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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Mouzakis, Dionysios E. , Kandilioti, Georgia , Elenis, Athanasios and Gregoriou, Vasilis G.(2006) 'Ultraviolet Radiation Induced Cold Chemi-Crystallization in Syndiotactic Polypropylene Clay-Nanocomposites', Journal of Macromolecular Science, Part A, 43: 2, 259 – 267

To link to this Article: DOI: 10.1080/10601320500437110

URL: <http://dx.doi.org/10.1080/10601320500437110>

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Ultraviolet Radiation Induced Cold Chemi-Crystallization in Syndiotactic Polypropylene Clay-Nanocomposites

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The effect of ultraviolet radiation on syndiotactic polypropylene (s-PP) and its nanocomposites with montmorillonite was studied by means of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Nanocomposite materials were manufactured by melt mixing of an organically modified montmorillonite (Cloisite[®]20A) with s-PP matrix. Several compositions of s-PP and montmorillonite were exposed to UV-C radiation (254 nm). The effect of chemi- or radiation-induced cold crystallization was confirmed for these nanocomposites by means of both DSC and DMA. Also, shifts in the glass transition temperature were discovered for the different compositions of clay. Finally, Fourier transform infrared spectroscopy (FT-IR) helped to identify and confirm the changes in the molecular structure of the irradiated s-PP matrix, providing confirmation of the cold chemi-crystallization effect.

Keywords chemi-crystallization, cold crystallization, nanocomposites, nanoclay, syndiotactic poly(propylene)

Introduction

The exposure to ultraviolet-radiation (UV) in many semi-crystalline polymers provokes a series of phenomena which result in the polymer molecular alteration, such as backbone chain scission, formation of radicals and functional groups like carbonyl (–C=O), aldehyde (–CHO) etc. These molecular alterations usually result in the change of the material mechanical properties (1, 2). Another interesting phenomenon reported in recent years is the raise in the material inherent crystallinity as measured after the exposure. A possible explanation for this is the formation of new more flexible chain segments after the main chain scission of the amorphous material areas by the

Received May 2005; Accepted June 2005.

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UV-radiation. These small but highly flexible segments tend to rearrange themselves into higher order formations, resulting in a phenomenon reported as chemi-crystallization (3, 4).

Since the introduction of metallocene catalysis in 1988 (5), the initially synthesized by Ziegler-Natta catalysis in 1960 (6) syndiotactic polypropylene is nowadays commercially available at high stereoregularities (>90%). Both the morphology (7) and crystallization kinetics (8–11) of syndiotactic polypropylene have been extensively studied in the past. It has been shown that the melting behavior in DSC experiments depends on the crystallization history, since a double melt endotherm is typical for this material (9–11) if a lower order crystalline form is allowed to form (12). In the open literature, four different crystal forms have been reported so far (13, 14). Forms I and II are characterized by chains in the helical, $(T_2G_2)_n$ conformation, whereas III and IV have their chains in trans-planar and $(T_6G_2T_2G_2)_n$ conformations, respectively. Also, the mechanical properties of this type of polypropylene have been examined by researchers, showing that they are dependent on the material crystallinity (15, 16).

Layered silicates such as montmorillonite, have been promisingly investigated as property enhancers for several polymers (17) and several studies have appeared correlating the structure and orientation of the nanosilicate fillers with the mechanical properties of nanocomposites based on both isotactic (18) and syndiotactic (19) polypropylene matrices.

Our aim in this work was to study the impact of UV-radiation on layered silicate nanocomposites based on syndiotactic polypropylene. The mechanical and thermal response in correlation to the molecular structure of these nanocomposites have already been reported in a recent work of our group (20).

Experimental

Syndiotactic polypropylene (s-PP) of high purity (MW = 130,000 g/mol, tacticity 68%) was used in the present study. Nanocomposite films were manufactured by melt mixing of an organically modified montmorillonite (Cloisite[®]20A) with the polymer matrix and subsequent hot pressing. s-PP and the dried nanoclay were mechanically mixed for 3 min prior to a 3 min melting phase at 170°C. The final melt mixing took 3 more minutes. Afterwards, the mixture was hot-pressed at 170°C with pressure of 20 bar for ca. 10 min and finally was quenched at 0°C. Thin films (200 μm) of s-PP nanocomposites with several compositions of montmorillonite, 0, 1, 3, 7, and 10 wt% were produced in this way.

