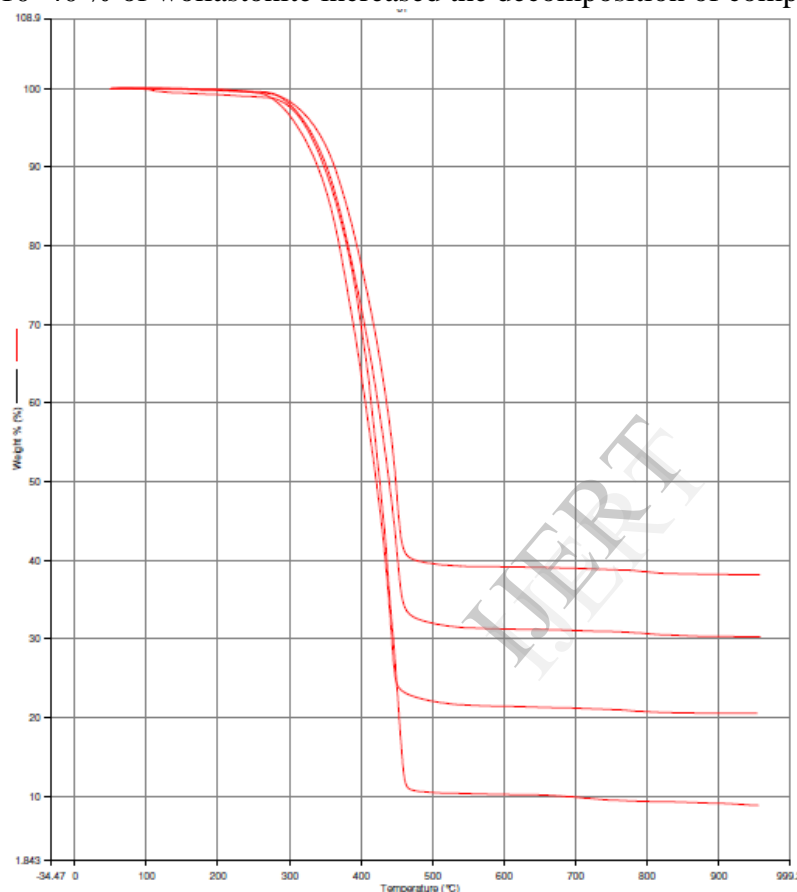


Fig-2: TGA data for the polypropylene composites having wollastonite at 10, 20, 30, and 40% with 5% silicon rubber.

FT-IR

The FTIR spectrum is equivalent to the "fingerprint" of the material and can be compared with cataloged FTIR spectra to identify the material. Shimadzu FTIR-8400S (Japan Make) was used to get the FT-IR graphs. All the SR1, SR2, SR3 and SR4 compositions identified by FTIR are given below.

The methyl groups of polypropylene give rise to two vibration bands, the asymmetric deformation band occupying at 1442 cm^{-1} and the symmetric band at 1350 cm^{-1} . The former band is overlapped by the $-\text{CH}_2-$ scissor vibration band occupying at 1442 cm^{-1} .

The -CH- stretching vibration occurs in the region $2985\text{-}2800\text{ cm}^{-1}$. The $\text{-CH}_3\text{-}$ asymmetric stretching vibration occurs at 2985 cm^{-1} and $\text{-CH}_2\text{-}$ absorption is about 2923 cm^{-1} of the stretching vibration. The -C-C- stretching absorption occurs in the region $1164\text{-}840\text{ cm}^{-1}$.

Fig-3 The -C=O- stretching vibration for carboxylic acid absorb very strongly in the region 1712 cm^{-1} . There is no absorption peak of malicanhydride in the blends. The bonds to the ester -C-O- stretching vibration are strong, partly due to an interaction with the -C-C- vibration and that occurs in the region $1311\text{-}1126\text{ cm}^{-1}$.

A strong absorption band due to Si-H stretching vibration is found at $2507\text{-}2044\text{ cm}^{-1}$. A sharp band is found at 1265 cm^{-1} , it may be the methyl groups attached to silicon atoms (Si-CH_3). The bond due to the asymmetric -Si-O-Si- stretching vibration is occurred in $1072\text{-}987\text{ cm}^{-1}$. The absorption peak at 1404 cm^{-1} may be due to -Si-CH=CH_2 group. Similar types of peaks are obtained in Fig-4 to Fig-6. It may be shift due to blend compatibility. The increase in the transmittance in the Fig 3 to 6 may be due to increase in % wollastonite.

