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Thermal Properties of Polypropylene/ Montmorillonite Nanocomposites

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Abstract

This research paper deals with the loading of different wt.% of Montmorillonite (MMT) thermal properties of polypropylene (PP). PP/MMT nanocomposites have been manufactured by melt blending method using maleic anhydride grafted polypropylene (MAH-g-PP) coupling agents. Melt blending was achieved by using twin screw extruder. The MAH-g-PP used as coupling agent and helped the good dispersion of the nanofiller in polymer matrix. The crystallization behavior of PP and its nanocomposites were studied by differential scanning calorimetry (DSC). DSC isothermal curves showed an increase in the crystallization temperature along with increasing degree of crystallinity. Thermogravimetric analysis (TGA) which indicated good thermal stability of PP matrix in Na⁺-MMT nanocomposites. Dynamic mechanical analysis (DMA) indicated significant improvement in the storage modulus and loss modulus compared with neat PP.

Keywords: Crystallization, Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimetry (DSC), Montmorillonite (MMT), Polypropylene (PP), Thermogravimetric Analysis (TGA).

1. Introduction

The incorporation of inorganic particulate fillers has been proved to be an effective way of improving the mechanical properties and in particular the toughness, of polypropylene¹. MMT is the most commonly used tool for the preparation nanocomposites. MMT possesses layered structure with an octahedral aluminium layer located between two layers of silicon tetrahedral. Each layered sheet is about 1nm thick with lateral dimensions of 100-1000 nm. Recently, MMT was used in the preparation of nanocomposites with polymers. In the case the platelets were nanoscale reinforcement for the polymer matrix. Nanoparticle filled polymers are attracting considerable attention since they can produce property enhancement that are sometimes even higher than the conventional filled polymers at low volume fraction range². Calcium carbonate nanofiller have resulted in some improvement in the mechanical properties of PP, namely the modulus and impact strength³. Incorporation of CaCO₃ nanoparticle into PP matrix can produce attractive polymer nanocomposites with improved modulus

and toughness⁴. The presence of SiO₂ nanoparticles in the polymer matrix led to an increase of both Young's modulus and impact strength⁵. Organomodified montmorillonite gives improved mechanical strength, higher fracture toughness and lower wear rates⁶. Polypropylene, talc filled polypropylene and silicate-clay filled polypropylene are strain rate sensitive material. The yield strength and modulus of material increase with increasing strain rate. Filling the talc particle into polypropylene can increase the modulus and decomposition temperature, but decrease yield strength and fatigue strength, has no effect on glass transition temperature and melt temperature. Silicate clay can increase the modulus, decomposition temperature, yield strength and fatigue strength, and has no effect on glass transition temperature and melt temperature⁷.

The purpose of this paper is to report the thermal and mechanical properties of neat PP and PP/Na⁺-MMT nanocomposites. Tensile, flexural and impact tests were performed to evaluate mechanical performance. Differential Scanning Calorimetric (DSC), Thermogravimetric Analysis (TGA) and Dynamic Mechanical

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Analysis (DMA) were performed to evaluate the thermal performance.

2. Experimental

2.1 Materials

The PP has grade of H110MA with density of 0.910g/cc and melt flow index (MFI) of 11g/10min, purchased from reliance Ltd, India. The coupling agent PP-g-MA purchased from Exxon mobile India Pvt.Ltd, India, with the grade name Exxlor PO 1020, with MFI 125gm/10 min with 0.75% of grafting. Nanoclay i.e. unmodified MMT having CEC 92.6 meq/100g, purchased from southern clay products Inc, USA.

2.2 Preparation of Nanocomposites

Melt mixing of PP, PP-g-MAH (10 wt %) and unmodified MMT of 1, 3, 5 and 7wt% carried out in counter rotating twin screw extruder. Prior to melt mixing, the PP and the nanofillers were preheated in a vacuum oven at 60°C for a time of 6 hours. PP was fed into the twin screw extruder at the rate of 5 kg/hour and the nanofillers were introduced subsequently at the melting zone. The process of manufacturing of PP/MMT nanocomposites were carried out at a two screw speed of 150 rpm and maintain the temperature difference of barrel in twin screw extruder were 160, 170 and 180°C between feed zones to die zone, followed by granulation in a pelletizer and drying. These pellets were injection molded by using injection moulding machine. The manufacturing of test specimens of tensile, flexural and impact strength as per ASTM D by using injection moulding machine with clamping force 800Kn fitted with dehumidifier at a temperature range of 195-220°C.

