

Preparation and Characterization of Injection-Homo-Polypropylene Filled with Nano-CaCO₃

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ABSTRACT: Nano-CaCO₃/homo-PP composites were prepared by melt-blending using twin-screw extruder. The results show that not only the impact property but also the bending modulus of the system have been evidently increased by adding nano-CaCO₃. The nano-CaCO₃ particles have been dispersed in the matrix in the nanometer scale which was investigated by means of transmission electron microscopy (TEM). The toughening mechanism of nano-CaCO₃, investigated by means of dynamical mechanical thermal analysis (DMTA) and scanning electron microscopy

(SEM), lies on that the nano-CaCO₃ particles take an action of initiating and terminating crazing (silver streak), which can absorb more impact energy than the neat PP. At the same time, the nano-CaCO₃ particles, as the nuclear, decrease the crystal size of PP, the results of which were investigated by means of polarized optical microscope (POM). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 911–916, 2010

Key words: polypropylene; dynamical mechanical thermal analysis; CaCO₃; nanocomposites

INTRODUCTION

Traditionally, inorganic particles (such as talc, calcium carbonate, clay, mica, etc) filled in polymer as fillers are primarily one purpose of cost reduction, which can also improve the hardness, Young's modulus and the thermal properties of polymer composites.^{1–3} In recent years, the nano-inorganic particles such as nano-CaCO₃,^{4–7} nano-clay,^{8–10} nano-SiO₂,¹¹ and nano-TiO₂,¹² and so on, have been developed. It is found that nano-sized inorganic particles especially nano-CaCO₃, have much more excellent properties than traditional micron-sized ones.

Homo-polypropylene (Homo-PP), a semi-crystalline polymer, is one of the most general-purpose plastic and widely used to make civil engineering clothes, packing, architectural materials, and other industrial applications, because of the high strength or density ratio. However, homo-PP is notch sensitive, brittle and large shrinkage. Blending PP with elastomer (such as ethylene-propylene rubber (EPR),¹³ Ethylene-propylene-diene terpolymers (EPDM),¹⁴ and ethylene-1-octylene copolymer

(POE)¹⁵) is an efficient and successful way to increase its toughness, but one drawback of this way is the significant loss of both tensile strength and stiffness of the composite. Incorporation of rigid nano-inorganic particles is a promising approach to improve both stiffness and toughness and decrease the shrinkage ratio of the composites simultaneously, the studies on the modification of PP by nano-inorganic particles are needed.

In this study, the mechanical and thermal properties of nano-CaCO₃/PP composites are investigated. The dynamical mechanical property of the neat PP and the nanocomposites is compared. The dispersion of nano-CaCO₃ is investigated by means of TEM and the fracture toughness of the nanocomposites is tested by SEM. The toughening mechanisms involved during the fracture of the nanocomposites are proposed.

EXPERIMENTAL

Materials

Homo-PP (71735), melting index of which is 35 g/10 min at 230°C and loading 2.160 kg, was supplied as pellets by Liaoyang Petrochemical Company, China.

The nano-sized precipitated CaCO₃ (cubic shape with an average primary particle size of 70 nm;

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TABLE I
Compositions of PP and Masterbatch

Sample	PP (wt. PHR)	Masterbatch (wt. PHR)
1	100	0
2	98	4
3	96	8
4	92	16
5	90	20
6	88	24

prepared by our research center) was coated with stearic acid to increase the compatibility with the polymer matrix and was designed to be a reinforcing additive to improve the properties of plastic materials.

The preparation of nano-CaCO₃ dispersed in homo-PP

To get a good dispersibility of nano-CaCO₃, the masterbatch was first prepared, which was obtained by melt-blending homo-PP with nano-CaCO₃ (mixing weight: PP : nano-CaCO₃ = 1 : 1) using a twin-screw extruder (PE-20, Keya Company, Nanjing, JiangShu, China). The temperatures of the extruder were ordinal 120°C, 165°C, 185°C, and 180°C.

The preparation of PP nanocomposites

The pellets of nano-CaCO₃/PP composites were prepared by melt-blending using the twin-screw extruder. Table I shows the mixing weight ratio of PP and masterbatch. The injection molding machine (JN88-E, Chen Hsong Machinery Co., China) was used for preparing the samples for mechanical and other tests, the operating temperatures of which were ordinal 145°C, 185°C, and 185°C.