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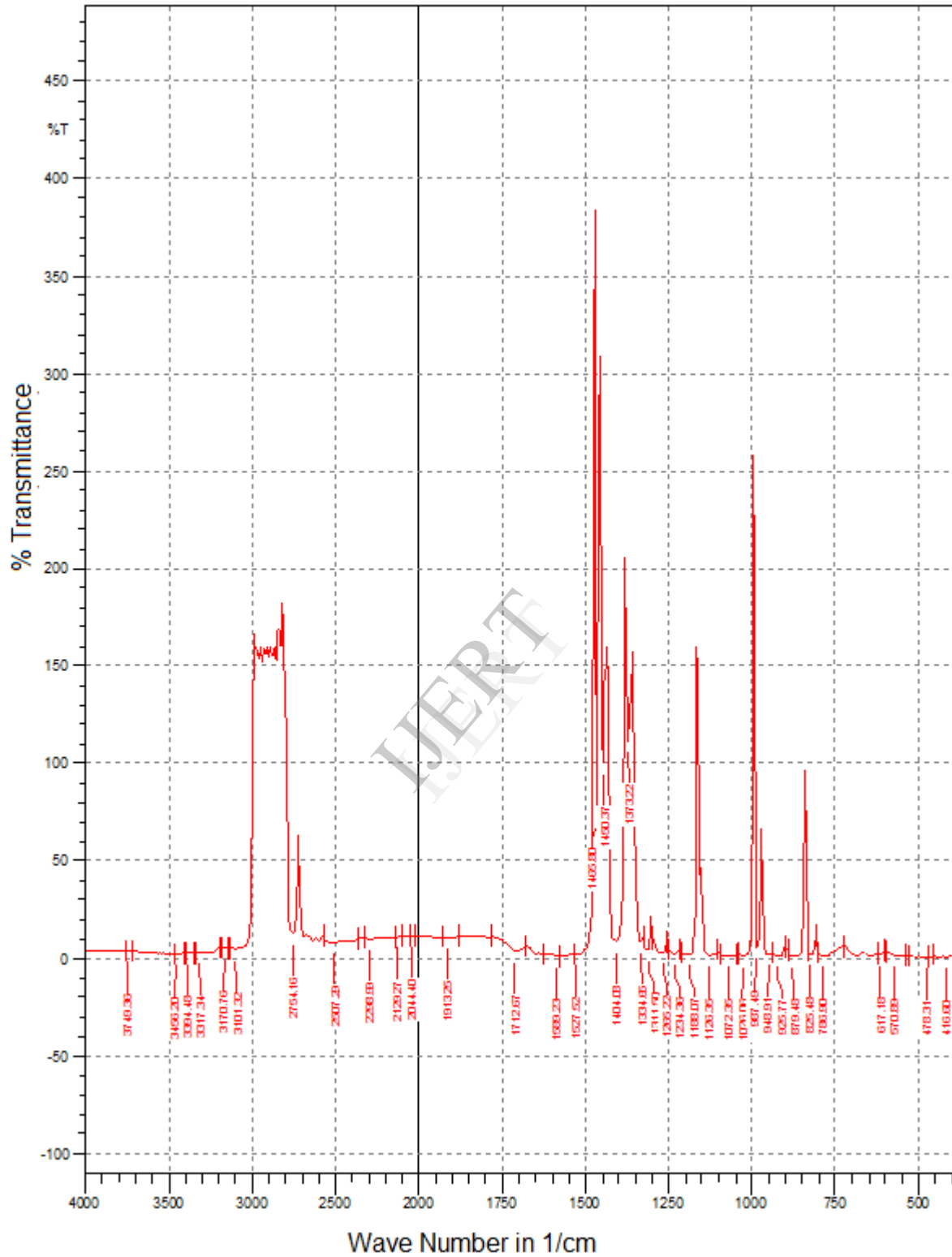


Fig-3: FT-IR data for the polypropylene composites having 10% wollastonite with 5% silicon rubber.