Both the pure s-PP and s-PP based nanocomposites were exposed to radiation in a self-devised chamber. Six UV-C Argon lamps of 6 watts each emitting at $\lambda = 254$ nm were installed in the chamber to provide the needed radiation. A built-in electric fan provided cooling and enough O₂ flow by constantly circulating the air inside the chamber in order to ensure photo-oxidation conditions. The specimens were exposed to UV-C radiation at 1 h intermittent intervals (1 h UV-on/1 h UV-off) for a total exposure time of 246 h.

A DMA Q800 of TA Instruments was used to obtain the dynamic mechanical spectra of the pristine and UV-aged s-PP based nanocomposites. Specimens were subjected to sinusoidal tensile stress at a wide range of frequencies from 0 to 30 Hz. In this way, the differences in material viscoelastic response due to UV-ageing were determined.

A DSC Q100 instrument (TA Instruments) was employed to study the thermal behavior of the pristine and UV-aged s-PP based nanocomposites. These types of

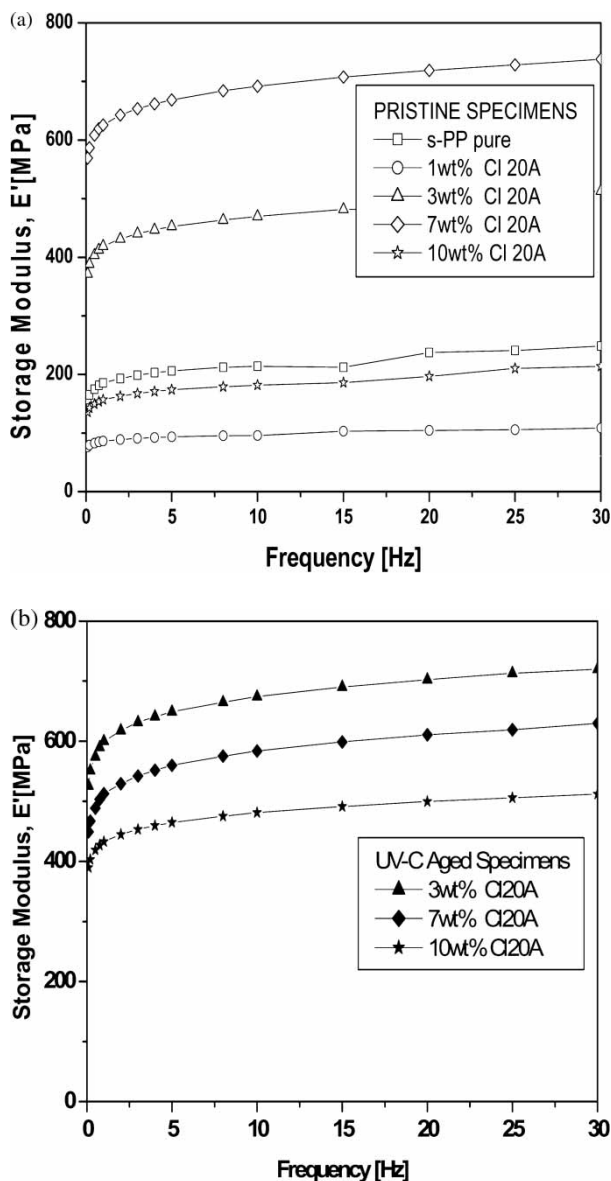


Figure 1. DMA spectra (E' vs. f) of (a) the pristine, and (b) the UV-aged layered silicate s-PP nanocomposites.

measurements are extremely useful to determine the variations in specimen, specific heat enthalpy and therefore, crystallinity prior and after exposure to UV radiation. In addition, possible shifts in the material glass transition temperature are followed. Thermal scans were performed from -30 to $+170^\circ\text{C}$ at a heat-cool rate of $10^\circ\text{C}/\text{min}$. The heat of fusion for the 100% crystalline material is $\Delta H_f^0 = 190.4 \text{ J/g}$ (21).

Finally, Fourier transform infrared spectroscopic studies were performed with a Nicolet 850 FT-IR spectrometer equipped with an MCT/A detector. 128 scans were accumulated for each spectrum, at 2 cm^{-1} spectral resolution.

