

Modeling of Polymer/Clay Nanocomposite Formation

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Received 22 October 2004; accepted 7 January 2005

DOI 10.1002/app.22196

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A statistical thermodynamic modeling of the formation of polymer/clay intercalation and nanocomposites was developed. The key factor in determining intercalation was an exothermic heat of mixing between polymer chains and the organically modified silicate surface. This was found to agree with previous experimental results in the

literature including halogenated polymers and acrylonitrile copolymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1657–1663, 2006

Key words: clay; nanocomposite; modeling

INTRODUCTION

The swelling mechanism of bentonite by various liquids would seem to have been first envisaged in 1949 by Jordan,¹ who associated swelling with polarity and high dielectric constant. This argument was further developed by Barshad² in 1952. The arrangement of polar molecules within the swollen clay was studied by earlier investigators^{3–6} but is most highly developed in a 1963 paper by Weiss.⁷ In 1960, Barrer and Kelsey⁸ described a lattice model of the statistical thermodynamics of the sorption of organic vapors by bentonite clay.

From the mid-1990s, after the Toyota R&D Center in Japan produced nylon 6 and its clay nanocomposite compound by absorbing caprolactam monomer into montmorillonite,⁹ many investigations have been carried out to produce polymer/clay intercalation with a melt-compounding process. Generally polar polymers such as polyamide 6,¹⁰ polyvinyl chloride (PVC),¹¹ poly(methyl methacrylate) (PMMA),¹² acrylonitrile butadiene rubber (NBR),¹³ and styrene acrylonitrile copolymer (SAN)¹⁴ have been melt compounded with montmorillonite to form polymer/clay nanocomposites. However, this process does not prove successful for polyhydrocarbons^{15,16} and various modified montmorillonites.¹⁷

In our previous studies,^{15–18} we produced polymer nanocomposites with many commercially available polar polymers such as chlorinated polymers (polychloroprene, chlorinated polyethylene, polyvinyl chloride, chlorinated polyvinylchloride, and polyvinylidene chloride), polyvinylidene fluoride (PVDF),

vinylidene fluoride (VDF) containing fluoroelastomers, styrene acrylonitrile copolymer (SAN), acrylonitrile butadiene copolymer (NBR), and hydrogenated NBR with various organic modified montmorillonite clays. From the experiments with the primary, secondary, tertiary, and quaternary organoclays, the most polar polymer NBR was the only one to form nanocomposites with secondary, tertiary, and quaternary organoclays. Nonpolar polymers [polyethylene (PE), poly(propylene) (PP)] or natural montmorillonite and primary organoclay could not produce intercalation. It was concluded that there are two critical factors to produce polymer/clay nanocomposite in melt compounding process. These are the polarity of polymers and the organophilicity of organic modified montmorillonite clay. The dielectric constant was used to indicate the degree of polarity. Organoclays were arranged by the organic surface area to represent the organophilicity.

There are two previous efforts—by Vaia and Gianellis¹⁹ and Balazs et al.²⁰—to develop theories of the formation of nanocomposites from polymer melts and clays. Both theories resemble our own considerations in the key role of enthalpic effects.

In this study, we explored a theoretical modeling of the formation of the polymer/clay nanocomposite in terms of statistical thermodynamic equilibrium principles. The strong interaction between polymer chains and clay surface was the focus of careful analysis.

MODEL

Formation of organoclays

We view the formation of organoclays from Na⁺ montmorillonite, following Smith²¹ and others,^{5,6} as a chemical reaction involving cation exchange. Initially a Na⁺ montmorillonite contains negatively charged

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silicate layers SiO_2^- and sodium Na^+ cations. Introduction of the organic amine salts $\text{R}_m\text{NH}^+\text{Cl}^-$ leads to the replacement of the sodium specifically. The reversible reaction occurs



This reaction is governed by an equilibrium constant K with²²

$$\Delta G^R = RT \ln K \quad (1)$$

where R is the gas constant and T is temperature.

$$K = \frac{a_{\text{R}_m\text{NHSiO}_2} a_{\text{Na}^+} a_{\text{Cl}^-}}{a_{\text{SiO}_2^-} a_{\text{Na}^+} a_{\text{R}_m\text{NH}^+\text{Cl}^-}} \quad (2)$$

where a_j is the activity of the y component.