Mechanical properties of the nanocomposites

The impact strength of nanocomposites was measured by Charpy pendulum impact testing machines (XJJ-5, ChengDe JinJian Testing Machine Company, HeBei, China.) at room temperature. The flexural (testing speed: 10 mm/min) properties was recorded by Instron universal testing machine (Instron 1185, Instron Company, England) at room temperature.

Dynamical mechanical thermal analysis of the composite

The dynamical mechanical thermal properties of composites were investigated by dynamical mechanical thermal analyzer (DMTA, Rheometric Scientific Inc., USA). The samples were tested in single cantilever bending mode under nitrogen from -100 to

150°C at the rate of 5.00°C/min. The frequency of bending was 6.28 rad/s 1 Hz.

Microstructure microscopy observation of the fracture section of the composites

The microstructure microscopy observation of the fracture section of neat PP and composites were evaluated by scanning electron microscopy (SEM). The surfaces prepared by impact testing machine were platinum/palladium sputter coated. SEM images are obtained by (Cambridge- S250MK3, England).

Crystallinity of the matrix

The samples were analyzed by the polarized optical microscope (POM) using a SM-LUX-POL (Leitz Company, West Germany). The samples were melted at 170°C, then hold for 5 min at 120°C in the stove. The specimen was subsequently cooled down to the room temperature.

Evaluation of dispersibility of the nano-CaCO₃ in PP matrix

The dispersion of the nano-CaCO₃ was evaluated by transmission electron microscopy (TEM, TEM images are obtained by Hitachi H-800 (Japan) with the acceleration voltage of 200 kV). TEM specimens were cut at -90°C using an ultra microtome (LKB-5, Switzerland) with a diamond knife.

RESULTS AND DISCUSSION

Mechanical properties of nano-CaCO₃/homo-PP composites

Figure 1 is the impact strength curve of nanocomposites changed by the addition of nano-CaCO₃. It

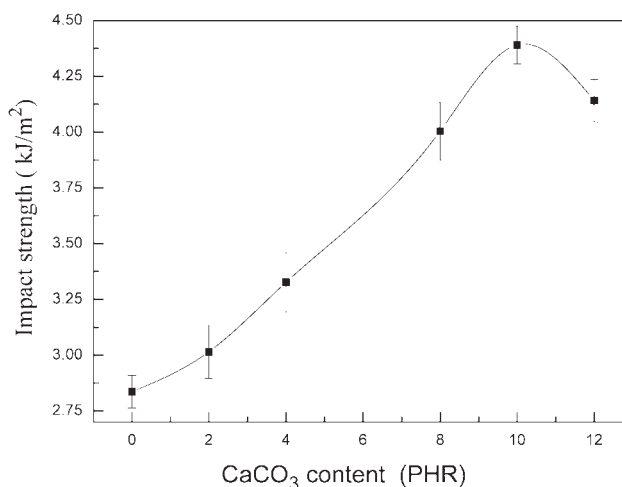


Figure 1 The impact strength of neat PP and composites.

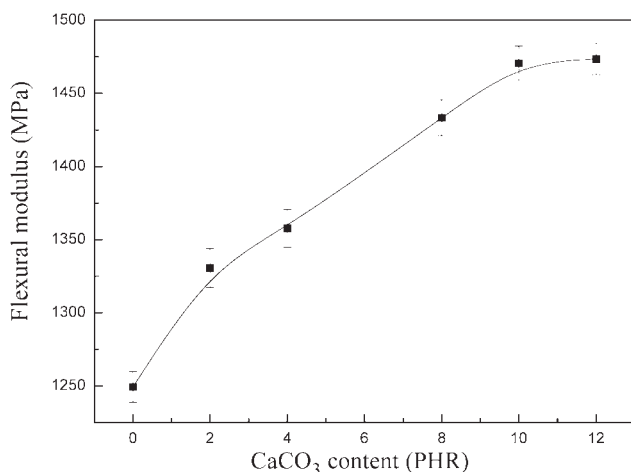


Figure 2 The flexural modulus of neat PP and composites.

shows that when nano-CaCO₃ particles were added from 0 to 10 PHR (Percent Hundred Resin), the impact properties of nanocomposites have an assurgent trend and when nano-CaCO₃ was added form 10 to 12 PHR, the impact properties of nanocomposites have a descending trend. Even though, the impact strength of nanocomposite filled with 12 PHR nano-CaCO₃ particles is higher than that of neat PP. The addition of 10 PHR nano-CaCO₃ particles eventuates the impact strength of nanocomposite get the maximum, which is about 1.55 times than that of neat PP.

