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Nanoclay and PMMA Granule: Influences on Mechanical and Thermal Properties of PVC

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ABSTRACT

This study aims to compare the mechanical and thermal properties of poly(vinyl chloride) (PVC)/poly(methyl methacrylate) (PMMA) blends, PVC/nanoclay binary composites and PVC/nanoclay/PMMA ternary composites. Also, the influence of component mixture sequences on the flexural strength of ternary composites is studied. Polymer blending is one of the most important ways for the development of new polymeric materials. On the other hand, using clay minerals it to have an effect because of their unique crystal structure and properties. Two component mixture patterns are investigated during the direct melting method PVC, including (a) an addition of PMMA granule then an addition of nanoclay, (b) a direct mixing of PVC and nanoclay then an addition of PMMA granule. The results indicate that using the component mixture pattern which nanoclay is mixed to PVC compound at first time (second pattern), has the best result for flexural strength of ternary composites. X-ray diffraction (XRD) technique and field emission scanning electron microscopy (FE-SEM) results demonstrate that PMMA granule in ternary composites causes no good interaction of nanoclay with PVC matrix. Thermo gravimetric analysis (TGA) indicates that there is a decreasing in the thermal stability of samples containing PMMA granule compared to the both binary composite and virgin PVC.

1. Introduction

A typical kind of PVC with a little or without plasticizer is used, named rigid. This kind is applied to provide waste pipe and window profile. There are some limitations for PVC such as brittleness and inferiority of thermal stability. However, this polymer has been extensively used in the industry. There are some methods to develop new PVC products with desirable properties that open new applications for PVC [1]. Acrylate groups used as impact modifers for PVC and PMMA are important member. PMMA has several desirable properties, including exceptional optical clarity, good weatherability, high strength, and excellent dimensional stability [2]. PMMA is completely amorphous and has solubility parameters very close to PVC which can have very suitable compatibility with PVC [3]. In spite of the fact that there have been a lot of articles about PVC/PMMA blends, the mixture ability of both has not been discussed yet [4-6]. The polymer/nanoclay composites are a kind of hybrid materials at which mineral filler with nano dimension is used in their matrix [7]. The MMT is a mica-type silicate that consists of sheets arranged in a layered structure [8]. The increased aspect ratio and low cost possible with nanoclay were important reasons to be considered for polymer/nanoclay composites

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[9]. few studies about PVC/MMT nanocomposites were performed about rigid PVC [10-12]. Blending of thermoplastics or nanofiller/polymer composites may generate materials with increased properties compared to main polymer. It is generally accepted that addition of fillers can dramatically increase the PVC composite stiffness compared to the PVC matrix [13]. In the recent years, some researchers were interested in ternary PVC composites [12,14-16]. Page et al. [12] reported on the basis of XRD technique and SEM results that the PMMA played an important role in the nanoclay dispersion. They found an overall increase in the properties of PVC/PMMA/MMT composites compared to the virgin PVC. The current paper focuses on the study of the mechanical and thermal properties on PVC/PMMA blends, PVC/nanoclay binary composites and PVC/ nanoclay/PMMA ternary composites, to show effects of both nanoclay and PMMA granule.

2. Experimental Procedure

2.1. Materials

In PVC compound: PVC powder with k-value 65 was taken from Bandar Imam Petrochemical Co. (Iran) and other additives such as thermal stabilizer based on Tin (Hampar Co.), DOP plasticizer and the processing aid based on acrylate about 2, 7 and 1.7 phr, respectively. PMMA granule (Acryrex®CM.205) was purchased from Chi Mei Corporation co. (Taiwan) with melt flow index of 1.8 g/10 min. The HB nanoclay with product number 682659 was purchased from Sigma-Aldrich Co. (USA).

2.2. *Preparation of the Samples*

The melt blending was run with laboratory two-roll mill Brabender (YAZD Radiation Application Research) at 180°C and 25 rpm of rotor speed. The nine samples are labeled, shown in table1.