The free energy of the reaction ΔG^R is negative. The Na^+ and Cl^- ions are readily extracted, thus pushing forward the R_mNHSiO_2 concentration.

Statistical thermodynamic principles

Modeling of equilibrium melt-intercalated polymer/clay nanocomposites should be developed based on thermodynamic concepts. To form an intercalated or exfoliated dispersion of silicate layers in a polymer matrix the overall Gibbs free energy change should be negative:

$$\Delta G = \Delta H - T\Delta S < 0 \quad (3)$$

which is needed to develop statistical thermodynamic models for ΔH and ΔS . ΔH may be obtained from energetic considerations. For a microcanonical ensemble^{23,24} S is

$$S = k \ln \Omega \quad (4)$$

where Ω is the number of configurations and k is Boltzmann's constant.

ΔH heat of formation/solution

From our experimental results,¹⁵⁻¹⁷ it is suggested that the process of polymer intercalation is driven by ΔH . The formation of intercalated structures for low molecular weight liquids—associated with polarity—was argued earlier by Jordan,¹ Barshad,² and Weiss.⁷ Some of these effects may involve cation exchange. They can be correlated with dipole moments and dielectric constants, which suggests an exothermic ΔH . Our experimental studies¹⁵⁻¹⁷ indicate similar behavior for polymers.

The interaction between adsorbed polymer and the silicate layer should play an important role for the change of enthalpy (ΔH). The treatment of natural montmorillonite clays with organic amines makes the silicate layer more organophilic, which is favorable to polymer chains. Polymers containing polar groups presumably have interactions with the organic ammonium compounds, leading to exothermic effects and negative ΔH .

There are two traditional approaches to heats of solution, one attributed to van Laar²⁵ (and successively generalized by Scatchard²⁶ and Hildebrand),²⁷ which considers a random solution with energies E_{11} and E_{22} between like molecules and E_{12} between unlike molecules. E_{11} and E_{22} are cohesive energies of individual components and E_{12} is the cohesive energy between two components. Generally E_{12} is taken as a geometric mean $\sqrt{(E_{11}E_{22})}$. This necessarily leads to an endothermic heat of mixing based on solubility parameters and the so-called regular solution.²⁵ This proved very useful in interpreting the characteristic of solutions of nonpolar molecules, although it would not seem a productive approach to the intercalation of liquids and polymer melts into clay.

A second approach is attributed to Dolezalek,²⁸ based on his explanations of the behavior of acetone-chloroform solutions. This involves considering a chemical reaction between "1" and "2" molecules to form "12" combinations. Presumably the energy of interaction was much greater in value than the geometric mean.

We may apply this idea to low molecular weight polar molecules and silicate surfaces. Liquids such as acetone, alcohols, and glycerols swell montmorillonite clays.² Clearly, for the low molecular weight polar molecule entering into the organoclay, $\Delta H < 0$ (exothermic), whereas for nonpolar liquids, $\Delta H > 0$ (endothermic).

The above formulation may be generalized to polymer solutions. A low molecular weight compound or polymer entering the gallery between the silicate layers can interact with either an organic amine or neat silicate layers. For polar polymers it produces an exothermic effect if it interacts with the organic amine and apparently an endothermic effect if it meets the bare silicate surfaces. The latter should be the reason for the Na^+ montmorillonite not to intercalate polymers. Thus

$$\Delta H = \beta \Delta H_{\text{coat}} + (1 - \beta) \Delta H_{\text{uncoat}} \quad (5)$$

where β is related to the extent of organic amine coating, being larger for amines with large organic groups; thus, β estimates the contribution of organophilicity of organoclays on the formation of polymer/clay nanocomposite. In a previous study,¹⁸ we calculated β from the structure and concentration of or-