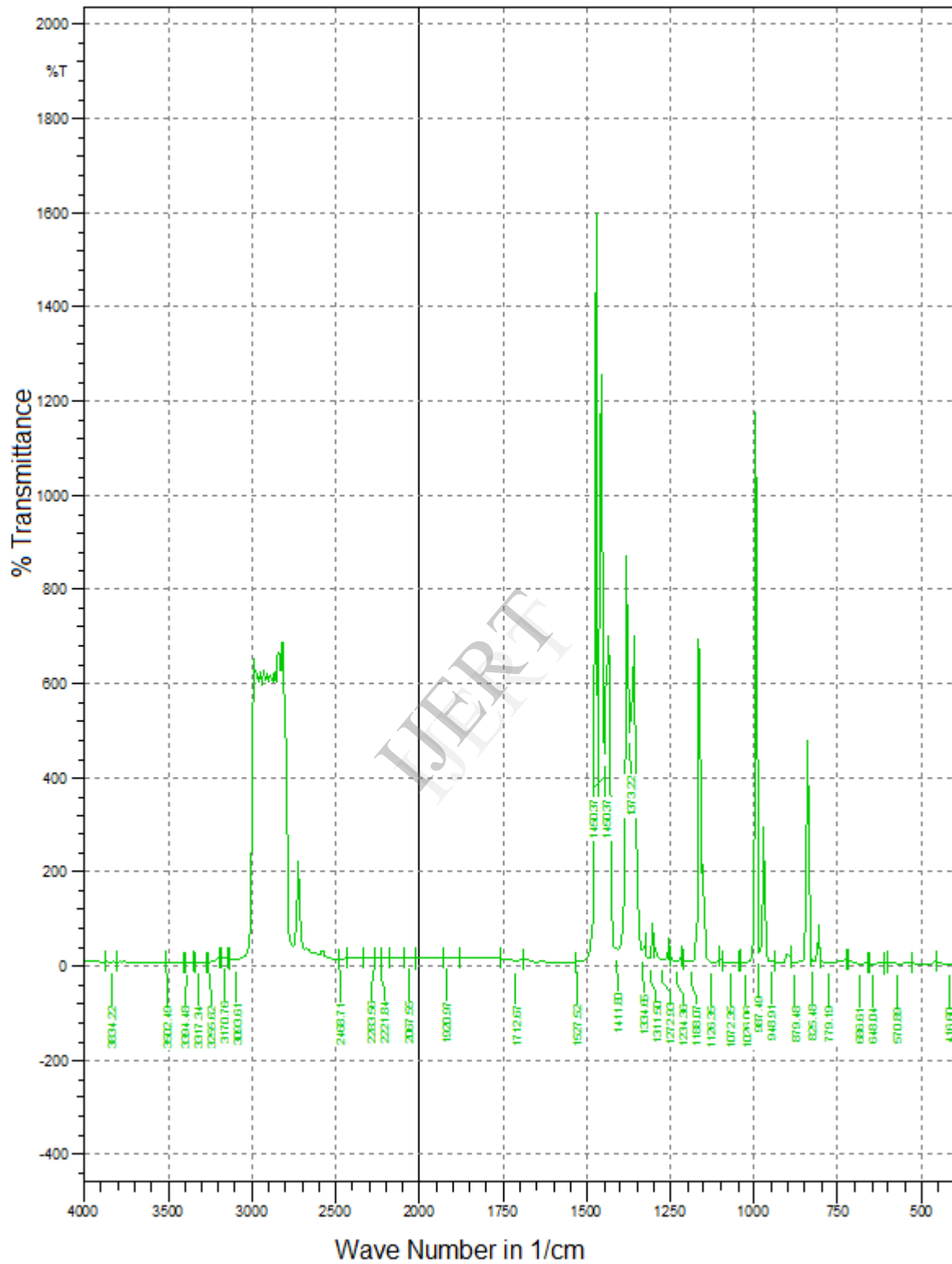


Fig-4: FT-IR data for the polypropylene composites having 20% wollastonite with 5% silicon rubber.

