Hybrid Organic−Inorganic Nanocomposites Formed from an Epoxy Polymer and a Layered Silicic Acid (Magadiite)

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Nanostructured hybrid organic−inorganic composites typically exhibit mechanical properties superior to the parent materials. One approach to preparing organic−inorganic nanocomposites is by the sol−gel processing method. In this method the inorganic phase is formed by the hydrolysis and condensation of metal oxide precursors while the organic matrix is being polymerized simultaneously. The size of inorganic building blocks is controllable and the interfacial properties can be improved by introducing covalent bonding between organic and inorganic phases. However, the sol−gel approach is limited by the evolution of volatile byproduct and shrinkage when the hybrid is molded at elevated temperature.[1,2]

Layered silicate nanolayers can be used as alternative inorganic components for the construction of nanostructured hybrid composites. The clay silicate nanolayers possess stable Si−O bonds and high particle aspect ratios comparable to conventional fibers.[3,4] Their interlayer surface is easily modified by ion-exchange reaction, and the gallery can be intercalated by organic polymer precursors for the formation of organic−inorganic nanocomposites.[5,6] The intercalation chemistry of layered silicate clays plays an important role in the formation of polymer−clay nanocomposites. Exfoliated clay composites contain single, 10 Å thick layers of clay dispersed in the polymer matrix.[7−12] Owing to the platy morphology of the silicate layers, exfoliated clay nanocomposites can exhibit dramatically improved properties such as barrier and mechanical properties that are not available for conventional composite materials.[13−16]

Toyota researchers first demonstrated that organoclay could be exfoliated in a nylon-6 matrix to greatly improve the thermal and mechanical properties of the polymer.[9,13] Although considerable research has been conducted on organic−inorganic hybrid composites in which smectite clays are used as reinforcement agents,[17] relatively little work has been devoted to derivatives of layered silicic acids that possess layered morphology and ion-exchange properties similar to smectite clays. The alkali-metal-ion forms of this layered silicate family include as members kanemite ($NaHSi_2O_5 \cdot nH_2O$), makatite ($Na_2Si_4O_9 \cdot nH_2O$), octosilicate ($Na_2Si_8O_{17} \cdot nH_2O$), magadiite ($Na_2Si_{14}O_{29} \cdot nH_2O$), and kenyaite ($Na_2Si_{20}O_{41} \cdot nH_2O$).[18−20] The detailed crystal structures of these layered silicates are still unknown, except for makatite.[21] In general, the structure of these layered silicates is built up of one or multiple sheets of SiO_4 tetrahedra with an abundant hydroxyl siloxane surface.[22,23]

The layers of alkali-metal silicates contain Q^3 ($\equiv SiO^-$) silicon sites in which the terminal oxygen is neutralized by alkali ions and protons. The alkali ions are exchangeable, and the intragalleries can be intercalated by various organic molecules and even pillared by inorganic pillaring agents.[24,25] Layered silicic acid derivatives are formed when the alkali-metal ions are replaced completely by protons. The special properties of the layered silicates include their basal plane hydroxyl groups and the variable thickness of the silicate layers (from 5.0 Å for makatite to 17.7 Å for kenyaite).[21] The active hydroxyl sites may provide enhanced bonding with the gallery intercalates, and the variable layer thickness may provide insights on the relationship between properties and aspect ratios. Although a large number of organic compounds have been intercalated into layered silicic acid derivatives,[18,26−28] the exfoliation of this family of materials in a polymer matrix has not yet been achieved.

In the present work we have extended the exfoliation chemistry of smectite clay in an epoxy matrix to include the layered silicate magadiite with a layer thickness of 11.2 Å. The chemistry elucidated for magadiite is likely to be applicable to other members of this mineral family for the formation of polymer−inorganic nanolayer composites.