Table 1. Samples information.

samples	PVC (phr)	PMMA (phr)	Nanoclay (phr)
S_0	100	0	0
S_1	100	5	0
S_2	100	10	0
S_3	100	0	3
S_4	100	5	3
S_5	100	0	5
S_6	100	5	5
S_7	100	10	5
S_8	100	10	5

Improvement of properties and the dispersion of nanoparticles in PVC composite are affected by the degree of gelation achieved in PVC compound during processing, which in turn depends on material combination method [11]. Hence, two patterns are performed for components mixture. In first pattern, PVC compound are poured between space in both cylinders of two-roll mill and the process is begun and after 1 minute, 10 phr PMMA granule is added and the process is continued forfurther 2 minutes. After this process, 5 phr HB is added and the process is finished after 2 minutes. The resulted sample from this pattern is abbreviated to S7 sample. In second pattern, the both PVC compound and 5 phr HB are poured between space in both cylinders of two-roll mill and the process is begun and after 3 minutes, 10 phr PMMA granule is added and the process is finished after 2 minutes. The resulted sample from this pattern is abbreviated to S8 sample.

2.3. Characterization

The XRD and Braggs's law ($n\lambda = 2d \sin \theta$) are used to determine the intercalation degree of PVC chains in silicate layers. X-Ray diffractometer is used with an angle amplitude of 2θ=1-10º. XRD measurements were carried out at room temperature using an X,pert Philips diffractometer (Holland, it was tested at the Tarbiat Modares University). X-Ray diffractometer worked with generator current of 30 mA and generator voltage of 40 kV. Special attention was paid to the low 2θ region for accurate determination of the(001) planes d-spacing nanoclay. The microstructure of the both binary and ternary composites was observed with a FE-SEM, Hitachi F4169 at 20 kV (Japan, it was tested at the University of Tehran). Prior to analysis, the test sample was cooled in liquid nitrogen, fractioned and sputtered with gold. Tensile tests were performed at room temperature at a crosshead speed of 10 mm/min using a tensile tester from HIWA200 (Iran) according to ASTM D 638M. According to ASTM D 790-92 standards, flexural properties test was performed using a Santam Co. (Iran, STM-50 Universal). The flexural test was conducted using the three-point bending experiment, in which the support span and the rate of crosshead motion were kept at 30 mm and 5 mm/min, respectively. Hardness of the all samples was determined by following the Shore D scale using Time TH3200 (China) according to ASTM D2240. The obtained samples were cooled at room temperature and the specimens for the tests were produced using warm press COLLIN (Germany), P200P, at 190°C.

TGA was performed using a TG-DTA (BAHR STA503, Germany) instrument to determine the thermal stability of polymer composites. The content of the used samples was about 22-23.5 mg from ambient temperature to 600 ºC in the air atmosphere. All of the four lasttest, were testedin the Khorasan Science and Technology Park.

3. Results and Discussion

3.1. Morphology

XRD characterization is generally based on a comparison between the (001) planes position of the nanoclay powder and that of the nanoclay in the polymer matrix [17]. Figure 1 shows the XRD results for nanoclay and S_5 sample. It is clearly seen from the spectra that nanoclay showed maxima at 7.11º, corresponds to the d-spacing of 1.24 nm. For S_5 sample, the peak characteristic of the d001 of nanoclay shifts to lower angle of $2\theta = 1.62º$ (5.43nm).

Figure 2 represent the XRD spectra for the S_3, S_4 and S_6 samples. The peak characteristic of the d001 of nanoclay disappears for the S_3 and S_4 samples. Interestingly, the characteristic peak for the nanoclay in the S_6 sample did not appear even at a 2θ value of 1º. With respect to XRD spectra of S_5 sample, it is seen that PMMA granule adding to this composite caused to highly exfoliation with gallery height (d-spacing) of more than 8.82 nm [18]. A peak revealed about 9-10º for the both S_4 and S_6 samples. It signifies that a structure containing agglomeration of nanoparticles is obtained [19]. Of course, this peak is like peek existed on PVC/MMT nanocomposites which is prepared by Peprnicek et al. [20]. They take that some MMT layers still keep their original crystal structure and remain in their primary particles. In other study, existence of the diffraction peak at 9.5º is attributed to the used compatibilizer in preparation of ethylene propylene diene terpolymer (EPDM)/organoclay nanocomposites [21]. Hence, with respect to absence of this peak for S_3 and S_5 samples comparing with composites contained PMMA granule, it is possible that PMMA granule effects appearance of this peak.