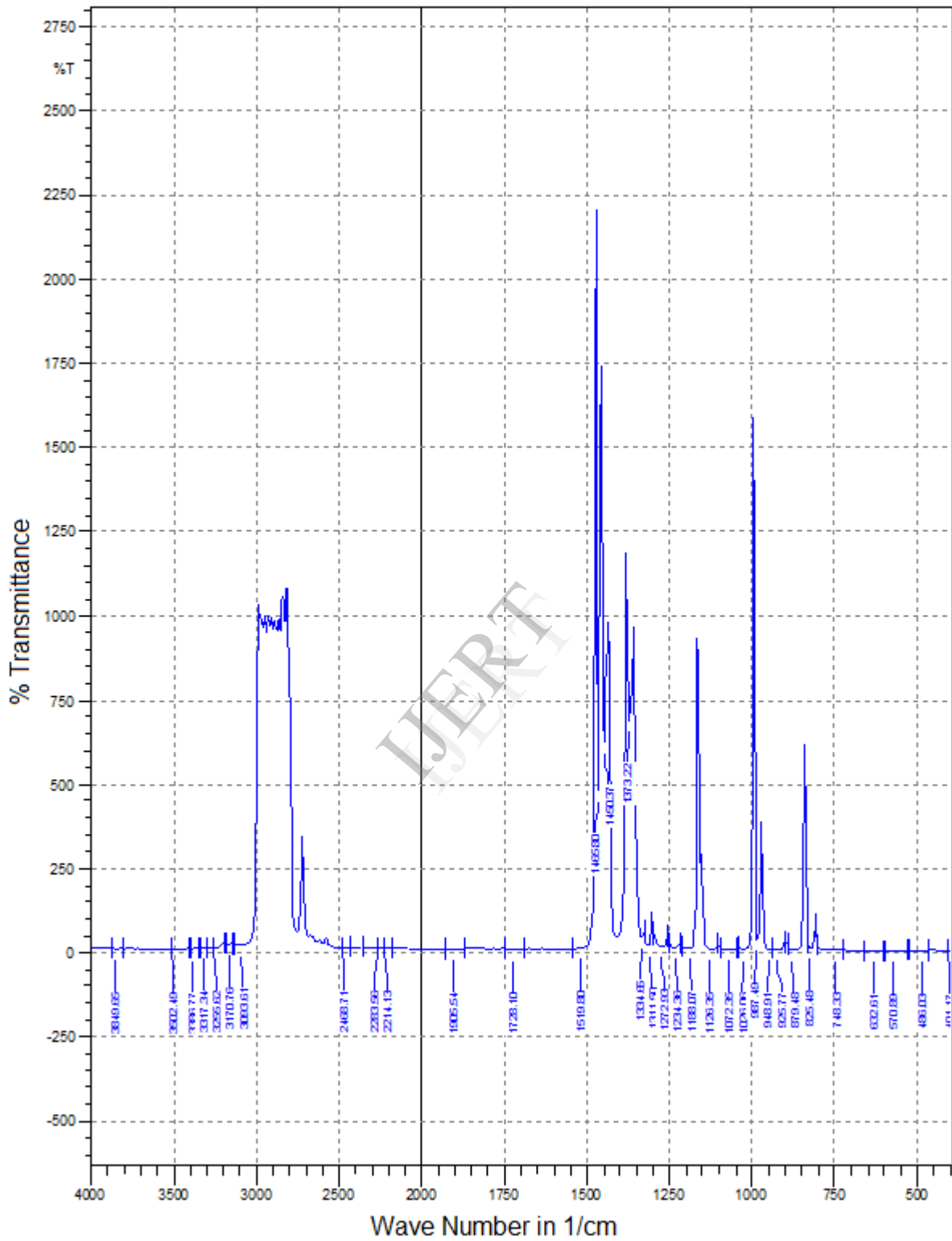


Fig-5: FT-IR data for the polypropylene composites having 30% wollastonite with 5% silicon rubber.