Na^+−magadiite was synthesized by the hydrothermal reaction of 60.0 g of silica gel with 300 mL of 1.11 M NaOH solution at 150 °C for 42 h according to previously published methods.[29] The Na^+ form of the silicate was then converted to a previously unknown mixed

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Table 1. Intercalates Formed by Reaction of Na^+−Magadiite with $C_{18}H_{37}NH_3^+Cl^-$ and $C_{18}H_{37}NH_2$

material designation	intragallery composition[a] per $Si_{14}O_{29}^{2-}$ unit cell	gallery structure	d_{001} (Å)
C18-magadiite-LM	$(CH_3(CH_2)_{17}NH_3^+)_{0.45}H^+_{1.55}$	lateral monolayer	14.0
C18-magadiite-PF	$(CH_3(CH_2)_{17}NH_3^+)_2(CH_3(CH_2)_{17}NH_2)_{0.48}$	paraffin	38.2
C18-magadiite-BL	$(CH_3(CH_2)_{17}NH_3^+)_2(CH_3(CH_2)_{17}NH_2)_{1.83}$	lipid bilayer	63.1

[a] The compositions were determined by CHN analysis and Si analysis.

$CH_3(CH_2)_{17}NH_3^+$−$CH_3(CH_2)_{17}NH_2$ intercalate by ion-exchange reaction in the presence of neutral amine. A 15.0-g quantity of air-dried Na^+−magadiite was added to 1.0 L of 0.14 M solution containing a 6:1 molar ratio of alkylammonium chloride and alkylamine in 1:1 (v:v) ethanol/water solution and stirred at 65 °C for 48 h. The onium ion exchanged magadiite was centrifuged, washed consecutively with 100% ethanol (1.0 L) once, 50% EtOH (750 mL) once, 25% EtOH (750 mL) twice, and water until free of Cl^-, and air-dried. A basal spacing of 38.2 Å was consistent with the paraffin structure of onium ions and neutral amine with an inclined angle about 65°.[18] This intercalated paraffin-like phase was designated C18-magadiite-PF. Elemental analysis and TGA results indicated the sodium ions were completely replaced by onium ions. This product also contained a small fraction of neutral primary amine which was essential for forming the paraffin structure, in addition to the primary onium ions.

Two previously known organo magadiite intercalates were also synthesized for comparison purposes. One was an organo magadiite with a 63.1 Å basal spacing, prepared using Lagaly's method of ion-exchange reaction of Na^+−magadiite with $CH_3(CH_2)_{17}NH_3^+$ and excess $CH_3(CH_2)_{17}NH_2$ (onium:amine molar ratio = 3:2) in aqueous ethanolic solution (10% ethanol).[18] The gallery of this organo magadiite contains a lipid-like bilayer structure of onium ions and neutral amine molecules. The sample was designated C18-magadiite-BL. This product should be regarded as octadecylamine-solvated octadecylammonium magadiite which contains near 100% neutral amine, except the alkylammonium fraction needed to balance the negative charge of the silicate layer. The other known organo magadiite phase was a 14.0 Å phase intercalated by a lateral monolayer of $CH_3(CH_2)_{17}NH_3^+$ ions. This monolayer phase, which was denoted C18-magadiite-LM, could be obtained by extensively washing C18-magadiite-BL and C18-magadiite-PF with ethanol/water or by direct ion-exchange reaction of Na^+−magadiite with $CH_3(CH_2)_{17}NH_3^+$ in ethanol/water (>1:1 vol) solution at a pH in the range 6−7. In this lateral monolayer structure the onium ion chains lie parallel to the interlayer siloxane surface.

The unit-cell compositions, basal spacings, and gallery structures for the three organo magadiite derivatives are summarized in Table 1. The powder XRD patterns for each phase along with that for Na^+−magadiite are given in Figure 1.

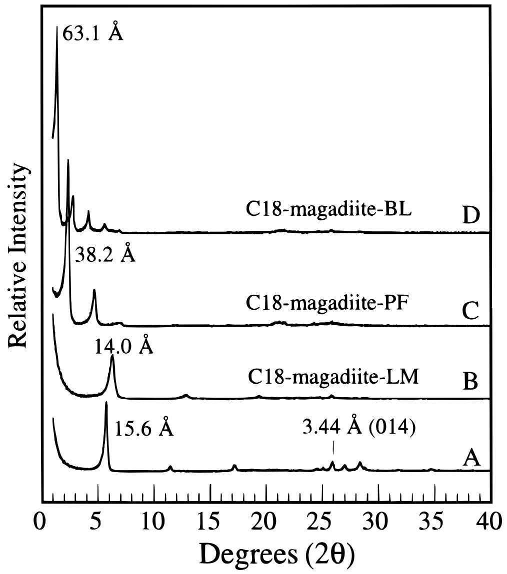
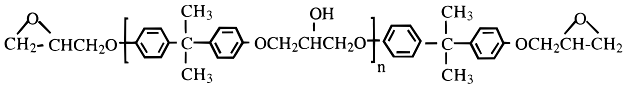
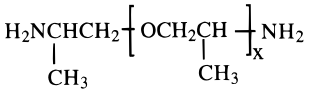