For more discussion, other methods should be used to complement the diffraction experiments. Figures 3 and 4 show FE-SEM images of S_5 and S_6 samples, respectively. Several studies have used FE-SEM microscopy for morphological characterization of polymer/MMT nanocomposites [22-27]. SEM images of S_5 sample indicate that in this composite nanoclay is fully covered by the polymer and show no phase separation. But FE-SEM images of S_6 sample indicate two phases. Presence of the voids around the polymers is distributed almost non-uniformly at the micro-level.

3.2. Influence of Component Mixtures Sequence

From table2, the S_8 sample is 4% larger than the flexural strength of the S_7 sample. The improvement of flexural strength can be attributed to components mixture pattern. Also, it can be attributed to a bad dispersion of HB in PVC matrix.

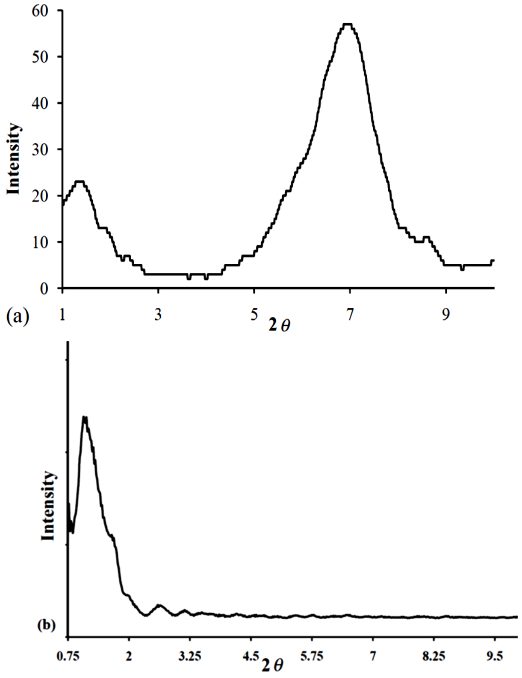

Figure 1. (a) XRD spectra of HB nanoclay. (b) XRD spectra of S_5 sample

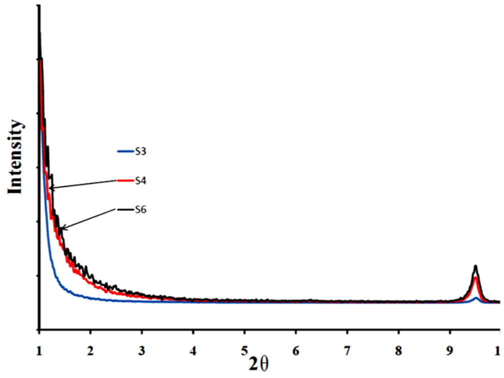

Figure 2. XRD spectra of S_3, S_4 and S_6 samples

Table 2. Influence of component mixtures sequence on flexural strength

samples	Flexural strength (MPa)
S_7	79.37
S_8	82.55

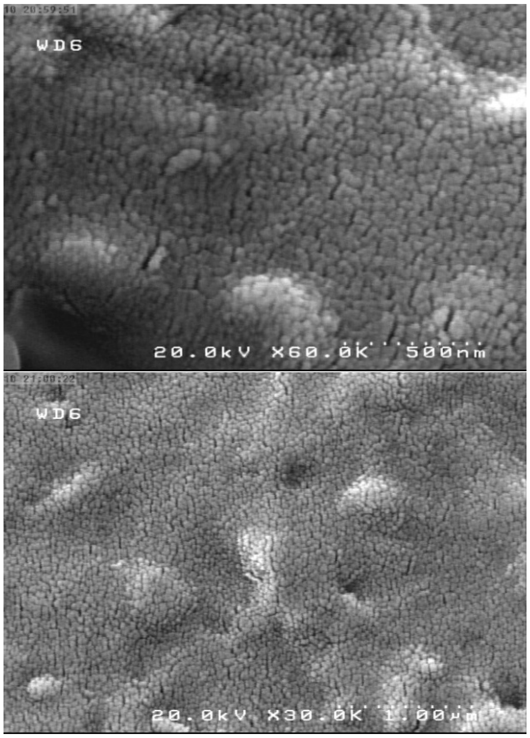

Figure 3. FE-SEM images of S_5 sample

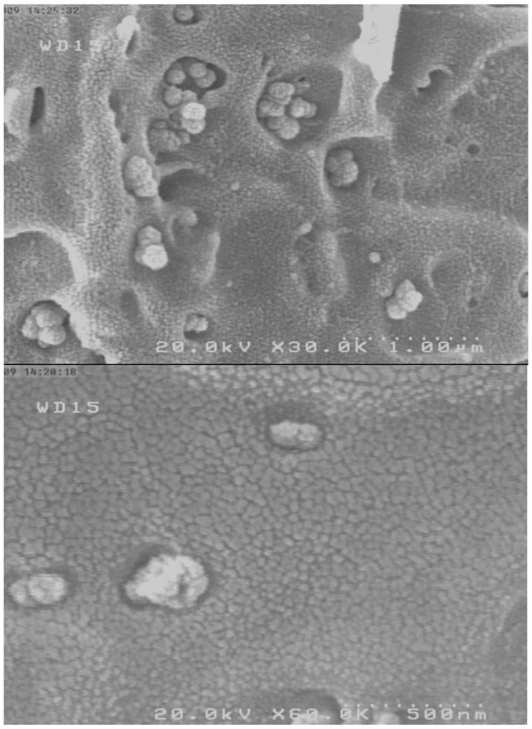

Figure 4. FE-SEM images of S_6 sample

In fact, PMMA granule does not allow HB to interact suitably with polymer matrix in first pattern.

3.3. Mechanical Properties

The PVC can be accounted as shape memory polymer [24]. The most common transformation of shape memory polymers is bending. So the bending and effect of its different parameters are very important. Various mechanical properties for all the samples are compared with S_0 as reference sample which are given in Table 3. It is clear that flexural strength of S_1 sample is higher than S_2 