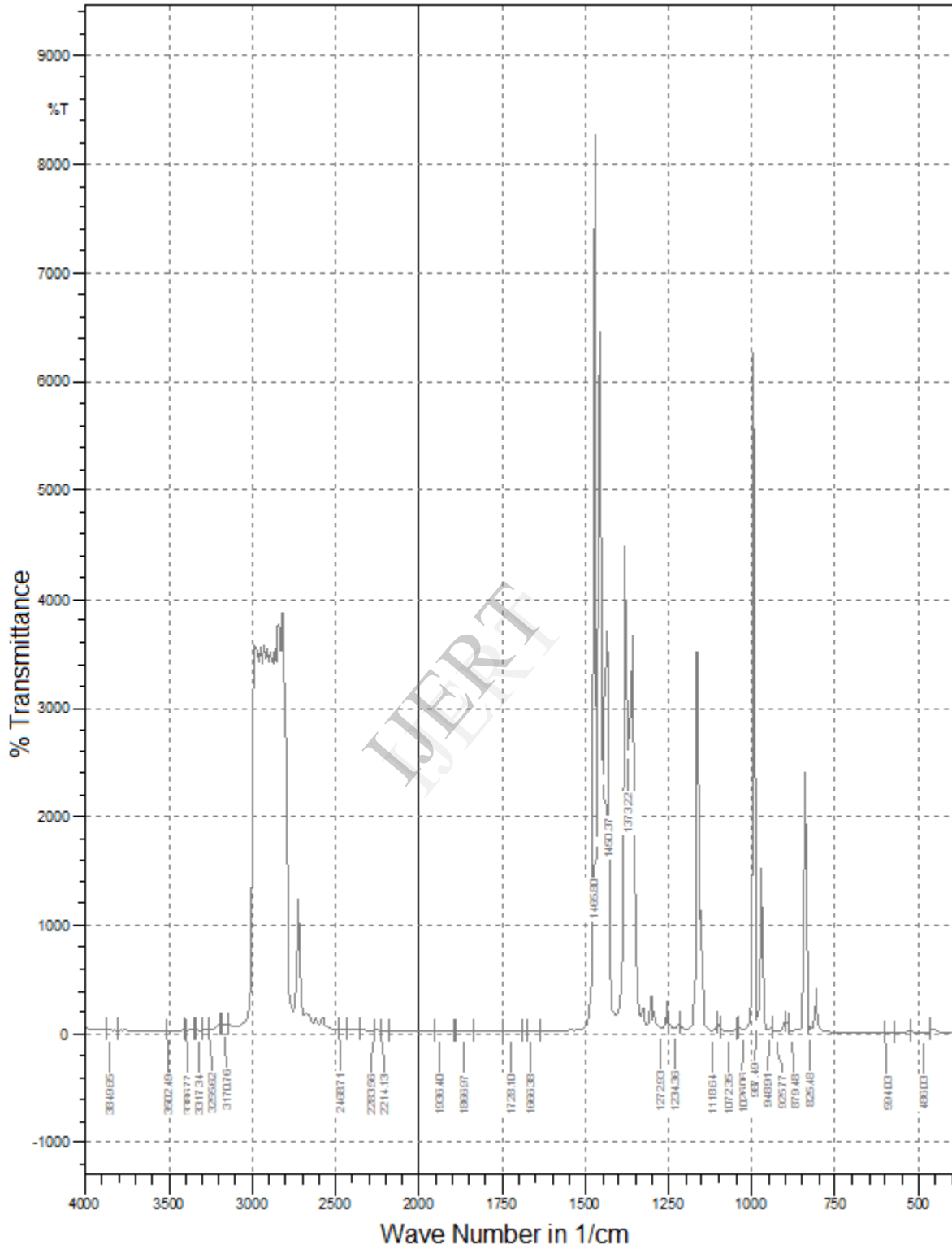


Fig-6: FT-IR data for the polypropylene composites having 40% wollastonite with 5% silicon rubber.

Results

All the compositions had a marginal difference of melting temperature (T_m),

Table-1 DSC Results

Sample No.	MATERIAL ← UNIT →	T_m	ΔH_m	H.D. T[28]	TENSILE STRENGTH	FLEXURAL STRENGTH	FLEXURAL MODULUS
		[°C]	[J/g]	[°C]	Kg/cm ²	Kg/cm ²	Kg/cm ²
SR1	PP+wollastonite-10%+silicon rubber 5%	163.94	56.664	105	300	409	5133
SR2	PP+wollastonite-20%+silicon rubber 5%	164.03	55.760	119	275	458	8872
SR3	PP+wollastonite-30%+silicon rubber 5%	164.26	53.259	128	275	499	10970
SR4	PP+wollastonite-40%+silicon rubber 5%	163.50	52.267	134	145	506	11840