Figure 1. X-ray powder diffraction patterns of (A) air-dried Na^+−magadiite; (B) $CH_3(CH_2)_{17}NH_3^+$−magadiite with a lateral monolayer (LM) structure. Patterns C and D are for mixed $CH_3(CH_2)_{17}NH_3^+$/$CH_3(CH_2)_{17}NH_2$−magadiite with a paraffin (PF) and a lipid bilayer (BL) gallery structure, respectively. The LM structure contains no free amine (0.45 onium ions/$Si_{14}O_{29}$ formula unit), whereas PF and BL structures contain neutral primary amine molecules, in addition to primary onium ions.

The epoxide resin used to for epoxy−magadiite hybrid composite formation was poly(bisphenol A-*co*-epichlorohydrin) (Shell, EPON 828), with a molecular weight of ~377: The curing agent was poly(propylene glycol) bis(2-aminopropyl ether) (Huntsman Chemical, JEFFAMINE D-2000), with MW ~2000:



n = 0 (88%); n = 1 (10%); n = 2 (2%).



$$H_2N\underset{CH_3}{CH}CH_2\left[OCH_2\underset{CH_3}{CH}\right]_x NH_2$$

Equivalent amounts of epoxide resin and poly(oxypropyleneamine) were mixed at room temperature for 30 min. The desired amount of organo magadiite was added to the epoxide−poly(oxypropyleneamine) mixture and stirred for another 60 min. This mixture was outgassed and poured into a stainless steel mold for curing at 75 °C for 3 h and, subsequently, at 125 °C for an additional 3 h.

Owing to the strong intragallery electrostatic interactions in C18-magadiite-LM, this structure cannot be further intercalated by epoxide resin or even by small polymer precursor molecules such as ϵ-caprolactam. However, both C18-magadiite-PF and C18-magadiite-BL with 38.2 and 63.1 Å basal spacing are readily swelled by polymer precursors and can be used to form hybrid composites. C18-magadiite-PF is much preferred over the BL analogue due to a much smaller amount of neutral amine (cf. Table 1), which can participate and interfere with the desired thermoset curing process. Unless otherwise indicated, all of the following experiments were carried out by using C18-magadiite-PF as a reinforcement agent. All effort to form a paraffin-like intercalate with onium ions and amines with chain

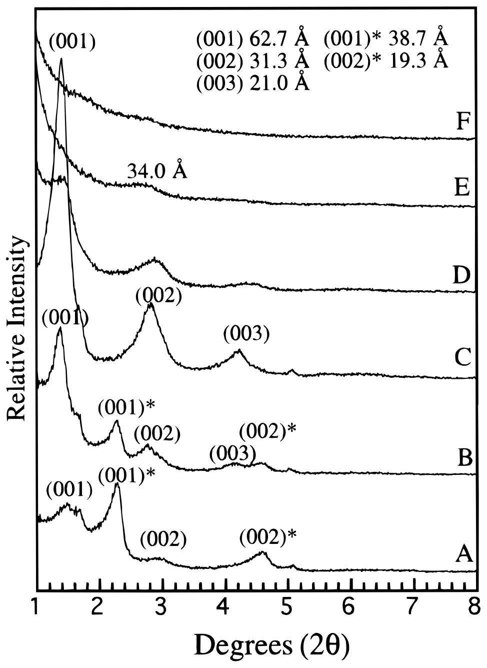


Figure 2. X-ray diffraction patterns of products prepared by reaction of C18-magadiite-PF (15 wt % loading) with epoxide resin and poly(oxypropyleneamine) curing agent at an epoxide group to amine group molar ratio of 2:1. Reaction conditions were as follows: (A) 25 °C, 60 min; (B) 75 °C, 5 min; (C) 75 °C, 15 min; (D) 75 °C, 3 h; (E) 75 °C, 3 h and 125 °C, 5 min; (F) 75 °C, 3 h and 125 °C, 10 min. The 00*l* lines marked with an asterisk are from the initial paraffin structure of the organo magadiite.

