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Effect of aspect ratio of clay on melt extensional process of maleated polyethylene/clay nanocomposites

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Summary

Maleated polyethylene composites with different aspect ratios of clays and SiO_2 were prepared by melt compounding. Aspect ratio of clay affects significantly the physical and mechanical properties of a nanocomposite. The composite with the highest aspect ratio of clay (Closite 20A) shows the higher storage modulus, complex viscosity, the higher melt tension of polymer and the longer drawability and lower neck-in during the melt processing than those with the low aspect ratio clay (SCPX2231) and SiO_2. It also shows an easy orientation in the polymer in melt drawing direction.

Introduction

Layered-silicate based polymer nanocomposites have attracted considerable technological and scientific interest in recent years [1-4], because they have shown the dramatic enhancements in physical, thermal and mechanical properties of polymers even with a very low loading of silicate [4].

Polyethylene is one of the most widely used polyolefin polymers. Since it does not include any polar group in its backbone, the homogeneous dispersion of the hydrophilic clay layers in polyethylene is not realized. Jeon and coworkers reported the intercalated morphology of HDPE nanocomposites prepared by solution blending of HDPE with sodium montmorillonite cation-exchanged with protonated dodecylamine[5]. However, the presence of fairly large stacks indicated a poor dispersion. Only when in-situ polymerization was performed, polyethylene/clay showed an exfoliated morphology [6-8]. Initial attempts to create the nonpolar polymer/clay nanocomposites by melt intercalation were based on the introduction of a modified oligomer to mediate the polarity between the clay surface and polymer [9-17].

Unfortunately, most of the previous works focused on the preparation and characterization of polymer-layered silicate nanocomposite. As a consequence, many fundamental questions concerning structures in polymer-layered silicate nanocomposites when submitted to an external force are far from clarity and need extensive investigations. The melt strength of a polymer has been recognized as one of the important parameters in melt processing operations where stretching or drawing is involved at one or more stages of the process. Typical industrial processes where stretching occurs along the streamline are melt spinning, blow molding, extrusion coating, film extrusion, fiber extrusion and thermoforming. The melt strength of a polymer is a measure of its resistance to extensional deformation. The melt strength parameter does not give a well-defined rheological property because neither the strain nor the temperature is uniform in the polymer melt being stretched. However, the test is useful in obtaining meaningful comparisons of the drawing behavior of different polymers [18,19]

The aim of this study is to investigate the effect of clay with different aspect ratios and conventional filler on the mechanical properties of a composite and the drawability during melt extrusion process.

Experimental

Materials and preparation of composites

Organically modified montmorillonite (Closite 20A) and laponite (SCPX2231) were obtained from Southern Clay Products as fillers and a maleic anhydride modified polyethylene (PEMA) purchased from Aldrich was used as a matrix resin. The montmorillonite(20A) had a high aspect ratio (100-200) and the laponite(Lapo) a low aspect ratio (20-30). The organic modifier for both organo clays was dimethyl dihydrogenated tallow ammonium ions. Tallow was composed predominantly of octadecyl chains with small amounts of lower homologues, e.g., the approximate composition of C_{18} 65%, C_{16} 30% and C_{14} 5%. The PEMA was the linear low density polyethylene (density = 0.930g/cc) grafted with 0.85wt% maleic anhydride. The conventional filler, SiO_2 (average particle diameter: 1.8μm) was purchased from Fuji Sylysia. The composites were prepared through melt compounding at 140°C, using a brabender mixer with the chamber size of 50cc. Screw speed was 60rpm and the mixing time was 20 min for all the cases.

Rheological Characterization

Rheological properties of all composites were measured in oscillatory mode by ARES (Advanced Rheometric Expansion System) with cone and plate geometry using 25 mm diameter and a cone angle of 0.04 rad at 210°C under nitrogen atmosphere.

