Structural, Morphological, and Dynamic Mechanical Properties of Zn-Filled Nylon 11

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ABSTRACT: Nylon 11 samples were filled with metal (Zn) fillers of two different concentrations (1 and 5% w/w) each. The samples in the form of disc were obtained by using hot press molder. The structural properties have been investigated using density measurement and wide angle X-ray diffraction (WAXD) technique. The morphology of pure and Zn-filled samples has been studied using scanning electron microscopy. Glass transition (T_g) temperature was determined using dynamic mechanical thermal analyzer (DMTA). The result shows that there is slight crystal modification due to the addition of metal fillers (Zn), and the crystallinity has improved. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3094–3098, 2007

Key words: nylon 11; metal filler; crystallization; morphology

INTRODUCTION

Many researchers have extensively carried out the structural and morphological studies of semicrystalline polymorph of Nylon 11.

Nylon 11 is known to exist in two crystal forms designated as α and γ.[1] The work of Slichter[1] reveals the existence of triclinic structure in Nylon 11 corresponding to α form, which was also proposed by Bunn and Ganner[2] for Nylon 6. Sasaki[3] reported the existence of γ-form in Nylon 11 from the wide angle X-ray diffraction (WAXD) for solution cast Nylon 11 films. The same structure in which pseudohexagonal lattice of γ form with the randomly distributed hydrogen bond in direction perpendicular to chain axis has been observed by Newman et al.[4] They also reported the relationship of pseudohexagonal lattice to triclinic unit cell of α phase. The temperature-induced phase transition $\alpha \rightleftarrows \gamma$ is general and occurs over a wide temperature interval. Researchers in Japan[5] have reported variety of alicyclic, aromatic, and fluorinated nylons wherein the physical properties are governed by the building blocks in the chains, such as methylene groups. They have further reported that Nylon 11 shows five polymorphs: α, α', δ, δ', and γ, out of these α (form I triclinic), δ (form II monoclinic), and γ (form III pseudohexagonal) have stable crystalline phase, whereas others have a metastable phase.[5,6] A mixture of phases can be obtained by different experimental techniques. The physical properties, such as crystallinity, kinetics of crystallization, moisture absorption, mechanical and dielectric relaxations, etc., are strongly affected by the structure of these materials.[7] It has also been reported that Nylon 11 is a semicrystalline polymer possessing both crystalline and amorphous regions.[7–10]

Literature survey for filled polymers has been carried out and almost all the work is concentrated upon the studies of electrical conductivity of filled polymers.[2–4] Further it was observed that conductivity of filled polymers increases abruptly above a certain concentration of fillers. This is the critical volume fraction (ϕ_c) of high conductivity component, at which the insulator to conductor transition occurs. Since the electrical conductivity of the filled polymer should be less, so that it will have a good dielectric properties, care was taken that volume fraction of added powder do not exceed the ϕ_c, so as to maintain its dielectric nature. Hence, the concentration of the added metal powder was kept low, i.e., 1 and 5% (w/w). Even though only two concentration (1 and 5% (w/w)) are used, they show quite interesting structural changes, which are worth reporting.

In the present work, an attempt has been made to understand the crystal structure of melt-crystallized pure and modified Nylon 11 at room temperature. The modification in pure Nylon 11 has been carried out by the addition of Zn fillers (1 and 5% w/w). The effect on structural and viscoelastic behavior of Nylon 11 after using fillers have been reported.

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EXPERIMENTAL

Materials

Nylon 11 (Sigma Aldrich CHEMIE GmbH, Germany) in the form of beads were used in the preparation of samples. Samples of pure and filled (1 and 5%, w/w) Nylon 11 were prepared in the form of circular discs, using hot press molding of nominal thickness of 1.5 mm. All the samples were stored in the desiccator.

Density measurement

Density of all the samples was measured by Sheldon's Floatation Technique,[11] using high precision electronic Metler Toledo PB153 S balance. For the measurement of density of pure and filled Nylon 11, a mixture of benzene and carbon tetrachloride was used.