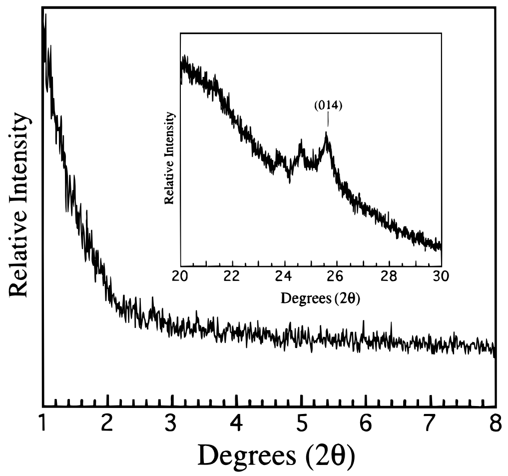


Figure 3. X-ray diffraction pattern of a cured epoxy polymer–magadiite nanocomposite prepared from C18-magadiite-PF. The organo silicate content was 15 wt %. Polymer curing was carried out at 75 °C for 3 h and followed by 3 h at 125 °C.

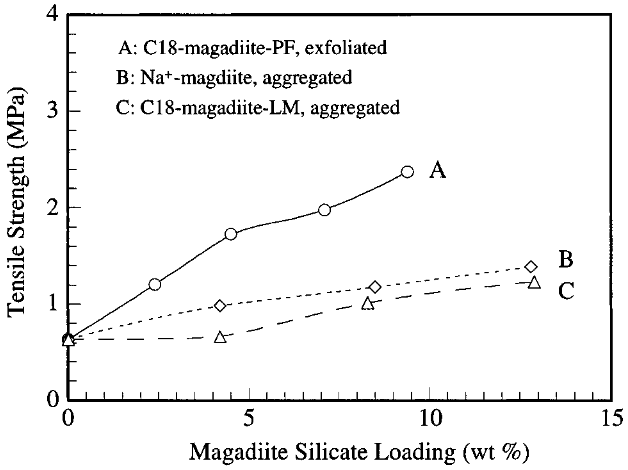


Figure 4. Comparison of the tensile strengths of an epoxy-exfoliated magadiite nanocomposite prepared from C18-magadiite-PF and conventional magadiite composites prepared from Na$^+$–magadiite and C18-magadiite-LM. The inorganic silicate loading was determined by calcining the composites in air at 650 °C for 4 h using a heating rate of 2 °C/min. The onium ion and amine content of the organo magadiite was counted as contributing to the stoichiometry of epoxide cross-linking.

length shorter than C_{16} resulted in intercalates with a lipid bilayer or lateral monolayer structure.

C18-magadiite-PF when mixed with epoxide resin at 75 °C undergoes a 4.3 Å increase in basal spacing from 38.2 to 42.5 Å. This indicates that the gallery onium ions change their orientation from an inclined to a vertical orientation to accommodate epoxide penetration into the gallery. Furthermore, the X-ray diffraction patterns in Figure 2 show the gallery also can be expanded by co-intercalation of epoxide and poly(oxypropyleneamine) mixtures. At room temperature, the gallery is only partially solvated due to the slow gallery diffusion of those macromolecules. This results in the presence of a 63 Å intercalate and the unintercalated initial phase. At elevated temperature (75 °C), the gallery is totally solvated within 15 min to form an intercalate with a very sharp d_{001} peak near 63 Å. This latter value is consistent with the reorientation of the onium ions into a bilayer structure when solvated by the resin and the curing agent (compare Figure 1D and 2C). The broadening of the first order peak upon further heating at 75 °C (Figure 2D) suggests that the gallery is further expanded by cross-linking polymerization. Upon further heating at 125 °C, the gallery continues to undergo expansion and the solvated phase basal spacing of 63 Å is replaced by the nearly amorphous phase characteristic of the exfoliated composite (Figure 2E,F).