Figure 2 is the bending modulus curve of the nanocomposites changed by the addition of nano-CaCO₃. It shows that with the addition of nano-CaCO₃, the bending modulus has evidently increased. The bending modulus of neat PP is 1249.3 MPa. When nano-CaCO₃ was added 10 PHR, the bending modulus of nanocomposite reaches 1470.5 MPa, which is 1.18 times than that of neat PP.

Ordinarily, the bending modulus of composites toughed by elastomers will unavoidably decrease because of the low modulus of elastomer. By contraries, using the nano-particles toughed the matrix can increase the toughness and stiffness evidently at the same time. This is the peculiarity and advantages of the nano-particles. The reason is that nanoparticles change the microstructure of polypropylene composites. In this article, the several analyses were used to discuss the mechanism.

Dynamical mechanical thermal analysis of the composites

The polymer and their polymer composite are typical viscous-elastic materials and it is very important to test the dynamical mechanical properties of them. The difference of the phase structure between the

neat PP and the nanocomposite phase structure is also determined synchronously.¹⁶

Figure 3 is the temperature dependency curve of the tan δ at 1 Hz of the neat PP and the composites filled with 10 PHR nano-CaCO₃ particles. The toughness of the materials can be characterized by the glass transition temperature (*T_g*).

In Figure 3, there are two peaks in every curve, which is corresponding to α transformation and β transformation. The neat PP is a semi-crystal polymer and α crystal belonged monoclinic crystal system, so α transformation is the point that segmer in the crystalline region can mobile and β transformation is *T_g* that segmer in the amorphous region can mobile.

From Figure 3(b), it is clear that the *T_g* of neat PP (22.236°C) is higher than that of nanocomposite (18.315°C) and the *T_α* of neat PP (78.918°C) is lower than that of nanocomposite (82.579°C). The results show that in the amorphous region, the segmer of the macromolecule chain of nanocomposite can move in the lower temperature than that of neat PP,

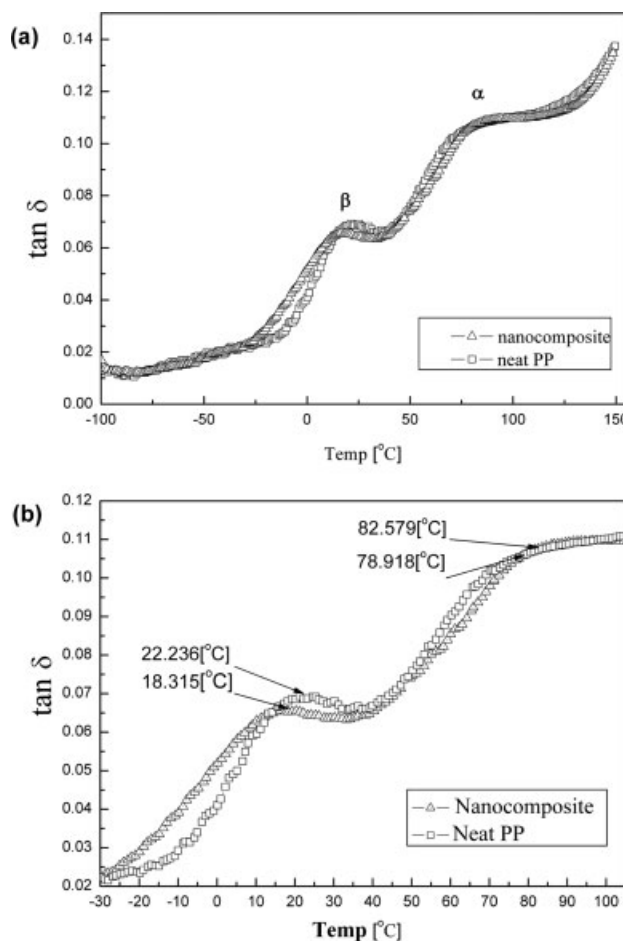


Figure 3 The temperature dependency of the tan δ at 1 Hz of neat PP and the composites filled with 10 PHR nano-CaCO₃.

