

Reinforcing Effect of Nano Kaolin Clay on Some Optical Properties of Poly (methyl methacrylate) for Medical Application

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Abstract

In this study, the effects of nano kaolin clay content on the optical properties of PMMA films are investigated. PVA solution used as a coated layer covered the nano-kaolin applied as filler. The reinforced nano-kaolin content of 1, 3, 5, and 7 wt%. Improve the absorbance of UV radiation for (PMMA/kaolin) nanocomposite films at 7 wt% allows use for protection purposes, such as solar radiation shield, in the manufacture of sunglasses to protect the human eye from UV radiation damaged to the tissues of the body and as packaging for storage drugs. The values of allowed and forbidden indirect transition optical energy gap decrease with increasing the rate of reinforced nano-kaolin up to (4.27, 3, 2.8, 2.49, 2.23 eV) and (3.99, 2.4, 2.1, 1.8, 1.3 eV) respectively. Refractive indexes, extinction coefficient of polymer reinforcement nano-kaolin were done.

Key words: PMMA, Nano-kaolin clay, Optical properties, Composite materials.

Introduction

Polymer nanocomposites consist of a polymeric substance and a nanoscale reinforcing material. These materials show considerable improvements in different properties; in mechanical properties, optical properties, thermal stability, chemical resistance etc....

The requirements of industrial development in the world led to the development of the science and technology of composite materials and the entry into the manufacture of new materials with special specifications determined by the required use [1].

PMMA is an amorphous thermoplastic polymer. It has good optical properties, but has a poor scratch resistance and a good weather resistance. PMMA is stable to alkalis and acid, and has good impact strength higher than that of glass or polystyrene.

PMMA is widely used in many technological applications because of its unique combination of excellent optical properties with chemical inertness, some good mechanical properties, thermal stability, electrical properties, and easy shaping [2]. Kaolin as a filler has characteristic of soft white color, and has melting point (1770°C) in case of purity [3].

Kaolin's structure is composed of silicate sheets (silica tetrahedral layer) Si_2O_5 bonded to aluminum Oxide / hydroxide layers $\text{Al}_2(\text{OH}_4)$ (Al-Octahedral layer) called gibbsite layers. The silicate and gibbsite layers are tightly bonded together with only weak bonding existing between these silicates /gibbsite paired layers (called s-g layers). The weak bonds between these s-g layers cause the cleavage and softness of this mineral [4, 5]. Kaolin does not swell because its structure doesn't have interlayer cations, and the water H_2O is chemically – bound in the structure as (OH) ions.

These minerals are non-expandable in water. Kaolin is widely used in the making of paper, rubber, paint, and many other products. Polymer - Clay nanocomposites are mostly attractive due to the low cost of filler and easy process ability. In this present work, we studied the effect of addition of nano-kaolin clay on the optical properties of Poly (methyl methacrylate).

Experimental

Raw Materials

The main material is Poly (methyl methacrylate) PMMA. A chemical structure of

the repeating unit of PMMA polymer shown in Fig. 1 [6]. The most important characteristics of the PMMA polymer are following [7]: It has glass transition

temperature TG (379 K), various molecular weights (g/mol), with a melting point (473 K), and refractive index (1.49).



Fig. 1: Poly (methyl methacrylate) structure [6]

The nano-kaolin clay used in this study was supplied by (SLGMA K7375 – 1KG, USA) with grain size $\sim 1\mu\text{m}$. His mineral analysis shows that the main component is aluminum silica hydroxide $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as it demonstrated by the results.

Method

The (PMMA/ Kaolin) nanocomposites are prepared by the following procedure: the granular sizes selected for nano kaolin clay is less than $0.1\mu\text{m}$ and the modified process was performed by additives of PVA at 80°C temperature for 4hr. The PVA addition has $\text{pH}=6$ (measured at room temperature), is one of the requirements to obtain the best adsorption on the surface of the clay before applied it as filler [8]. The mixture was mixed by a magnetic stirrer type –Strut- Germany manufacture under 80°C temperature continued to get slurry form and to insure homogeneity with high viscosity (the mixing process was adopted according to the method of green land [9]), then dried, milled and sieved to granular size $\sim 0.1\mu\text{m}$.