The X-ray diffraction pattern of epoxy-exfoliated magadiite composite completely cured at 125 °C for 3 h is shown in Figure 3. The absence of the 00*l* diffraction peaks provides strong evidence that the silicate layers of magadiite have been exfoliated in the thermoset curing process. However, the magadiite 2-dimensional structure is still retained in the exfoliated state, as indicated by a d_{014} reflection at 3.4 Å. As indicated by the XRD data in Figure 2, the key to achieving an exfoliated composite structure is to first load the magadiite gallery with mobile onium ions and amine guest species and then expand the gallery region to a “critical gallery height” by replacing the amine with epoxide and poly(oxypropyleneamine) precursors. This expansion of the gallery by the precursors allows the intragallery and extragallery curing of the polymer to occur at comparable cross-linking rates.

The benefit of magadiite exfoliation in polymer reinforcement is illustrated by the tensile strength vs loading curves in Figure 4. The tensile strengths of the exfoliated magadiite nanocomposites are superior to conventional composites prepared from both Na$^+$-magadiite and C18-magadiite-LM. In obtaining these curves, we adjusted the stoichiometry of epoxide and poly(oxypropyleneamine) by including the intragallery onium ion and amine as curing agents. The results are

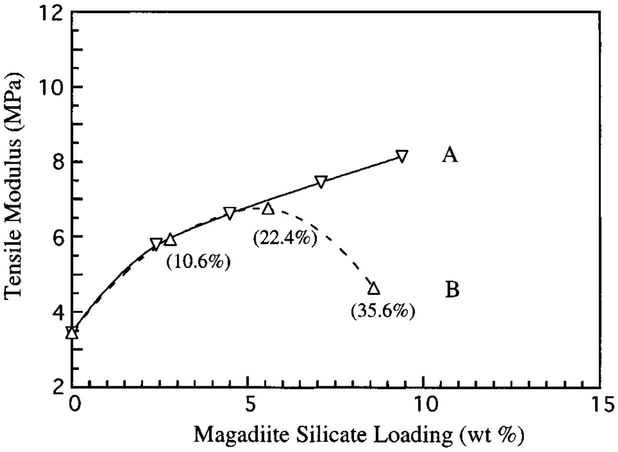


Figure 5. Effect of octadecylammonium and octadecylamine on the tensile modulus of epoxy-exfoliated magadiite nanocomposites prepared from C18-magadiite-PF. The solid line is for composites formed by including the onium ion and neutral amine content of the organo magadiite as a curing agent for epoxide cross-linking and reducing the amount of poly(oxypropyleneamine) accordingly; the dashed line is for composites formed by disregarding the cross-linking reactivity of the gallery onium ion and amine in the initial intercalate and curing the resin with 1 equiv of poly(oxypropyleneamine). The values given in parentheses for curve B are the molar fractions of excess alkylamine functional groups contributed by the onium ions and free amine relative to poly(oxypropyleneamine).

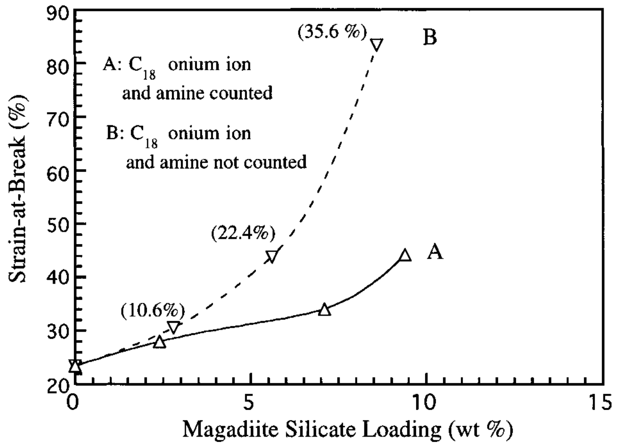


Figure 6. Effect of octadecylammonium and octadecylamine on the strain-at-break values of epoxy-exfoliated magadiite nanocomposite prepared from C18-magadiite-PF. The dashed line is for composites formed by not counting onium ion and amine content of the organo magadiite as contributing to the stoichiometry for epoxide cross-linking, the solid line is reversed. The values in parentheses give the amount of excess amine curing agent due to the organo magadiite component.