Melt Tension Measurement

The melt tension was measured by using a Gottfert "Rheotens" Melt Strength Tester. It consists of a pair of rollers rotating in opposite directions that are mounted on a balance beam. Capillary viscometer provides a polymer melt strand with a constant output rate at 150°C. A polymer melt strand from a capillary die was extruded into air at room temperature and drawn by the rotating rollers whose velocity increases at a constant acceleration rate. The tensile force in the strand measured by the balance beam could be plotted as a function of velocity of the rollers or elongation ratio. The elongation ratio was defined as the ratio of velocity of strand at the wheel nip to velocity of strand when the tensile force on the strand was zero.

Neck-in Test

The composite was prepared using twin screw extruder(Gottfert Corp., screw diameter:19mm) at a constant rotating speed of 30rpm and the barrel (L/D=25) temperature profile of 140-180°C, and pelletized before neck-in test. The filler content in PEMA was held at 1 volume% (vol%). The reaction mixtures was premixed in a Henschel mixer before it was fed into the twin extruder.

Neck-in test was carried out on a brabender extruder with 19mm screw diameter and T-type die with width 10cm and gap of 1mm. All neck-in data were obtained at a die temperature of 180°C. Extruder output rate was 1.5kg/hr. Neck-in was measured in terms of the width of sheet with take-up speed of 10m/min and 60m/min.

X-ray diffraction

The X-ray data of composites after neck-in test were obtained using Simens GADDS(General Area Detection Diffraction System) two-dimensional detector. X-ray pattern was collected in transmission with CuK_α(λ= 0.15406nm) radiation. The distance from sample to detector was 120mm.

Results and Discussion

Preparation of nanocomposites with different aspect ratio clays

We prepared two kinds of nanocomposites with a high aspect ratio clay "20A"(PEMA/20A) and a low aspect ratio clay "Lapo"(PEMA/Lapo) and one macrocomposite with SiO_2 (PEMA/SiO_2) by melt compounding. X-ray diffraction (XRD) profiles and transmission electron microscopy (TEM) image of the two nanocomposites show the exfoliation state [20]. Clay layers were homogeneously dispersed in the PEMA. The dispersion mechanism is highly dependent on the hydrophilicity of polyethylene grafted with maleic anhydride and the hydrophobicity of the organically modified clay. When polyethylene has a higher grafting level of maleic anhydride than the critical grafting level of 0.1 wt% and the number of methylene groups in alkylamine chain(organophilic modifier of clay) has more than 16, polyethylene/clay nanocomposites are completely exfoliated [21]. In PEMA/SiO_2 macrocomposite, irregular sizes of SiO_2 particles were detected, indicating the aggregation and poor dispersion of SiO_2 particles [20].

Rheological properties of composites

Fig. 1(a) show storage moduli of composites of PEMA with 1 vol% of filler measured at 210 □. PEMA/20A shows higher storage moduli at all frequency range than the others. PEMA/SiO_2 shows the least increase in storage moduli. PEMA/20A nanocomposite shows the highest values of complex viscosity (η^*) and PEMA/SiO_2 macrocomposite shows a little higher values than PEMA in Fig. 1(b). PEMA/Lapo has intermediate values in storage modulus and complex viscosity between PEMA/20A and PEMA/SiO_2 because Lapo has the intermediate aspect ratio between 20A and SiO_2.