Wide angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) is a widely used technique to study the crystallinity of a polymer. Phillips difffractometer with Cu Kα radiation was used in this study. WAXD of pure and filled Nylon 11 were recorded at room temperature with $1°$/min scan over a range of 2θ from $15°$ to $40°$.

From the radial scans of intensity versus 2θ, the lateral order or crystallinity index was determined using Manjunath's formula. According to the method suggested by Manjunath et al.,[12] for any polymer, the resolution of the peak R is given by,

$$R = \frac{m_1 + 2m_2 + \cdots + m_{n-1}}{h_1 + h_2 + \cdots + h_n} \qquad (1)$$

where $m_1, m_2, \ldots$ are the heights of minimum between two peaks, and $h_1, h_2, \ldots$ are the heights of peak from the baseline.

Then $(1 - R)$ gives the lateral order or the index of crystallinity.

Scanning electron microscopy

It is one of the most important techniques used for the investigation of morphology of polymers. During the present work, the morphology was investigated using Leo 435 VP 501B Philips SEM.

The samples to be examined were made conductive by depositing a very thin layer of gold of thickness 800 nm on the surface. Initially, large area of the samples was observed at low magnification and then the selected area was studied at higher magnification.

Dynamic mechanical thermal analysis

The dynamic mechanical thermal analysis (DMTA) studies were conducted by a Rheometric Scientific DMTA apparatus. Experiments were carried out on a dual cantilever arrangement in bending mode in the temperature range from $-10°C$ to $130°C$ at a heating rate of $5°C$/min. Cooling was achieved by pumping liquid nitrogen through the accessories provided in the instrument. Samples were scanned with an imposed frequency of 1 Hz. Plots of tan δ were recorded as a function of temperature. Measurements of all samples were made in identical conditions for a valid and reliable comparison of the results.

RESULTS AND DISCUSSIONS

The values of density are calculated by considering the filled samples to be a physical mixture of Nylon 11 and Zn. This has been confirmed from the FTIR spectra of pure Nylon 11 and Zn-filled samples of Nylon 11. From Table I, the calculated values of density therefore show a proportionate increase in the values of density for 1% Zn and 5% Zn-filled Nylon 11. The experimental values of density, however, show that the density of 1% Zn-filled sample is slightly more than that of pure Nylon 11. The experimental value of density for 1% Zn-filled sample is much less than the expected (calculated) value. This decrease in the experimental value of density is rather surprising because, from WAXD results, it is clear that the crystallinity of this sample has increased. The increase in crystallinity shows that the density of Nylon 11 component of the mixture must have increased. Hence with addition of 1% Zn powder to Nylon 11 should have shown more value of experimental density. The decrease in the experimental value of density for 1% Zn-filled sample must be due to possibility of increase in volume (volume expansion) by filler addition or due to presence of voids. However, the scanning electron micrographs do not show the presence of voids. Hence, the decrease in value of density can be correlated with volume expansion of the polymer crystallites caused due to addition of fillers. For 5% Zn-filled sample, similar clarification can be given.

It was observed that by the addition of metal (Zn) fillers (1 and 5% w/w), the IR spectra does not show much difference as expected, since the metal particles do not form any type of bonding with Nylon 11. Hence, FTIR spectra using filled metal particles have not been depicted.

Figure 1 shows the X-ray scans for the pure Nylon 11 and Zn-filled samples. The X-ray scan of pure Nylon 11 shows three small peaks, two peaks at

TABLE I
Measurements of Density, Order of Crystallinity, and T_g

Samples	Density (g/cc)		Order of crystallinity	Glass transition temperature (T_g, °C)
	Calculated	Experimental		
Nylon 11	1.05	1.051	0.37	73.26
1% Zn	1.059	1.0512	0.52	34.419
5% Zn	1.094	1.063	0.53	58.564

$2\theta = 20°$ and $20.8°$ correspond to α crystal form and the third peak at $2\theta = 21.2°$ corresponds to γ form.