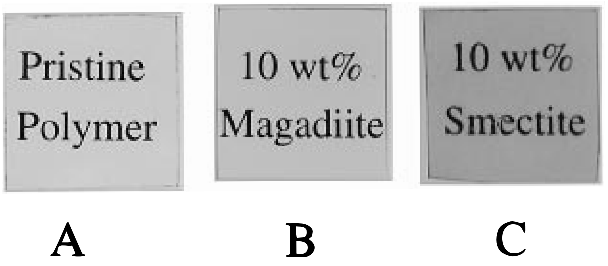


Figure 7. Comparison of the optical properties among (A) a pristine epoxy polymer, (B) an epoxy-exfoliated magadiite nanocomposite prepared form C18-magadiite-PF, and (C) an epoxy-exfoliated smectite clay nanocomposite prepared from $CH_3(CH_2)_{17}NH_3^+$ ion-exchanged montmorillonite (from Wyoming, cf. ref 15). The thickness of each sample is ~1 mm. Polymer curing was carried out at 75 °C for 3 h, followed by 3 h at 125 °C.

very predictable. Since the single silicate nanolayers have been dispersed into the polymer matrix, the exfoliated nanocomposite is more or less microscopically homogeneous relative to the macroscopic homogeneity of conventional composites. Thus each nanolayer of the exfoliated composite contributes to the reinforcement effect.

Examples of epoxy hybrid composites based on smectite clay intercalates have been reported previously.[14,30] In comparison to the results obtained for epoxy–smectite clay nanocomposites, the reinforcement provided by magadiite is not as significant at higher loading. The difference in the charge density between magadiite and smectite results in different loading of alkylammonium ions. It is quite likely that the onium-exchange ions function as curing agents in the process of polymer cross-linking. This hypothesis was supported by an experiment wherein C18-magadiite-BL was swelled by epoxide and poly(oxypropyleneamine). The series of sharp XRD reflections present at the swelling stage disappear upon complete curing (cf. Figure 3). This result signifies that C18-magadiite-BL can also be exfoliated in an epoxy–polymer matrix. Therefore, it was necessary to investigate the effect of alkylammonium ion chain length on the mechanical behavior of our nanocomposites.

The dashed line (curve B) in Figure 5 shows the results obtained if we do not compensate for the alkylammonium and alkylamine content of the organo magadiite curing agent and use the stoichiometry amounts of epoxide resin and poly(oxypropyleneamine). The tensile moduli of the resulting nanocomposites exhibit a maximum. At low organo magadiite loading, the effect was minimal due to reinforcement contribution of the layers, but at high loading, the effect of the gallery onium ion and amine is significant. Although the polymer network maintains its continuity, the excess amine weakens the composite and reduces the benefit derived from exfoliation of the silicate layers. However, we still obtain some benefit from the effect of excess alkylamine in nanocomposite formation. The stain-at-break is significantly improved by the excess alkylamine provided by the organo magadiite (Figure 6). A very elastic nanocomposite with higher tensile strength and modulus is obtained. Significantly, this plasticizing effect cannot be achieved by adding an excess of poly(oxypropyleneamine) in the absence of magadiite reinforcement.

The most significant result we derive from the epoxy–magadiite system relative to epoxy–smectite nanocomposite is the unique transparent optical properties. As shown in Figure 7, the magadiite composites are much more transparent than the corresponding smectite composites at the same loading. This result suggests the refraction index of magadiite more nearly matches that of the organic matrix or that the magadiite is more fully exfoliated than smectite. Future studies will address the transparent properties, which represent a significant milestone in the development of polymer–clay nanocomposites.

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In conclusion, three organo magadiite intercalates have been synthesized. The lateral monolayer intercalate, which contains only intercalated onium ions and no free amine, is not organophilic enough to be intercalated by epoxy monomer and curing agent. The lipid bilayer intercalate can be exfoliated into the epoxy matrix, but the high gallery concentrations of onium ion and free amine compromise the properties of the matrix by participating in the curing process. Thus, the reinforcing benefit of the nanolayers is diminished. The paraffin intercalate is best suited for exfoliation into an epoxy matrix, because the gallery concentration of onium ion and free amine is sufficient to impart a hydrophobic environment and allow monomer intercalation without greatly disrupting the integrity of the polymer network. The transparent properties of the composites, together with the anticipated barrier film properties of these materials should make them especially attractive for packaging materials and protective films.

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