A solution has been prepared by solving 2g of PMMA in 30ml of the chloroform and using magnetic stirrer to mix the materials to obtain more homogeneous solution at $70\text{--}80^\circ\text{C}$ temperature for 30 minutes. The reinforced nano-kaolin content of 1, 3, 5 and 7 wt %, were added to PMMA and mixed for (50-60) minutes, even get a homogeneous solution white color. The casting method is used to get the nanocomposites cast on glasses petri dish, and left for two days to dry. The choice of the casting method in the preparation of PMMA and (PMMA/kaolin) nanocomposites was due to the require no advanced techniques and complex devices, and by which they can prepare samples with a large area and equal thickness.

The absorption spectrum of (PMMA/kaolin) nanocomposites at thickness $25\text{--}30\mu\text{m}$ have been recorded in the wavelength range (200-1100)nm by using the double beam spectrophotometer (Shimadzu, UV-1800 Å, Japan).

Basic Relation

The absorption coefficient (α) can be calculated from the equation [10]:

$$\alpha = \ln(1/T) / t \quad (1)$$

Where t is the sample thickness.

The reflectance (R) of thin films was calculated from the equation [10]:

$$R = 1 - \sqrt{T \exp(-\alpha t)} \quad (2)$$

The refractive index (n) was calculated from the equation [10]:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (3)$$

The extinction coefficient (K) is related to the exponential decay of the wave as it passes through the medium and it is defined to be [11]:

$$K = \frac{\alpha \lambda}{4\pi} \quad (4)$$

Where λ is the wavelength of the incident radiation.

The optical energy gap (E_g^{opt}) for indirect transition type is given by [12]:

$$ah\nu = B(h\nu - E_g^{\text{opt}} \pm E_{\text{ph}})^r \quad (5)$$

Where E_{ph} energy of phonon, (-) when phonon absorption, and (+) when phonon emission, r is the exponential constant; its value depends on the type of transition, $r=2$ for the allowed indirect transition and $r=3$ for the forbidden indirect transition.

Results and Discussion

The metallic analysis of nano-kaolin clay was characterized by x-ray diffraction technology (XRD). The mineral analysis shows that the

main component is aluminum silicate hydroxide $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as presented in Fig. 2.