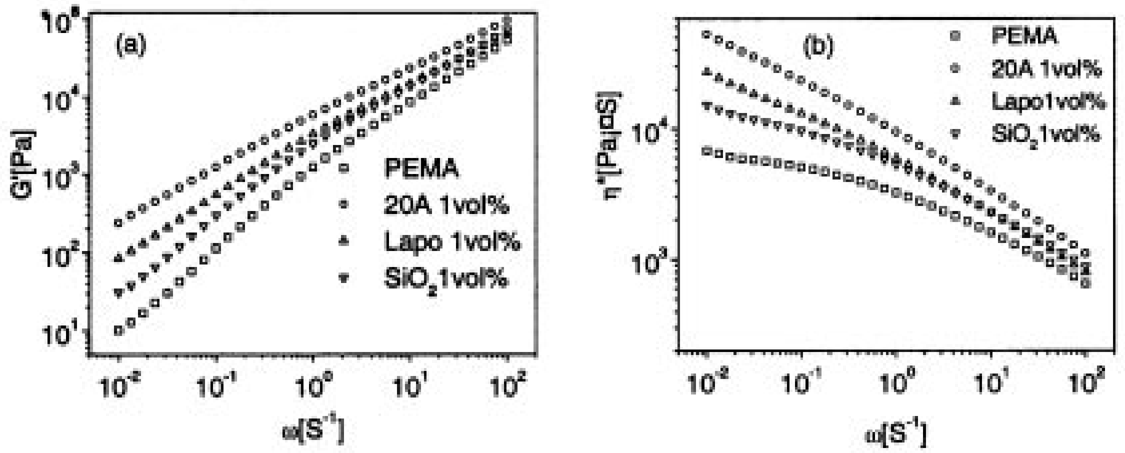

Fig. 1 Rheological properties of composites measured by a cone and plate rheometer at 210°C; **a** Storage moduli, **b** Complex viscosity

Melt Tension test

Fig.2 shows the tensile force at break of simple melt extensional fiber during the spinning in tensile tester. The point of a fiber rupture indicates a relative measure for the drawability and the tensile strength of the melt under test [22]. The maximum elongation ratio is regarded as a drawability of the melt under the test conditions. PEMA/20A nanocomposite shows higher melt tension (tensile force) and elongation ratio (better drawability than the others). PEMA/SiO_2 has the lowest drawability and

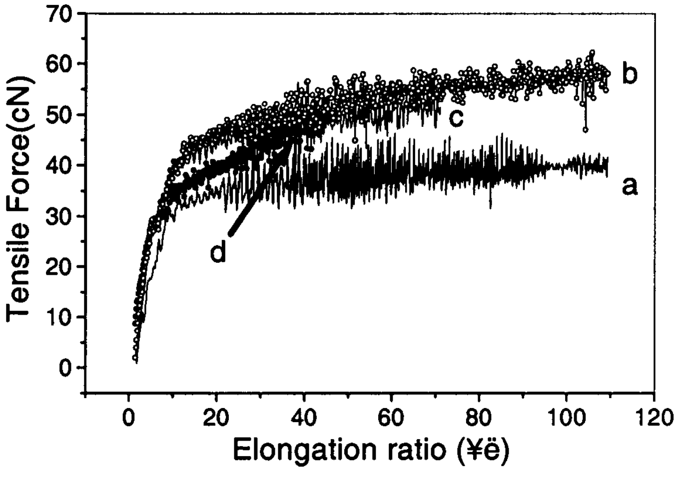

Fig. 2 Melt tension of composites with 1vol% of filler at 150°C **a** PEMA, **b** PEMA/20A, c:PEMA/Lapo, d: PEMA/SiO_2

lower melt strength than other nanocomposites. The high melt tension is caused by a strong interaction between polymer and layers of clay 20A. The high aspect ratio, good dispersion (exfoliation) and strong interaction of clay 20A in PEMA matrix enhance its storage modulus, viscosity, melt tension and drawability.

Neck-in test

For an inelastic material the 'neck-in' increases with extrusion rate. But the material with high elasticity appears to have an increased resistance to simple extension at a high stress, so the 'neck-in' is reduced [23]. Tablel shows the results of neck-in test of composites with 1vol% fillers. At the same extrusion rates, all composites give wider width than PEMA sheet. PEMA/20A nanocomposite shows the widest width of extruded sheet. Especially at high extrusion rate, it has 1.3 times wider width of sheet than PEMA. PEMA/Lapo nanocomposite has a low drawability and a higher neck-in than PEMA/20A. PEMA/Lapo is not greatly different from PEMA/SiO_2. This result is consistent well with the storage moduli behavior of Fig. 1(a) and melt tension behavior of Fig. 2. Polyethylene nanocomposite with high aspect ratio clay can be used widely in commercial application to gas barrier packaging, flame retardation and high modulus composite. The addition of clay with a high aspect ratio into polyethylene is useful for extrusion coating, bottle & film blowing and foam packaging because of its good processability.