sample. It indicates more compatibility between the two polymers when PMMA granule is used in low content [27]. In S_5 sample which only uses HB, we find that increasing in the flexural strength occurs for other samples and also is 21.5% larger than S_0 sample. This increasing can be attributed to the interfacial interaction between nanoclay and polymer matrix [28].

Combination of nanoclay and PMMA granule in ternary composites has been able to increase the mechanical properties of the reference sample but decrease when compared to binary composites. It can be ascribed to poor interaction between nanoclay and polymer matrix in ternary composites from FE-SEM results. The caused increase of tensile and flexural strength in ternary composites than S_0 sample can be related to PMMA granule existence rather than nanoclay in these composites. This increase may be due to hydrogen bonding between the hydrogen of vinyl chloride and the ester carbonyl group of acrylic polymer, which reduces the sliding of the PVC chains when an external force is applied to the resin [29]. The maximum elongation at break is obtained in S_3 sample that maybe it exfoliates the structure.

The hardness of all samples increases almost than S_0 sample. Because of the stiff and rigid PMMA phase,

Table 3. Mechanical properties of samples

sample	Tensile strength (MPa)	Flexural strength (MPa)	Elongation at break (%)	Hardness Shore D
S0	26.48	75.78	6.51	79.4
S1	31.24	82.89	7.99	80.9
S2	-	78.55	-	81.5
S3	30.97	88.43	9.76	81.05
S4	29.68	84.32	7.12	79.9
S5	34.32	91.95	9.58	80.7
S6	30.9	87.54	8.57	80.32

Most content of PMMA granule leading to more compactness and the rise in specific gravity lead to increase in hardness for PVC/PMMA blends [3]. Also, because of the inherently rigid and hard layered silicate, hardness of PVC/nanoclay composites increases than S_0 sample.