Table 1
E' @ 20 Hz for the as-molded and UV-aged nanocomposites

| | %wt in clay | | | | |
|----------|-------------|------|-----|-----|-----|
| | 0 | 1 | 3 | 7 | 10 |
| Pristine | 237 | 105 | 482 | 719 | 197 |
| UV-aged | n.a. | n.a. | 702 | 611 | 499 |

Results and Discussion

Typical DMA spectra of the dynamic storage modulus (E') plotted against frequency are shown in Figure 1(a) for the as-molded specimens. This specific viscoelastic parameter reflects the material stiffness under dynamic loading conditions. It can be easily deduced that the optimum stiffness for these composites is obtained at 3 and 7 wt%, whereas for all the other, compositions fall below the pure s-PP data at all frequencies. DMA tests were also run for the UV-aged specimens, Figure 1(b); however films of 0 and 1 wt% clay were not possible to be measured since UV-ageing resulted in their extreme embrittlement.

Only the samples with 3, 7, and 10 wt% of clay survived UV-ageing as shown in Figure 1(b) by the related DMA graphs. Table 1 above presents all storage moduli @ 20 Hz. Two main observations can be made. First, a material stiffening effect can be confirmed for the samples that survived the irradiation treatment, except for the sample with 7 wt% of clay. Certainly, the effect of UV-radiation is great with respect to material viscoelastic response for both 3 wt% and 10 wt% samples. It is expected that this will reflect changes in the material microstructure.

Results obtained from the DSC scans confirmed the findings of the differentiating material response due to UV-radiation. Table 2 shows the glass transition temperatures and the shifts that were observed after the UV-C ageing of the s-PP nanocomposites. Although the neat s-PP matrix does not appear to be much affected by the irradiation (small rise in the T_g), the T_g 's of the nanocomposites shift to lower temperatures. This effect shows the impact of the UV-C radiation to these samples as it probably inflicts chain scission and creation of smaller flexible radicals, which mobilize at lower temperatures. The shift lies at a range of 3°C for most nanocomposites as seen in Table 2 below. The least sensitive nanocomposite with respect to T_g reduction, is the 7 wt% in clay. It is

Table 2
Glass transition temperatures for the as-molded and the UV-aged nanocomposites

| | %wt in clay | | | | |
|---------------------|-------------|-------|-------|-------|-------|
| | 0 | 1 | 3 | 7 | 10 |
| Pristine T_g (°C) | -5.43 | -2.67 | -3.00 | -3.51 | -3.42 |
| UV-aged T_g (°C) | -4.74 | -5.82 | -5.72 | -5.24 | -6.71 |
| Shift (°C) | +0.7 | -3.1 | -2.7 | -1.7 | -3.3 |

expected that these shifts in the glass transition temperature will reflect in the other properties as well. It should be reminded here that the 7 wt% in clay nanocomposites showed only a small reduction in the storage moduli after ageing as seen both in Table 1 and Figure 1, so the impact of UV-radiation does not appear to be great for this material.

Figure 2(a) and (b) presents the DSC scans of the as-molded and the UV-aged specimens. A secondary relaxation endotherm at ca. 50–55°C is observed for both the aged and pristine specimens indicating that a softer phase of the matrix material is present. This endotherm has been also reported in previous work (22) and was attributed to the partial melting of the s-PP trans-planar mesophase.

No large variation in the material crystallinity was found between the as-molded specimens respective to the content of clay as depicted in the large melt-endotherms @