From Figure 1, it has also been observed that by the addition of 1% Zn in Nylon 11, the α peak disappears, while there is an increase in intensity of γ peak at $2\theta = 21.2°$. Another small peak at $2\theta = 21.8°$, corresponding to γ form starts appearing. Thus, the increase in intensity of the γ peak and shifting of peak indicates change of structure from α to γ form.

Similarly, from the Figure 1, it has been observed that by the addition of 5% Zn in Nylon 11 again, only two peaks appear; there is an increase in the intensity of the α peak at $2\theta = 20.8°$, while the γ peak corresponding to $2\theta = 21.2°$ is slightly shifted to larger angle at $2\theta = 21.6°$. Thus, for 5% Zn-filled sample, α and γ form exists. It can be observed that the intensity of the peak increases with increase in concentration of metal (Zn) fillers.

The crystallinity index of the pure and Zn-filled Nylon 11 samples were calculated using Manjunath's formula,[12] and the results are tabulated in Table I. Thus, by the addition of Zn fillers in pure Nylon 11, it is observed that the crystallinity of the filled samples increases as compared with that of the pure Nylon 11. The crystallinity index has been found to increase by the addition of Zn powder, i.e., addition of metal powder pushes the chains of Nylon 11 and arranging them in more ordered form. It is also evident from WAXD that addition of 1% Zn powder transforms the α-crystalline structure of pure Nylon 11 into γ-form. It appears that the added powder must be entering into the crystalline region of Nylon and slightly pushing the chains apart, and thus changing the form of crystalline phase from triclinic α form to hexagonal γ form. The volume expansion of crystallite has also been established from density measurements.

Similarly, the addition of 5% Zn powder does not increases the order of crystallinity much above than that of 1% Zn-filled Nylon 11. But, the crystalline form presumes both phases α and γ as in case of pure Nylon 11.

Thus, the additional powder seems to have again entered into the crystalline part of Nylon 11, and thus pulling the chains partly into α and γ form.

One interesting feature that is observed in case of these samples is that order of crystallinity changes much more when 1% Zn powder is added, but if the percentage of Zn powder in Nylon 11 is increased to 5% then the order of crystallinity remains nearly same as that of 1% Zn added Nylon 11 samples. At 1% Zn content, there is tremendous enhancement of crystallinity as compared with pure Nylon 11. This may be due to catalytic effect of small amount of Zn powder. When Zn content increases, the polar interaction between components restricts the crystalline arrangement, causing a minor increase in the crystallinity.

The surface morphology of Zn-filled samples was investigated and is given in Figure 2. It has been observed that no voids were present in the samples. In melt cast pure Nylon 11, large number of platelet like crystals have been observed.

From Figure 2, it is revealed that, by the addition of filler (both 1 and 5%), the platelet structure becomes more prominent and crystallinity also increases with increase in concentration of Zn fillers.

The measurement of DMTA is used for measuring the glass-transition temperature of the polymers. In the present work, pure and Zn-filled Nylon 11 have been investigated (Fig. 3). A plot of loss maximum tan δ with temperature was used to measure the glass-transition temperature, T_g. From Table I, it can be observed that the glass-transition temperature of Nylon 11 generally reduces after filling Zn particles.
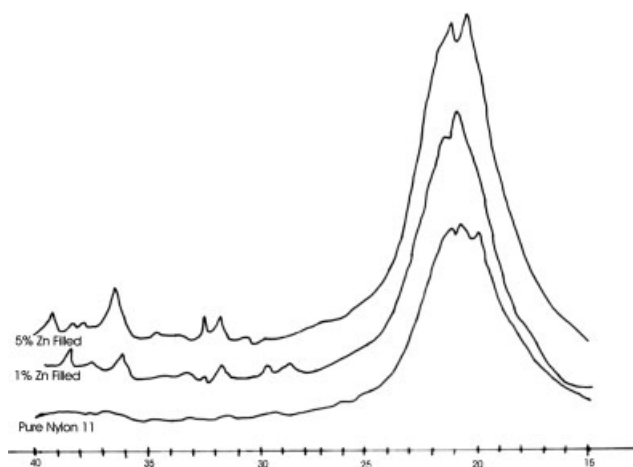

Figure 1 WAXD pattern of pure and Zn-filled Nylon 11.