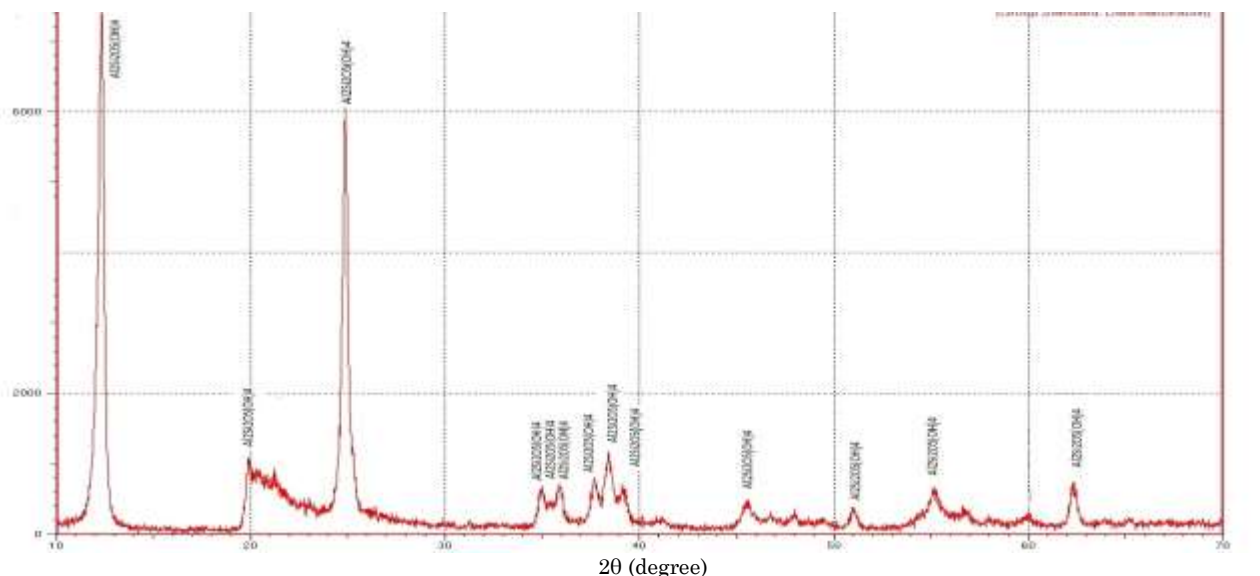


Figure (4) shows the optical absorbance spectrum versus wavelength of incident light for PMMA nanocomposite with nano-kaolin clay content of 1, 3, 5, and 7 wt% together with the pure PMMA as a reference. The highest absorbance value appears in the UV region of the electromagnetic at nano-kaolin content of 7 wt%.

The pure PMMA has low absorbance because there is no free electron (i.e. electrons are linked to atoms by covalent bonds) [13], and the increase in absorbance value of PMMA is caused by the added kaolin nanoparticles which contains electrons outside orbits can absorb the electromagnetic energy of the incident light and travel to higher energy levels.

This process is not accompanied by emission of radiation because the traveled electron to higher levels have occupied vacant positions of energy bands, thus part of the incident light is absorbed by the substance and dose not penetrate through it. This is agreeing with previous research related to it [14].

This result is very important in industrial and medical applications. Improve the absorbance of UV waves allows use for protection purposes such as solar radiation shield, so it is works as filters, and antireflection coating. It can also be used for medical purposes such as the manufacture of sunglasses to protect the human eye from ultraviolet radiation damaged to the tissues of the body, and as packaging for storage drugs.

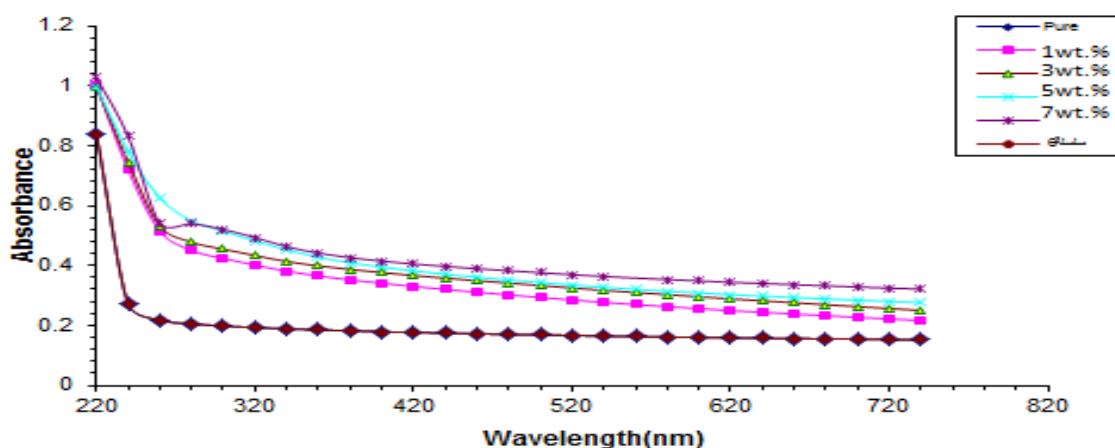


Fig.4 : The absorbance spectrum versus wavelength of PMMA and (PMMA/kaolin) nanocomposite films

Figure (5) shows the optical transmittance versus wavelength of incident light for PMMA nanocomposite with nano-kaolin clay content of 1, 3, 5, and 7 wt% together with the pure PMMA as a reference. The optimum value of

transmission about 75% for pure PMMA film at high wave length (VIS-NIR).The transmittance of the films is increases with increasing wave length. This is agreeing with previous research related to it [14].