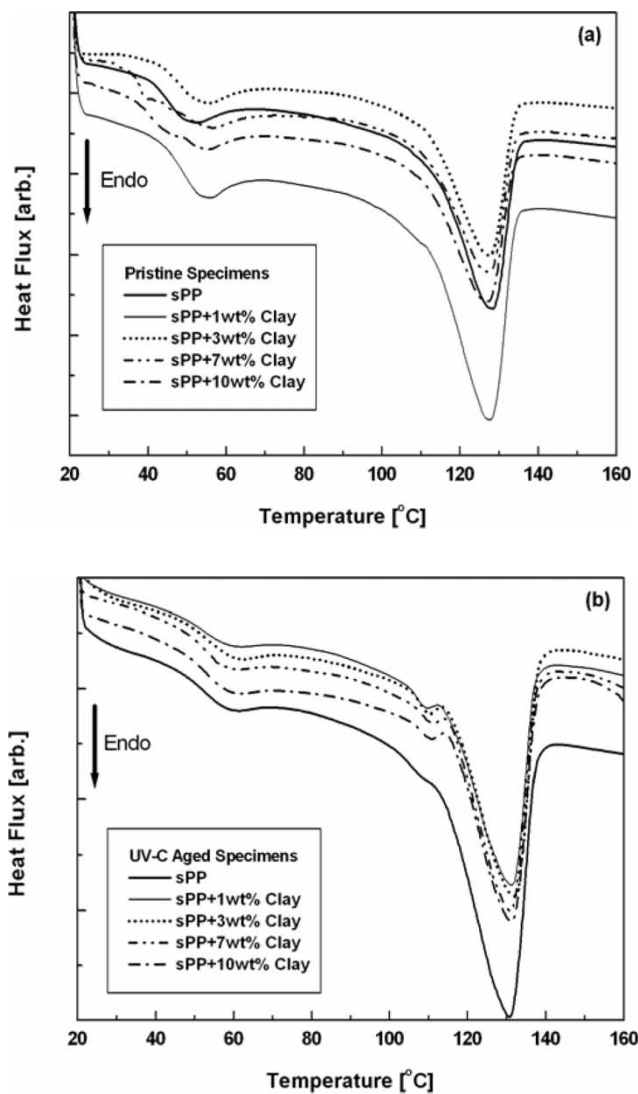


Figure 2. Typical DSC graphs $\Delta H(T)$, of (a) the pristine, and (b) the UV-aged, layered silicate s-PP nanocomposites.

ca 125°C. However, interesting variations in the material thermal behavior were discovered after the UV-ageing procedure. A small endotherm is seen for all the nanocomposites and the neat s-PP prior to the main melt-endotherm. This small lump can be attributed to the melting of the disordered form I (12), which is formed upon exposure to UV-radiation.

Table 3 depicts the overall % crystallinity grades for all nanocomposites, prior and after ageing, as calculated by the specific heat of fusion from the DSC curves. Also, the increase in crystallinity is calculated by these data. Clearly, an increase in the material crystallinity appears for all compositions after the ageing procedure. It is noteworthy to mention here that the 7 wt% shows very little differentiation. These findings are in agreement with the results presented in Table 2 for the T_g shift for this nanocomposites. On the other hand, pure s-PP matrix shows a large increase in relative crystallinity, whereas its T_g was not much affected by the UV-irradiation. Consequently, the stiffening effects observed by DMA should be related to the rise in crystallinity. This phenomenon is more profound for the 3 wt% and 10 wt% specimens which have shown a significant increase of the storage moduli after the UV-radiation.

Considering the fact that room temperature conditions were ensured in the UV-chamber during the specimen ageing, the crystallinity enhancement cannot be related to any thermal effect. Therefore, the “cold” achievement of a higher order of the s-PP matrix originating from the UV-radiation should be related to this phenomenon. Indeed, in the literature, a similar effect is reported for isotactic polypropylene (3, 4). It seems that the UV-radiation causes scission of the backbone chain and/or formation of radicals. The smaller amorphous chain segments tend to rearrange themselves into higher ordered chains resulting in a phenomenal higher material crystallinity. This effect referred to as “cold- or chemi-crystallization” (3, 4) has been lately reported for pure UV-irradiated s-PP too (23).

As far as the amount of reinforcement with respect to nanofiller content is concerned, there are some major conclusions to be drawn here: DMA testing has shown that only some compositions survived the UV-irradiation procedure. Since it was shown that the sPP matrix did not survive for mechanical loading the nanocomposites should show a superior behavior. Indeed, some of the compositions like the 3 and 10 wt% survived but became stiffer. The 7 wt% specimen showed that it remained largely unaffected (crystallinity and T_g) except for the small deterioration in E-moduli. So, this might be the optimum composition with respect to UV resistance in terms of retaining the original properties.

Figures 3 and 4 present the FT-IR spectra of the pristine and irradiated neat s-PP and its nanocomposite with 1 wt% nanoclay, respectively. It can be noticed that the molecular structure is influenced by the UV-radiation, since the peak at 811 cm^{-1} , which corresponds

Table 3
Crystallinity (%) variations for the as-molded and UV-aged nanocomposites

| | %wt in clay | | | | |
|-----------------|-------------|-------|-------|-------|-------|
| | 0 | 1 | 3 | 7 | 10 |
| Pristine | 19.01 | 18.63 | 17.15 | 18.26 | 18.60 |
| UV-aged | 26.59 | 23.51 | 23.83 | 20.66 | 21.29 |
| Increase in Cr% | 7.6 | 4.9 | 6.7 | 1.4 | 2.7 |