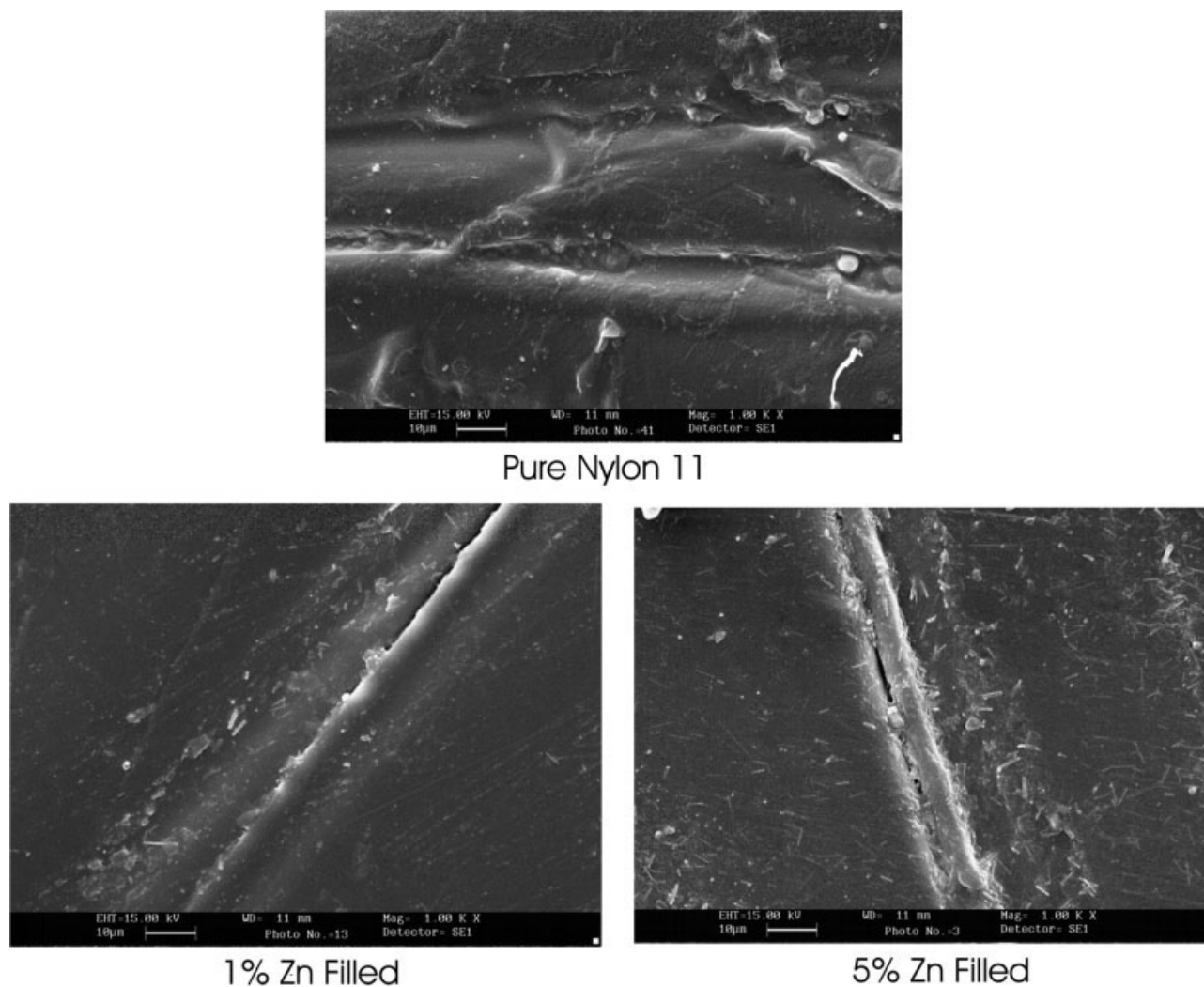Pure Nylon 11

1% Zn Filled

5% Zn Filled

Figure 2 scanning electron micrographs.