2.3 Characterization

2.3.1 Differential Scanning Calorimetry (DSC)

The thermal characterization of PP and PP/MMT nanocomposites were determined by using a TA Q-10 thermal analysis apparatus. The temperature range was used 40 ~ 220°C at a scan rate of 10°C/min under nitrogen atmosphere. In the first heat run, all samples were annealed at 220°C for 5 min to eliminate the thermal history. The degree of crystallinity (X_c) of PP and its nanocomposites was calculated from the heat of fusion (ΔH_m) of the second heating cycle with the following relation.

$$X_c = (\Delta H_m / (1 - \Phi) \Delta H_m^0) \times 100\%$$

Where, ΔH_m^0 is the heat of fusion for 100% crystalline PP, which has taken as 209 J.g⁻¹ and Φ the weight fraction of the filler in the composites. Subsequently, the samples were cooled to 40°C at the rate of 10°C/min cooling rate and the corresponding melting temperature (T_m), crystallization temperature (T_c) and degree of crystallinity were recorded from the heating and cooling curves.

2.3.2 Thermogravimetric Analysis (TGA)

The thermal stability of PP and PP/MMT nanocomposites were studied from TGA curves employing Perkin Elmer pyris-7 TGA equipment. samples of ≤ 5 mg were heated from 40°C to 500°C at a heating rate of 10°C/minute in nitrogen atmosphere and corresponding weight loss recorded.

2.3.2 Dynamic Mechanical Analysis (DMA)

Viscoelastic properties such as storage modulus (E'), loss modulus (E'') and mechanical damping parameter ($\tan \delta$) as a function of temperature were measured in a dynamic mechanical thermal analyzer (Netzsch DMA 242-C) with the temperature range from -150° ~ 150°C. The frequency used was 1 Hz and the heating rate, 10°C/min. The specimen dimension was 60X10X3mm.

3. Results and Discussion

3.1 Thermal Properties

Nonisothermal crystallization of PP and its nanocomposites was studied and DSC curves are presented in Figure 1(a, b, c, d and e). Heating scans were analysed for the melting temperature, T_m , heat of fusion, H_m , and the degree of crystallinity, X_c , while cooling scans were used to obtain the crystallization temperature, T_c , and the degree of super cooling, $\Delta T = (T_m - T_c)$. The heat of fusion was determined by integrating the heat flow at 40-220°C. The result clearly indicated that nanoclay in PP could improve the crystallization of polymer matrix, since the crystallization temperature increased by 1.5°C. The degree of crystallinity of PP in PP/MMT composites also increased especially at the higher nanoclay content (the degree of crystallinity increased by 25.86%). Table 1 also shows that the ΔT of nanocomposites is smaller than that of neat PP, which indicates that the addition of nanoclay into PP increased the rate of crystallization of PP. It can also be seen from Table 1 that the melting temperature

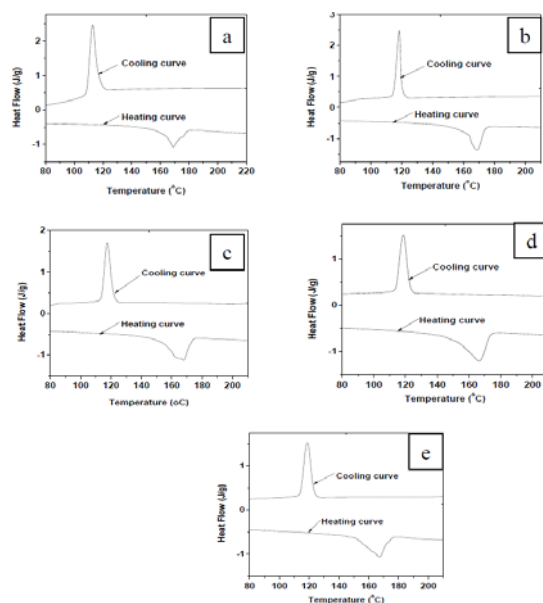


Figure 1. DSC thermogram of PP and PP/MMT nanocomposites a) PP, b) 1%MMT, c) 3%MMT, d) 5%MMT and e)7%MMT

(T_m) remained unaltered after the addition of nanoclay, which means that the crystal size of PP did not change.