TABLE I
Organic Surface Area of Organoclays

Clay	Organic modifiers	d_{001} (Å)	Δd (Å)	Organic surface area (%)
12-ALA	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_{11}\text{COOH} \end{array}$	14.0	4.4	50
DOA	$\begin{array}{c} \text{H} \\ \\ \text{H} \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	14.8	5.2	50
TOA	$\begin{array}{c} \text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{H}-\text{N}^+-\text{(CH}_2\text{)}_7\text{CH}_3 \end{array}$	15.8	6.2	70
Cloisite [®] 30B	$\begin{array}{c} \text{(CH}_2\text{)}_7\text{CH}_3 \\ \\ \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3-\text{N}^+-\text{T} \end{array}$	18.5	8.9	70
Cloisite [®] 20A	$\begin{array}{c} \text{CH}_2\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \\ \\ \text{CH}_3-\text{N}^+-\text{HT} \\ \\ \text{HT} \end{array}$ <p>T (\approx 65%C18; \approx 30%C16; \approx 5%C14) HT (\approx 65%C18; \approx 30%C16; \approx 5%C14)</p>	24.2	14.6	120

ganic modifier (Table I). Basically we lay out the organic amine on the silicate surface and calculate the fraction of the surface it coats from its concentration. For large organic amines, β converges to 1 and $\Delta H \rightarrow \Delta H_{\text{coat}}$.

As we found in our experiments, the polarity of polymer chains is critical in the formation of polymer/clay nanocomposite in the melt-compounding process. The range of polarity of polymeric materials may be estimated by the dielectric constants and dipole moment of each polymer molecule. We have found experimental data for dielectric constants.

The Clausius–Mosotti equation is

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N}{3} \alpha \quad (6a)$$

which expresses the dielectric constant for nonpolar materials. Here ε is the dielectric constant, α is the molecular polarizability, and N is the number of molecules per unit volume.

The influence of dipole moment on the dielectric constant has been proposed by various researchers beginning with Debye. Specific theoretical interpretations of polar molecules were first modeled by Debye,²⁹ who devised the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N}{3} \left[\alpha + \frac{\mu^2}{3kT} \right] \quad (6b)$$

where μ is the dipole moment. It may be seen that μ enhances the dielectric constant. Subsequent modifications of Debye's formulation have been given by Onsager³⁰ and Kirkwood.³¹

Table II details the dielectric constants and dipole moments of various polymers as well as values of the latter determined from the work of Debye,²⁹ Onsager,³⁰ and Kirkwood.³¹

Exothermic heats of solution and dipole moments

Generally when solutions are formed from molecules with dipoles the heat of solutions is exothermic. We are especially interested here in solutions of amines. We consider butylamine ($\mu = 1.32$) and triethylamine ($\mu = 0.75$).

Heat of mixing of amine compounds with a range of organic liquids can be obtained from the literature. Table III shows the heat of mixing of butylamine and triethylamine with organic liquids. Generally high dipole moment polar organic liquids such as water, 1-butanol, ethanol, methanol, 1-propanol, and trichlo-

TABLE II
Dipole Moment of Polymers

Polymer	Dielectric constant	Dipole moment (unit: Debye)			
		Debye	Onsager	Kirkwood ($\delta = 1$)	Table of dipole moments ³³
PE	2.30	0.07	0.07	0.28	0.0
PP	2.25	N/A	N/A	0.32	0.34
PS	2.80	0.42	0.42	0.80	0.25
SAN	3.10	0.55	0.54	0.87	1.07
PVC	3.40	0.52	0.53	0.79	1.44
PMMA	3.60	0.86	0.88	1.25	—
PVDF	8.40	0.89	1.15	1.60	1.37
NBR	13.0	1.17	1.74	2.61	1.50

roethane exhibited exothermic heat of mixing with both amine compounds. Nonpolar organic liquids such as decane, heptane, methyl cyclohexane, hexane, and benzene exhibit endothermic heat of mixing. Figure 1 clearly shows the exothermic and endothermic heat of mixing of polar and nonpolar organic liquids with organic amines.