The reduction in glass-transition temperature (T_g) has been associated with the plasticization effect of plasticizer.
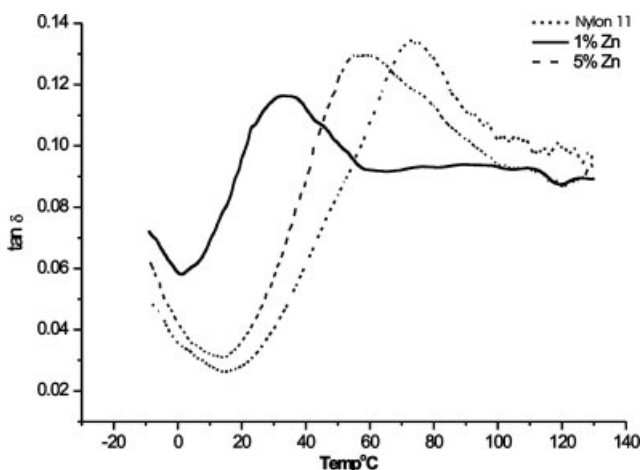

Figure 3 Plot of temperature versus tan δ for pure and Zn-filled Nylon 11.

The plasticization and antiplasticization effect has been studied by many researchers.[13–15]

It is known that, when a polar plasticizer is introduced into a polar polymer, the polar groups of polymer strongly bind with one or two plasticizer molecules. Shielded by the plasticizer molecules, the polar groups of the neighboring polymer chains cannot interact with each other, and also, the number of polar groups on the polymer chains becomes smaller, and hence the polymer passes into the glassy state, i.e., hardens at lower temperature.

True plasticizing action of the plasticizer is the weakening of second-order (van der Waal's) attraction forces between the polymer chains because of the interposition of the plasticizer molecules. The screening of the polar groups takes place up to a certain extent. It is necessary that the plasticizer should form a complex.

In the present work, added Zn powder does not form any complex with Nylon 11 and remains as dispersed particles in Nylon 11 matrix. Chemical bonds

are not formed between the polymer chain and metal particles.

The addition of Zn powder remains a physical mixture in Nylon 11. However, the effect of addition of Zn powder on Nylon 11 is similar to that of plasticizer.

In the present work, in case of 1% Zn-filled Nylon 11, the added Zn particles enter into the crystalline phase of Nylon 11, as is evident from WAXD analysis. WAXD studies (Fig. 1) reveal that the phase transformation from α to γ has taken place. The interposition of Zn particles in between the Nylon 11 chains, therefore, can have the effect of weakening of second-order (van der Waal's) attractive forces between the polymer chains. Hence, the glass transition temperature reduces.

As the concentration of Zn in Nylon 11 is increased to 5%, it is observed from WAXD analysis that this sample contains the presence of both α and γ phase. The crystallinity has also increased slightly as compared to 1% Zn-filled sample. In this case, therefore, one can say that the interposition of Zn particles in-between the Nylon 11 chains must have taken place, so as to form the α phase of Nylon 11, along with the γ phase of Nylon 11. The van der Waal's force between the polymer chains as far as α phase is concerned becomes stronger as compared with that of 1% filled Nylon 11, where only γ phase is present. Thus, with further addition of Zn powder, there is Zn/Zn interaction and reduced Zn/Nylon interaction. Therefore, the glass-transition temperature (T_g) for 5% Zn-filled Nylon 11 is more than that for 1% Zn-filled sample.

CONCLUSIONS

It has been observed that there is a slight crystal modification due to the addition of metal fillers (Zn) in pure Nylon 11, and the crystallinity has improved. Even, when the added Zn powder forms a physical mixture with Nylon 11, still phase transformation from α to γ has taken place, thereby weakening the second-order (van der Waal's) attractive forces between the polymer chains, thereby reducing the glass-transition temperature T_g.

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