because the amorphous region dimension of nanocomposite is bigger than that of neat PP, which was approved by POM images. However, in the crystalline region, the nano- CaCO_3 particles, as the heteronuclei, have increased the crystallizing point of the crystalline region of polymer, which have immobilized the segment of the macromolecule chain; consequently, the T_α of neat PP is higher than that of nanocomposite. As a result, the addition of the nano- CaCO_3 particles has caused the polymer matrix has a much larger and broader elastomer transition zone, which makes the composites has a better toughness. Compared with Premphet and Horanont,¹⁶ nanoparticles have higher performance than microparticles.

Microstructure microscopy of the fracture section of the composites

Figure 4 is the SEM images of the neat PP (a) and the nanocomposite (b,c). It is clear that the neat PP has the typical brittle fracture, because the surface appeared relatively flat and no significant whitening was observed. However, in Figure 5(b,c), the fracture surface of the nanocomposite had some extensive plastic deformation characterized by ductile fracture, which means that the nano- CaCO_3 particles in the matrix had effect on initiating and terminating the crazing (silver streak), which can absorb more energy coming from the impact.

Crystallinity of the matrix

Figure 5 is the POM images of the neat PP and the nanocomposites. With the different conditions of the crystallization, the homo-PP can form three kinds of crystal lattices— α , β , and γ crystal lattice. α crystal lattice which the most common crystal and existed as spherocrystal in the Homo-PP, is monoclinic lattice. Under POM, the image of the spherocrystal is black cross-shaped extinction.

The neat homo-PP exhibits a common spherocrystal structure with a diameter of 40–50 μm and the interfaces between the spherocrystal were clear and sharp. When 10 PHR of the nano- CaCO_3 was added, the size of homo-PP spherocrystal was reduced and the homo-PP spherocrystals were distorted and interlaced with one another. It is clearly that the presence of the nano- CaCO_3 has greatly affected the crystallization of the homo-PP by acting as heteronuclei, leading to more spherocrystals in a limited space. At the same time, more spherocrystals are not grown perfectly. Thus, the birefringence of the spherocrystals became obscure and blurring and their dimensions are reduced to 20 μm or less. In fact, the number of nano- CaCO_3 particles was so huge that only a small fraction served as hetero-

