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Polymer mica: layered polymer with nanometer sized interlayer gaps

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The unique stacked-layers structure of naturally occurring mineral mica [1] is largely responsible for its good thermal and electrical properties. We have been able to create a corresponding structure in polymers with similar results. Layered polymers with nanometer sized interlayer gaps filled with gas have been produced such that the energy transfer between the polymer layers has to occur through the intervening gas layer, thereby giving this morphology superior insulation properties. The insulation efficiency of layered polymers is much higher than that of polymer foams whose properties are density dependent [2, 3]. The layered structure is achieved by first making a template containing regions of weak chain-entanglements and then severing these entanglements by gas nucleation and expansion [4]. A typical morphology consists of stacked polymer layers, around 10 μm thick, and the interlayer gaps, about a few nanometer thick. It is similar in appearance to mica, but can be produced in a controlled way. Here we present the technique for producing the multilayered polymer, and the unique properties associated with such structures.

The polymer was produced by compression molding 40 μm polystyrene beads from Scott (C-35) at 200 °C into 0.74 mm thick sheet, exposing the sheet to CO₂ at 60 atm and 24 °C for 24 h, and then heating it to 35 °C under ambient pressure. The resulting sample was fractured at liquid nitrogen temperature and room temperature, respectively, prior to the morphology study with SEM (Jeol, JSM-5300). The interlayer gaps were analyzed using small angle X-ray diffraction (SAXD, Rigaku diffractometer), and the optical measurement was done with Perkin-Elmer UV/VIS/IR spectrometer Lambda 19 at a scanning rate of 120 nm/min. No correction was made for the surface light scattering.

Fig. 1 is a schematic summarizing the method used in producing multilayered polymer with nano-interlayer gaps. Polymer beads or stacked polymer thin films are compression molded at a suitable temperature for a certain holding time into transparent sheets. The polymer sheets are then exposed to CO₂ under certain pressure until a thermodynamic equilibrium is reached, followed by a quick pressure release. Any alternative gas can be used in place of CO₂ if it can achieve a solubility above 4 wt% in the polymer. The polymer saturated with CO₂ or an alternative gas is then heated to a temperature below the glass transition temperature

(T_g) of the polymer-gas system for a certain period to produce multilayered polymers. The weak entanglements are introduced into the polymer during the compression molding step by controlling inter-diffusion of the macromolecular chains with appropriate selection of processing temperature and time. These weak entanglements are periodically distributed throughout the polymer at the interfaces between the films or the beads. On exposure to compressed gas, the T_g of the polymer is depressed [5, 6], the extent of depression depends on the polymer-gas system, and gas pressure and temperature used. When the gas-saturated polymer is heated to a temperature below the T_g of the polymer-gas system, the gas is driven out from the polymer matrix to nucleate and expand in the regions where chain entanglements are weak. Such entanglements cannot hold the gas pressure and, therefore, the chains in these regions are pushed apart by the expanding gas, resulting in the layered morphology. Layered morphologies with various geometries can be produced by using appropriately designed compression molds or by deforming

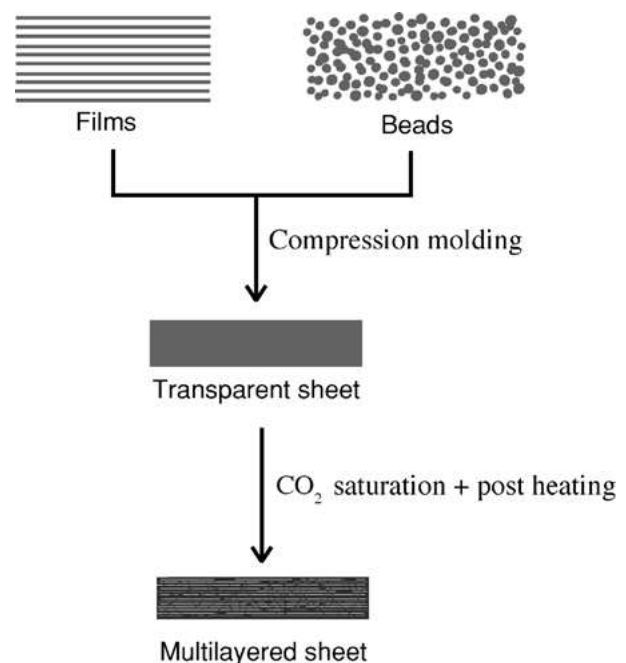


Figure 1 A schematic of the process used in producing multilayered polymer.