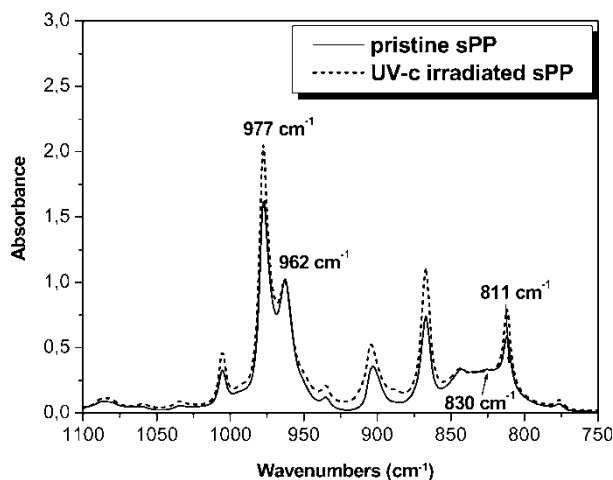


Figure 3. FT-IR spectra of the pristine and UV-C aged s-PP samples.

to the helical form I of s-PP increases in both samples, and also in all the rest compositions of clay (not shown here). In contrast, the peak at 830 cm^{-1} , which is related to the trans-planar conformation decreases upon irradiation. This implies that the UV-radiation procedure induces chain scission of the segments characterized by trans-planar conformation, which are reorganized in new small chains preferentially in the helical form. The same effect is observed for a second pair of bands at 977 cm^{-1} (form I) and 962 cm^{-1} (form III). After irradiation, the absorbance of the band at 977 cm^{-1} is enhanced, which again implies an increase of the content of the chains in the helical form. On the other hand, the band typical of the trans-planar conformation (962 cm^{-1}) decreases.

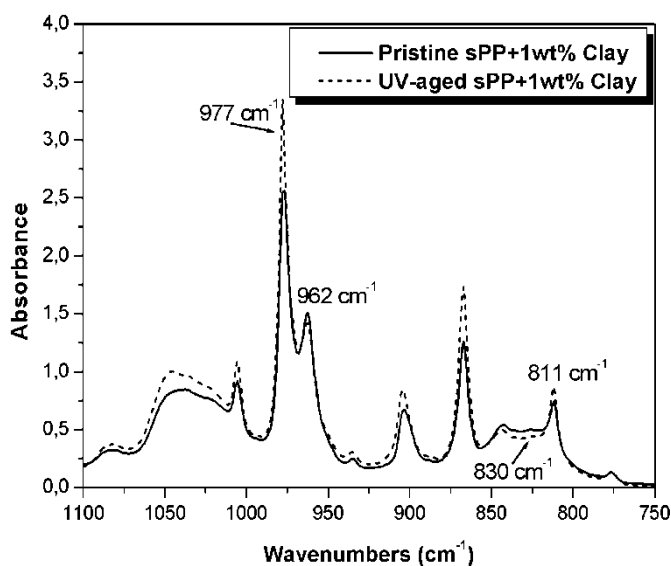


Figure 4. FT-IR spectra of the pristine and UV-C aged s-PP samples with 1 wt% clay.

Summarizing, the impact of the UV-C radiation on the phase conformation of s-PP and its nanocomposites appears to enhance the content of chains in the helical form with simultaneous reduction of the chains exhibiting trans-planar conformation. This is a direct confirmation of our findings from the DSC scans as presented in Table 3. The phenomenon of the increase of the overall material crystallinity is not thermally activated and is due to the rearrangement in the helical conformation of the shorter s-PP segments resulting from chain scission. It can be termed therefore, as a “cold”, “chemi”- crystallization procedure as seen in other works as well on i-PP and s-PP (3, 4, 23).

Conclusions

The effect of UV-C irradiation was studied for syndiotactic polypropylene based nanocomposites with an organically modified montmorillonite. Dynamic mechanical analysis showed a stiffening effect due to the impact of UV radiation on the s-PP matrix for the samples with 3 and 10% wt clay. Differential scanning calorimetry scans showed a rise in the material crystallinity as a result of the UV-C radiation. This effect was attributed to the formation of small, mobile chain segments produced by scission due to UV-radiation. This phenomenon was confirmed by means of FT-IR spectroscopy. It was found that in all nanocomposites, the helical form of s-PP was increased upon the irradiation of the specimens, while the amount of segments characterized by trans-planar conformation were decreased. The increase in crystallinity termed to as: “chemi crystallization” in the literature, can also be called a “cold chemi-crystallization” since it is being activated at room temperatures under the influence of UV-radiation on this polymer.

Acknowledgements

We are grateful to the Greek Ministry of Development for support via the research grants Program PENED 2001 (PENED136) and EPAN E13.

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