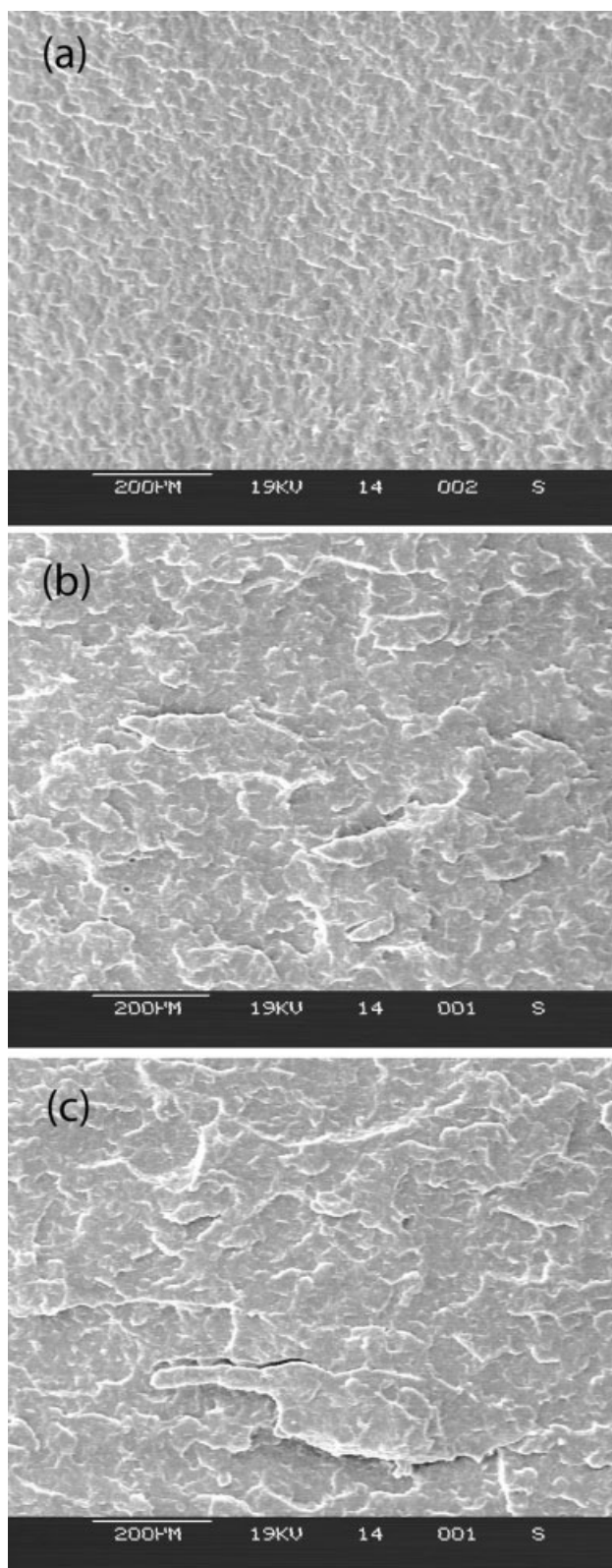


Figure 4 The SEM image of neat PP (a) and the composite filled with 10 PHR nano- CaCO_3 (b and c).

nucleating agents, and most particles restrict molecular movement and hinder orderly packing of molecular segments. The size-reduction of the crystal is

another reason for the improved toughness of the nanocomposites.¹⁷

Dispersibility of the nano-CaCO₃ in PP matrix

It is known that the better dispersion of the nano-inorganic particles in the polymer matrix, the better