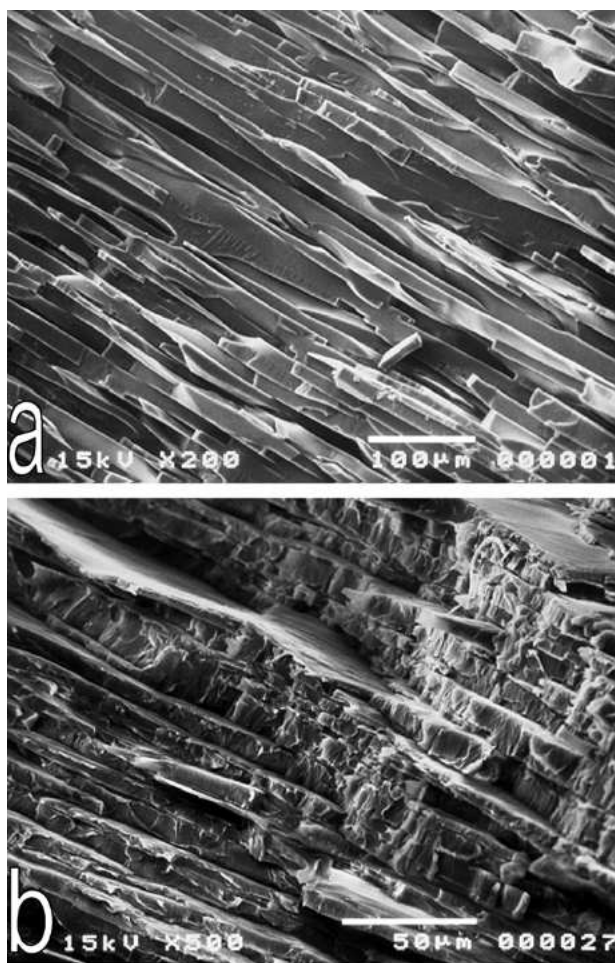


Figure 2 SEM photograph of multilayered polystyrene: Sample was fractured at (a) liquid nitrogen temperature (b) room temperature.

the compression-molded sheets prior to their exposure to gas. Furthermore, the layered polymers can be produced in various sizes whereas such a flexibility in shape and size does not exist in the naturally occurring mica.

Fig. 2 shows the SEM cross views of the multilayered polystyrene produced from a sheet molded from polystyrene beads. The fractured surface in Fig. 2a was prepared after the sample was frozen in liquid nitrogen while that in Fig. 2b was prepared at room temperature. A stacked-layer structure with layer thickness around $10\ \mu\text{m}$ can be clearly seen. A similar morphology can be achieved from the sheet molded from stacked films. The thickness of the polymer layer in the multilayered morphology depends on whether the starting material is beads or films. The smaller the beads or the thinner the original films, the thinner the layers in the multilayered polymer. In addition, processing conditions, such as temperature and mold pressure, affect the layer thickness; higher temperatures and higher pressures lead to thinner layers. It was found that most thermoplastics can be processed to give multilayered structure. We term this multilayered morphology with intervening gaps as *polymer mica* because of their stacked layer structure and silvery opaque appearance.

A detailed SEM analysis of the surface of the polymer layer in the multilayered polymer showed that the weak chain-entanglement distribution in the molded polymer

is planar and that the breakage of the entanglements follows a brittle fracture mechanism. Meanwhile, it should be noted that the nano-interlayer gaps are discontinuous because there are dense, interconnections in-between the adjacent layers that keep the material intact, Fig. 2. In addition, an intact skin layer, which is thicker than the internal stacked layers, is formed around the multilayered polymer. This skin layer is caused by the rapid desorption of gas from the surface when gas pressure is released and the sample is transferred into heating bath, and its thickness can be controlled by simply changing the time allowed for gas desorption. The multilayered polymer is much stronger than polymer foams. For instance, in the layer direction, multilayered polystyrene keeps 100% of the tensile modulus and 80% of the tensile strength of the compression molded polystyrene. It was also found that multilayered polymer has higher layer peeling resistance than mica does, indicating that the strength provided by the physical links in the multilayered polymer is more than that provided by electric charge-based interlayer interactions in mica [1].