3.4. Thermal Property

The thermal stability of samples in TGA test is demonstrated in Figure 5. The data including the temperature at which 10% degradation occurs (T_{10}), the temperature at which 50% degradation occurs (T_{50}) and the fraction that is non-volatile at 600 ºC (char percent) are presented in Table 4.

The onset thermal decomposition temperature (T_{10}) and char percent of S_5 sample are higher than those of S_0 sample but, the mid-point of decomposition temperature (T_{50}) of S_5 sample is close to S_0 sample. Enhancement of the thermal stability of S_5 sample could be related to presence of silicate layers in PVC matrix. It can act as a barrier to minimize the permeability of volatile degradation products out of the material during the thermal decomposition of PVC [30]. For the samples containing PMMA granule, T_{10}, T_{50} and char percent are lower than those of S_0 sample. A major change is seen in the degradation pathway with addition of PMMA granule. This may be due to phase aggregation tendencies of the components in samples that result in lesser interaction between the degrading products from the two polymers thus reducing the mutual stabilizing effect [31].

On the other hand, the addition of nanoclay to any samples containing PMMA granule enhances the thermal stability but very lower than S_0 sample.

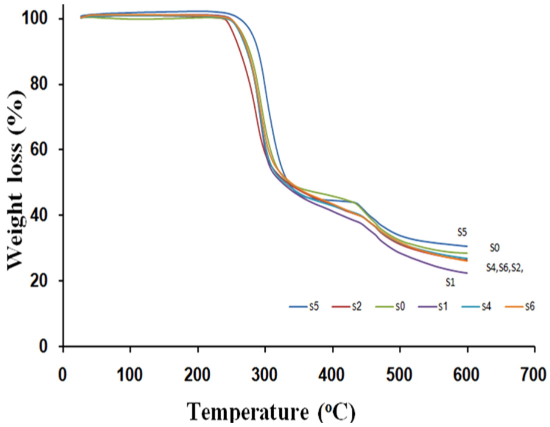

Figure 5. TGA curves of samples

Table 4. Data from TGA analysis

Sample	S_0	S_1	S_2	S_4	S_5	S_6
T_{10} (ºC)	277	273	263	274	290	273
T_{50} (ºC)	337	326	333	329	336	337
Char at 600 ºC (%)	28.5	22.5	26.4	26.9	30.7	26.1

1. Conclusions

PVC compound filled with two types of additives, nanofiller and acrylate polymer, was prepared via a direct melting method. The ternary composites were formulated with two patterns mixing components. The composite of second pattern had better flexural strength.This increase can explain the more PVC chains intercalation into the interlayers of nanoclay in composite of second pattern. According to XRD patterns, the addition of PMMA granule increased d-spacing of nanoclay but according to FE-SEM images, it reduced interaction between nanoclay and PVC matrix. Also, the mechanical properties of ternary composite were diminished than binary composites. The improvement of mechanical properties of the samples containing PMMA granule compared to reference sample can be attributed to hydrogen bonding between molecules of the constituent PVC and PMMA. Increasing the mechanical properties of PVC/PMMA blends is dependent on the composition and level of compatability. The main problem in the ternary composites is the inferior thermal property. The PMMA granule in PVC compound implies a major change in the degradation pathway. The presence of PMMA granule in samples causes aggregation of other components and decreases thermal stability than reference sample. But in the ternary composites, the presence of nanoclay increases thermal stability than binary blends. Both mechanical and thermal properties of binary composites containing nanoclay are higher than other samples due to the interfacial interaction between nanoclay and polymer matrix. The overall results, the mechanical properties are affected by the amount of nanoclay in the PVC matrix and PMMA in the form of granule does not allow nanoclayto interact with polymer matrix well.

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Nomenclature

PVC	Poly (vinyl chloride)
PMMA	Poly(methyl methacrylate)
MMT	Montmorillonite
XRD	X-ray diffraction
SEM	Scanning electron microscopy
DOP	Dioctylphtalate
HB	Hydrophilic bentonite
FE-SEM	Field emission-scanning electron microscope
TGA	Thermogravimetric analysis

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