Tablel Neck-in test results

	Take up speed	Sheet width after extrusion in T-die extruder
PEMA	10 m/min	5cm
	60 m/min	2.5cm
PEMA/20A	10 m/min	5.7cm
	60 m/min	3.3cm
PEMA/Lapo	10 m/min	5.2cm
	60 m/min	2.7cm
PEMA/SiO_2	10 m/min	5.0cm
	60 m/min	2.7cm

Test condition: 19mm screw diameter and T-type die with width 10cm. All data were obtained at a die temperature of 180°C and a die gap opening of 1mm. Extruder output rates of 1.5kg/hr were controlled to constant.

Shear - induced ordered structure

A question arises in why the nanocomposite with high aspect ratio clay gives a longer drawability and a lower neck-in than the nanocomposite with low aspect ratio clay.

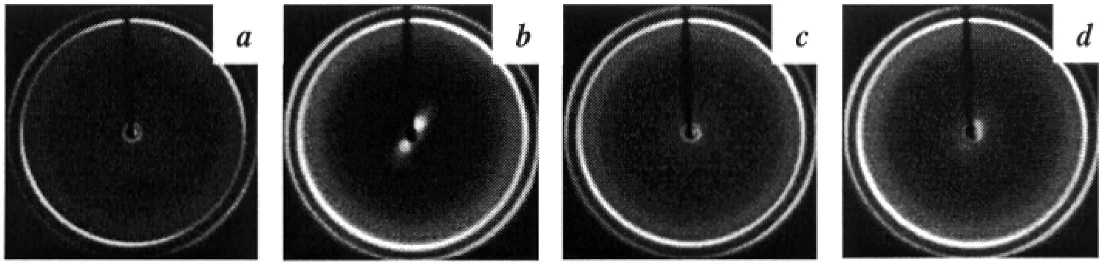

Fig. 3 X-ray diffraction of T-die extruded sheet at 180°C **a** PEMA/20A through direction, **b** PEMA/20A edge direction, **c** PEMA/Lapo through direction, **d** PEMA/Lapo edge direction

(⤡ sheet rolling direction)

Fig.3 shows XRD pattern of the through and edge direction of PEMA/20A and PEMA/Lapo nanocomposite sheets. Here through and edge directions are normal to sheet surface and parallel to sheet rolling direction, respectively. The through-view patterns show no reflection of clay in both PEMA/20A and PEMA/Lapo. But the edge view pattern of PEMA/20A in Fig.3(b) reflects strongly the orientation of clay around the beam stopper. Similar reorientation behavior of clay during melt deformation is also found for Nylon-6 and polystyrene nanocomposites [24-28]. The patterns of PEMA/Lapo ((d) in Fig.3) and PEMA/SiO_2 (not shown here) do not show the reflection pattern. It indicates almost no orientation of fillers in polymer matrix. Even though the Lapo with a low aspect ratio clay is exfoliated in polymer matrix, it is not oriented during extrusion.

Conclusions

PEMA/20A(high aspect ratio clay) and PEMA/Lapo(low aspect ratio clay) nanocomposites show the exfoliated state. PEMA/20A nanocomposite shows higher storage moduli and complex viscosity than PEMA/Lapo and PEMA/SiO_2. It shows the highest melt tension among the composites. It also shows a longer drawability than the others in melt extensional fiber spinning tensile tester. It has the lowest neck-in and shows the orientation of clay layers during melt processing. All these properties of PEMA/20A seems to be caused by the highest aspect ratio clay.

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