ΔS entropy of formation

An entropy change occurs in the absorption/adsorption of molecules into the galleries between silicate layers. The entropy of formation of chain structures in clay silicate layers has been described notably by Barrer and Kelsey.⁸ We consider that there are two steps. The first is the formation of an organoclay by the absorption of low (modest) molecular weight organic amine into the galleries with the elimination of sodium and potassium cations. The second is the absorption of the polymer chains into these same galleries. The entropy change requires the evaluation of Ω , which has the form

$$\Omega = \frac{1}{N_p!} \prod_{i=1}^{N_p} \nu_i \quad (7)$$

where ν_i is the number of configurations for each chain introduced and N_p is the number of indistinguishable polymer chains.

In our analysis we seek to determine ν_i and Ω for polymer chains entering a partially empty gallery containing organic amines tethered to some of the silicate layers. ν_{i+1} is obtained in the following manner. N_0 represents the total sites that are available in the gallery. There are already N_{org} number of organic molecules fixed to the silicate sheets. There are $(N_0 - MN_{\text{org}})$ cells available for polymer chains, where M is the number of cells occupied by each organic amine molecule. After i polymer chains, each having m segments and introduced, there will be $(N_0 - MN_{\text{org}} - im)$ sites. The number of configurations ν_{i+1} for the $(i + 1)$ th polymer chain is

$$\nu_{i+1} = (N_0 - MN_{\text{org}} - im)z(z - 1)^{m-2}(1 - f_i)^{m-1}g^a \quad (8)$$

TABLE III
 ΔH of Amine Compounds

Organic liquid	Dipole moment ³⁰	Heat of mixing (J/mol) ³⁴		
		Butylamine	Triethylamine	
Water	H ₂ O	1.82	-3401	-2163
1-Butanol	C ₄ H ₁₀ O	1.81	-2894	-1495
Ethanol	C ₂ H ₆ O	1.73	-2954	-1336
Methanol	CH ₄ O	1.71	-3829	-1889
1-Propanol	C ₃ H ₈ O	1.70	-3068	-1429
Ethane, 1,1,1-trichloro	C ₂ H ₃ Cl ₃	1.75	—	-175
Cyclohexane	C ₆ H ₁₂	0.61	1199	225
Decane	C ₁₀ H ₂₂	0	1449	135
Heptane	C ₇ H ₁₆	0	1269	88
Cyclohexane, methyl	C ₇ H ₁₄	0	1129	82
Hexane	C ₆ H ₁₄	0	975	82
Benzene	C ₆ H ₆	0	678	330
Toluene	C ₇ H ₈	0.43	611	132
Benzene, 1,4-dimethyl	C ₈ H ₁₀	0.37	635	45

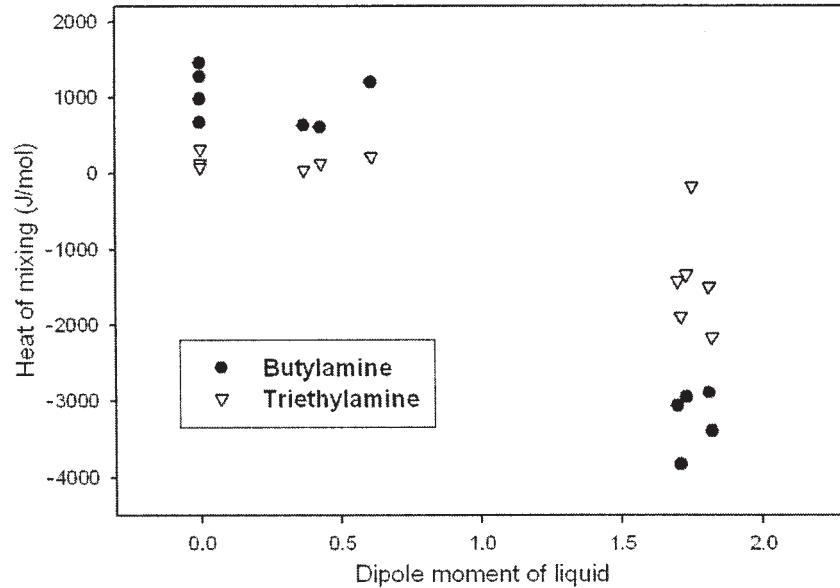


Figure 1 ΔH of butylamine and triethylamine with various alcohols and trichloroethane.