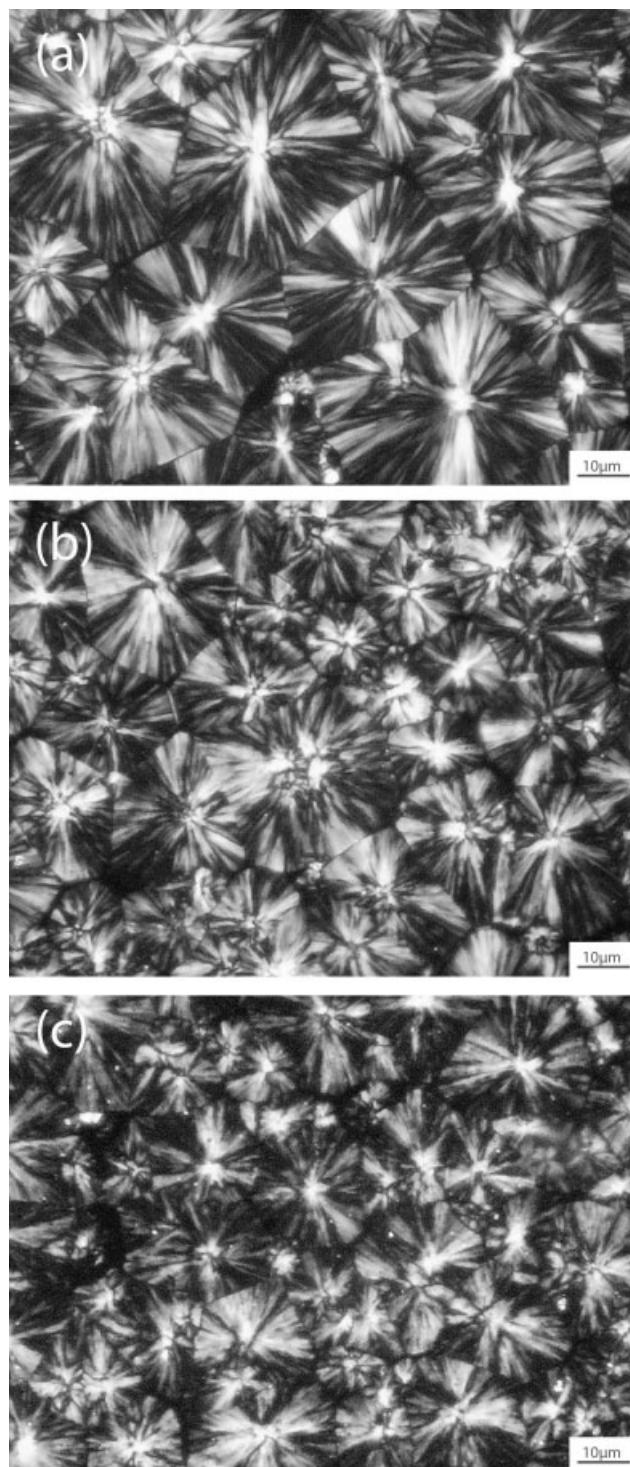


Figure 5 The POM image of neat PP (a) and the composite filled with 10 PHR nano-CaCO₃ (b and c).

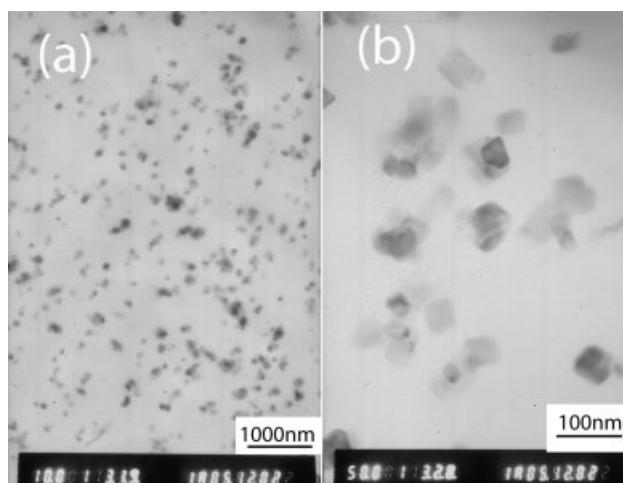


Figure 6 The TEM image of the nanocomposite filled with 10PHR nano-CaCO₃.

mechanical or other properties of the nanocomposites. However, the dispersion of the nano-inorganic particles in a thermoplastic is not an easy process because the nanoparticles have a strong tendency to agglomerate. To have a good dispersion, the surface modification of particles must be done.

Figure 6 is the TEM image of nanocomposites filled with nano-CaCO₃(10 PHR). Figure 6(a) is magnified by 10 k times. Figure 6(b) is magnified by 50 k times. Figure 6(a) shows that the nano-CaCO₃ has been dispersed in the polymer matrix in the nanometer scale. Because the dispersion of particles in matrix only occurred in the twin-screw extruder and the blending time was transitory, some of the nano-CaCO₃ particles existed as aggregates. With the addition of the nano-CaCO₃, the distance between the nano-particles became smaller, the re-congregating chance of the nano particles was added, which leads poor dispersion of the nano-CaCO₃ particles.

Figure 6(b) shows most of the nano-CaCO₃ particles are broken down and existed in the polymer matrix in a primary particles state. Even in the aggregate, the nano-CaCO₃ particles were not connected tightly, which aggregated unconsolidated.

CONCLUSION

PP-based nanocomposites were prepared by melt-blending using twin-screw extruder. The results show that the nano-CaCO₃ particles added to the thermoplastics can evidently increase the toughness and stiffness of the composites at the same time. The nanocomposites structure is demonstrated by TEM, which shows that most of the nano-CaCO₃ particles dispersed in the matrix in a primary particles state. The DMTA results show that adding nano-CaCO₃ particles, the glass transition temperature (T_g) has

decreased and the T_{α} has increased, which is the reason for the toughness increasing. From the SEM images of the fracture section of the matrix, the nano- CaCO_3 particles have an effect on initiating and terminating the crazing. The crystal properties of the composite have been tested by POM, which shows that the nano- CaCO_3 can be heterogeneous nucleus effect on neat PP, which results in a reduction of the spherocrystals size and an imperfection of the spherocrystals. That is another reason increasing the toughness of the nanocomposites. This work also shows that nano- CaCO_3 /PP composites can be prepared in ordinary machines, which provides a general concept for manufacturing polymer nanocomposites by direct melting-blending.

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