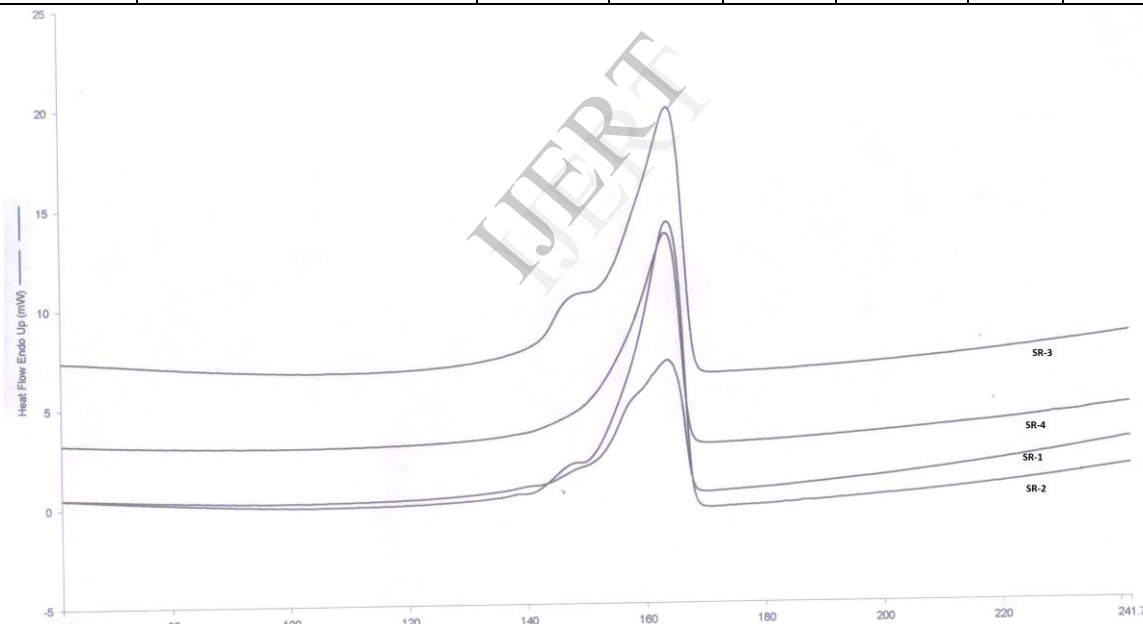


Fig-7: DSC data for the polypropylene composites having wollastonite at 10, 20, 30, and 40% with 5% silicon rubber.

Compared to neat PP with composite, PP had the lowest T_m (163.1°C) [27] and the composites had the highest T_m (164.26°C). The increased loading level of wollastonite had no significant effect on the T_m of composites. At 10, 20, 30, 40% loading of wollastonite, the T_m increased up to 0.84, 0.93, 1.16, 0.4°C respectively, which is not significant. The enthalpy (ΔH_m) of caloric processes was determined at the heating rate of 10°C/min (Table 1). The ΔH_m of neat PP at transition temperature was 81.8 J/g, but the ΔH_m with different loading of wollastonite in composition SR1, SR2, SR3 and SR4 loading levels are 56.664, 55.760, 53.259 and 52.267 J/g respectively, indicating an increase in thermal stability. This result indicates that wollastonite absorbed more heat energy in the melting of the composites as the ΔH_m of wollastonite was

much lower than that of neat PP. Fig- 1 (a, b, c and d) presents morphologies of fractured surfaces of the SR1, SR2, SR3 and SR4 composites, respectively. From all SEM micrographs, typically acicular, needle-shaped particles of the wollastonite filler could be seen. Furthermore, the filler particles are randomly dispersed in the PP matrix and they are mostly oriented in the direction of the melt flow in all composites due to the similar processing conditions. Micrographs of different composites show the compatibility of PP and Silicon rubber with untreated Wollastonite on addition malicanhydride. The fibrous filler wollastonite particles were randomly dispersed in the PP matrix, lumps formation of silicon rubber and compatibility of silicon rubber and wollastonite in all compositions were observed. As shown in Figure 1a, the visible acicular, needle-shaped particles of wollastonite covered with silicon rubber from the surface indicates adhesion at polymer/filler interface. Fig-1 b depicts lumps formation of the silicon rubber and some wollastonite particles in the polymer matrix. Fig-1 c is also showing the compatibility of wollastonite with rubber and polymer matrix Fig-1 d shows the lumps of silicon rubber and needle shaped wollastonite particles. From the morphological observation it could be expected that the observed differences in composite morphology would be confirmed by mechanical measurements.

Conclusions

1. Some novel polypropylene composites having wollastonite at different compositions of 10%, 20%, 30% and 40% were prepared by compounding with and without 5% silicon rubber. Subsequently, thermal, morphology and FT-IR analysis were done to evaluate the degradation temperature, Delta H compatibility and chemical changes.
2. An increase of wollastonite amount in the polypropylene, in general, resulted into increase in thermal degradation in TGA observation, which may increase HDT of the composite.
3. Addition of 5% rubber in the polypropylene composites having wollastonite at different compositions of 10%, 20%, 30% and 40% provided, in general, reduce ΔH_m . This result indicates that wollastonite absorbed more heat energy in the melting of the composites as the ΔH_m of wollastonite was much lower than that of neat PP.
4. FT-IR study shows that there is no change in chemical structure of the composite.

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