where $N_0 - MN_{org}$ is the total available number of possible sites in the gallery for polymers; f_i is the probability of an adjacent site being occupied; g is the factor specifying unavailability of sites on the far side of the surface; and $a = 2m/q$, where q is the number of sites equal to the distance between two separated silicate surface. Now taking $(1 - f_i)$ to be $(N_0 - mi)/N_0$, where $N_0 = N_0 - MN_{org}$, leads to

$$\Omega \cong \frac{(N_0^0 - 1)!}{(N_0^0 - mN_p)!} \left(\frac{z - 1}{N_0^0} \right)^{(m-1)N_p} g^{N_p a} \quad (9)$$

Using Stirling's approximation, the configuration entropy S becomes

$$S \cong -k \left[N_1 \ln \frac{N_1}{N_1 + mN_p} + N_p \ln \frac{1}{N_1 + mN_p} - N_p(m - 1) \ln(z - 1) + mN_p - N_p a \ln g \right] \quad (10)$$

where $N_1 = MN_{org}$.

The entropy of disorientation is the case where $N_{org} = 0$

$$S_d = kN_p [\ln mN_p + (m - 1) \ln(z - 1) - m + a \ln g] \quad (11)$$

The entropy of mixing in the gallery is

$$\Delta S_M = S - S_d = -k \left(N_{org} \ln \frac{MN_{org}}{MN_{org} + mN_p} + N_p \ln \frac{mN_p}{MN_{org} + mN_p} \right) \quad (12)$$

which is essentially the well-known Meyer-Huggins-Flory form for polymer solutions.^{23,27,32}

ΔG free energy of formation

The free energy of formation eq. (3) of the intercalated structure can be rewritten with eq. (5) as

$$\Delta G = \beta \Delta H_{coat} + (1 - \beta) \Delta H_{uncoat} - T \Delta S \quad (13)$$

where ΔS is given by eq. (12). The values of ΔH_{coat} , ΔH_{uncoat} , and β determine whether ΔG is positive or negative.

For a polymer in Na^+ montmorillonite $\beta = 0$,

$$\Delta G = \Delta H_{uncoat} - T \Delta S \quad (14)$$

For organoclay where β becomes large ($\beta \sim 1$), eq. (13) becomes

$$\Delta G \rightarrow \Delta H_{coat} - T \Delta S \quad (15)$$

COMPARISON WITH EXPERIMENT

Values of parameters

$$\Delta G = \beta \Delta H_{coat} + (1 - \beta) \Delta H_{uncoat} - T \Delta S \quad (16)$$

To estimate ΔH_{coat} and ΔH_{uncoat} , we need to consider the organophilic and polar-polar interactions expressed in four different cases.

Case 1. Polar polymer and organic ammonium surface, $\Delta H_{coat} < 0$, organophilic and polar interactions

Case 2. Nonpolar polymer and organic ammonium surface, $\Delta H_{coat} > 0$, organophilic but not polar interaction

Case 3. Polar polymer and inorganic clay surface, $\Delta H_{\text{uncoat}} > 0$, polar interaction but not organophilic

Case 4. Nonpolar polymer and inorganic clay surface, $\Delta H_{\text{uncoat}} > 0$, not organophilic and polar interaction

For organoclays where the surface is completely coated, $\beta = 1$. If the organic surface is 70% coated, $\beta = 0.7$, and the effect of the 0.7 portion of ΔH_{coat} and the 0.3 portion of ΔH_{uncoat} on the free energy change. For sodium natural montmorillonite clay (Cloisite[®] Na⁺) without organic modifier, $\beta = 0$.

To estimate overall free energy change for a polar polymer in a clay with organic amine coated galleries, we used the heat of mixing ($\Delta H_{\text{coat}} = -175$ J/mol) of triethylamine and trichloroethane for the (Southern Clay, now Rockwood Specialties, Princeton, NJ) Cloisite[®] 20A and 30B organoclays and chlorinated polyvinylchloride (CPVC) or polyvinylidene chloride (PVDC). These polymer compounds CPVC and PVDC possess a chemical structure that is roughly similar to that of trichloroethane.