Thermal stability of PP and PP/MMT nanocomposites were studied by TGA as shown in Figure 4. From the observation it is clear that the thermal stability of the base polymer increased with nanoclay loading.

3.2 Dynamic Mechanical Analysis (DMA)

The storage modulus curve and values of PP and PP/Na+MMT nanocomposites are represented in Figure 3(a), which displays the variation of storage modulus as a function of temperature at a temperature range of -150°C to +150°C. Storage modulus of PP as well as its nanocomposites decreases with increase in temperature. It is observed that storage modulus of PP decreases with the increase in temperature, which is mainly attributed to

Table 1. DSC melting and crystallization parameters for PP and nanocomposites

sample	T_m (°C)	T_c (°C)	ΔT (°C)	ΔH_m (J.g ⁻¹)	X_c (%)
PP	168.95	117.09	51.86	35.72	17.09
1%MMT	168.58	118.34	50.24	52.53	25.13
3%MMT	167.82	117.60	50.22	49.09	23.48
5%MMT	166.31	118.61	47.7	54.05	25.86
7%MMT	167.36	118.83	48.53	36.13	17.28

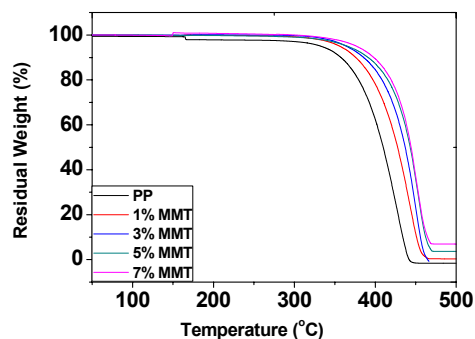


Figure 2. TGA Thermogram of PP and PP/MMT nanocomposites

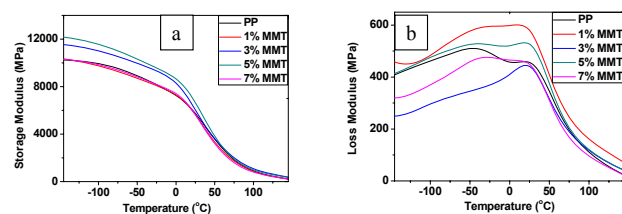


Figure 3. a) Storage modulus and b) Loss modulus of PP & PP/MMT nanocomposites.

the polypropylene molecules in the glassy region where as above glass transition temperature. However, reinforced the nanofillers into the PP molecules resulted in an increase in the storage modulus of the PP/MMT nanocomposites over the entire range of temperature. The E' curves display a rubbery plateau, indicating that addition of clay induces a reinforcing effect. The improvement in storage modulus of the nanocomposites over their pristine counterpart is more prominent in the rubbery region because in this region the material is soft and flexible. The enhancement of storage modulus strongly depends on the aspect ratio of the dispersed clay particles and intercalation of the polymer chains inside the clay matrix. When polymer matrix is reinforced with nanoclay, the polymer interface adjacent to the clay particle is highly restrained mechanically. Platelet edges of the clay particle act as a weak point and are sites of high stress concentration for the matrix. As aspect ratio of this filler increases, weak points decreased which results in the higher amount of stress transfer between the matrix and filler particles. Loss Modulus (E''). If the applied mechanical energy (work) is not stored elastically, it must be lost and converted to heat through molecular friction that is viscous dissipation within the material. The loss modulus curves of virgin PP

and the nanocomposites are illustrated in Figure 3(b). The lower temperature relaxation peak is primarily associated with the T_g (0°C) of the virgin matrix. The nanocomposites have lower T_g (5 to 2°C) than PP, which varies with the different weight fraction of clay. The decrease in T_g in the nanocomposites indicates that the amorphous molecules become mobile at lower temperature as compared with virgin PP which is probably due to the existence of low molecular weight surfactants in the nanoclays. The difference in T_g in the nanocomposites can be attributed to the different types surfactant applied to the surface of nanoclays.

4. Conclusion

We have shown that PP/MMT nanocomposites can be prepared by a melt compounding technique with compatibilized PP-g-MA. The non-isothermal crystallization studies showed an enhanced crystallization of PP. DMA indicated 100% improvement in loss modulus for 5% PP/MMT composites compared to neat PP at -40°C . Thermal stability of the base polymer increased with nanoclay loading.

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