The layers in the multilayered polymer are separated by some very narrow gaps filled with gas and the polymer has a silvery opaque appearance under visible light as mica does. The interlayer gaps were analyzed using small angle X-ray diffraction. The average gap size in the multilayered polystyrene, as shown in Fig. 2, for instance, was measured as 5.4 nm thick. Consequently, the polymer is called multilayered polymer with nano-interlayer gaps.

Layered polymers have unique insulation properties in the direction vertical to the layers. As reported previously [4], both the thermal conductivity and dielectric constant of the layered polystyrene with a density of $0.914\ \text{g}/\text{cm}^3$ are much lower than those of neat polystyrene with a density of $1.05\ \text{g}/\text{cm}^3$. The insulation efficiency of layered polystyrene is three times that of closed cell polystyrene foam with a density of $0.025\ \text{g}/\text{cm}^3$. Therefore, a layered polymer can become a good insulator with a small sacrifice in material density, in contrast to foams which do so only at much lower density whereby the loss in mechanical and electrical properties, and dimensional stability becomes considerably higher. Another interesting property of a layered polymer is that its morphology, and thus its properties, are reversible. The stacked layer structure reverts to the dense state without any gaps after the polymer is heated to a temperature above its T_g . Fig. 3 shows the light transmission through a layered polystyrene at two wavelengths after it was annealed at various temperatures for 15 min. The polymer which was initially opaque became transparent at annealing temperatures above its T_g of $105\ ^\circ\text{C}$, and the light transmission achieved by annealing above T_g reached the same level as that of molded sheet without the interlayer gaps. It was found that the interlayer gap size decreased as the annealing temperature approached the T_g . For instance, the gap size was reduced from 5.4 nm to 3.6 nm after the polymer was annealed at $75\ ^\circ\text{C}$ for 15 min, and the decrease in gap size increased as the annealing temperature was raised. The gaps disappeared completely when the annealing temperature was at or above

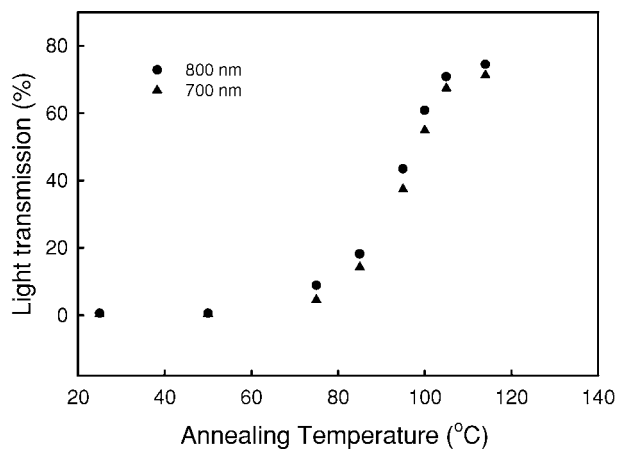


Figure 3 Light transmission through layered polystyrene at different wavelengths as a function of annealing temperature: Layered polystyrene sheet produced was annealed at various temperatures for 15 min prior to the optical measurement.

the T_g because the polymer chains reestablished the regular degree of entanglements between the adjacent layers due to the translational mobility gained at the higher temperatures. However, if the process in Fig. 1 is repeated, interlayer gaps can again be introduced into the annealed polystyrene. Natural mica does not have such characteristics.

The mechanism leading to production of layered morphology also offers an opportunity to detect regions

of weak chain-entanglements in a polymer. Though chain entanglements are mainly responsible for the materials aspects of polymers, there does not exist any method which can be used to locate the weak chain-entanglements. Based on the method described above, compressed gas can be used as a probe to identify regions of weak chain-entanglements.

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