For Cloisite[®] 20A organoclay, which is completely covered by organic modifiers, eq. (15) should be valid. Here $\Delta H_{\text{coat}} < 0$ and ΔS is positive, and the free energy change is negative.

For this case, we may do rough conclusions using the data given above. If we consider PVDC/Cloisite[®] 20A (10 wt %) compound, 90 g of PVDC polymer was compounded with 10 g of organoclay: 90 g of PVDC (average molecular weight of two repeating units = 78 g/mol) has 1.15 mol, which corresponds to $\Delta H = -175$ J/mol \times 1.15 mol = -201 J. For ΔS , $n_M = 0.0095$ mol and $n_P = 1.15$ mol, if $d = 1$ for modifier and polymer, $\Phi_M = 0.1$ and $\Phi_P = 0.9$, $R = 8.314$ J/K mol, $\Delta S = 1.19$ J/K, $T\Delta S = 355$ J, $\Delta G = -201 - 355 = -556$ J.

Because the organic surface of Cloisite[®] 30B organoclay is 70%, $\beta = 0.7$. The free energy change is

$$\Delta G = 0.7\Delta H_{\text{coat}} + 0.3\Delta H_{\text{uncoat}} - T\Delta S \quad (17a)$$

where ΔS is given by eq. (12). For the PVDC polymer, the heat of formation of the coated surface is $\Delta H_{\text{coat}} < 0$. The heat of formation of the uncoated surface is $\Delta H_{\text{uncoat}} > 0$ because there is no organophilic interaction.

For the PVDC/30B (10 wt %) compound, $0.7\Delta H_{\text{coat}} = 0.7 \times -201 = -141$ J and $-T\Delta S = -352$ J. Because our experimental result confirmed the intercalation of PVDC/30B and the tendency to form a nanocomposite, we can assume the positive $0.3\Delta H_{\text{uncoat}}$ contribution is smaller than the sum of $0.7\Delta H_{\text{coat}}$ and $-T\Delta S$. The overall free energy change ΔG is negative.

In the case of natural montmorillonite clay (Cloisite[®] Na⁺) and PVDC compound, $\beta = 0$.

$$\Delta G = \Delta H_{\text{uncoat}} - T\Delta S > 0 \quad (17b)$$

ΔH_{uncoat} is positive for polar PVDC polymer because there is no organophilic interaction and $-T\Delta S < 0$. The overall free energy change depends on the value of enthalpy and entropy changes. In our experiment with PVDC polymer and Cloisite[®] Na⁺, the free energy change is positive, which means no intercalation.

We can compare the PVDC and Cloisite[®] 30B organoclay compound to the case of polyethylene (PE) and Cloisite[®] 30B compound. The heat of mixing ($\Delta H_{\text{coat}} = 135$ J/mol) of triethylamine and decane can be used for PE and Cloisite[®] 30B compound. Because the organic surface area of Cloisite[®] 30B is 70%, $\beta = 0.7$. Once again we obtain eq. (17a).

Because polyethylene is a nonpolar polymer, $\Delta H_{\text{coat}} > 0$ and $\Delta H_{\text{uncoat}} > 0$. If we use 10 g of organoclay and 90 g of polyethylene, $0.7\Delta H_{\text{coat}} = 0.7(135$ J/mol \times 3.21 mol) = 303 J and $-T\Delta S = -890$ J. If we know the value of $\Delta H_{\text{uncoat}} (>0)$ we obtain a positive free energy change.

As we described above, for the PVDC and Cloisite[®] 30B compound, $0.7\Delta H_{\text{coat}} = -141$ J and $-T\Delta S = -352$ J. If we know the value of $\Delta H_{\text{uncoat}} (>0)$ we can determine whether the free energy change is negative.

CONCLUSIONS

The formulations we present here are similar to but simpler than earlier theories described by Vaia and Giannelis¹⁹ or Balazs et al.²⁰ The conclusions are similar and illustrate more simply the "polarity" and "heat of solution" mechanism for forming intercalated structures of polymers' intersilicate layer galleries in clay. The existence of an exothermic heat of solution between the organic amine and the polymers seems to be the key to intercalation of the polymer melt.

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