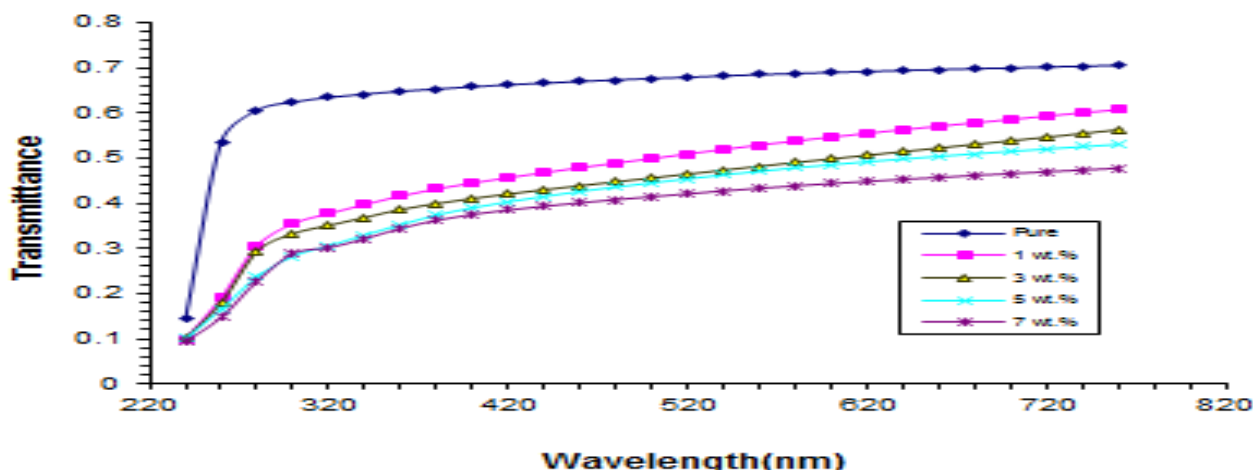


Fig.5: The transmittance versus wavelength of PMMA and (PMMA/kaolin) nanocomposite films

Figure (6) shows the absorption coefficient α (cm^{-1}) versus photon energy for (PMMA/kaolin) nanocomposite films. It can be seen that the absorption coefficient is the smallest at a low energy. This means that the possibility of electron transition is little because the energy of the incident photon is

not sufficient to move the electron from the valence band to the conduction band. While at high energies we find that absorption is good. The values of the absorption coefficient is less than $(10^4) \text{ cm}^{-1}$. This explains that the electron transition is indirect.

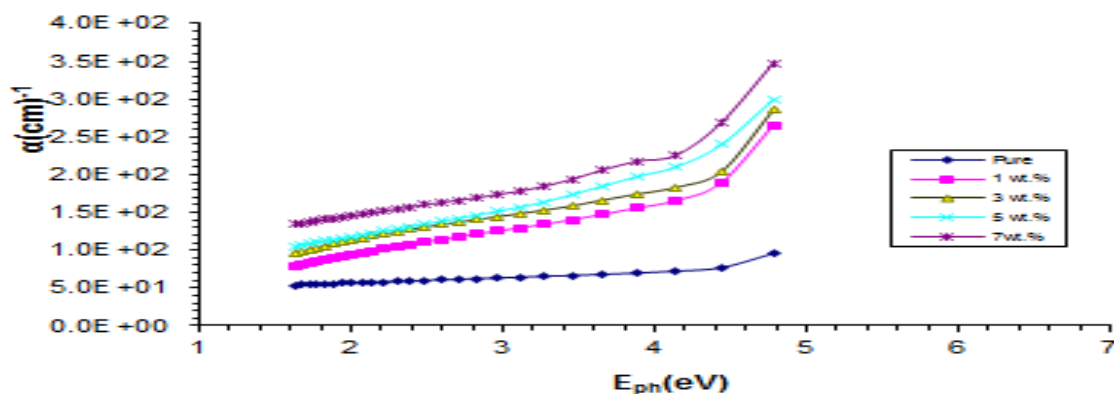


Fig.6: The absorption coefficient $\alpha(\text{cm})^{-1}$ versus photon energy for PMMA and (PMMA/kaolin) nanocomposite films

Both the allowed and forbidden indirect transition optical energy gap is shown in Figs. 7, and 8 respectively. The optical energy gap values decrease with increasing reinforced nano-kaolin content (see

Table 1). This attributed to the creation of localized levels in the forbidden energy gap. According to this result it is possible to apply in transistor, capacitors, and solar cells.

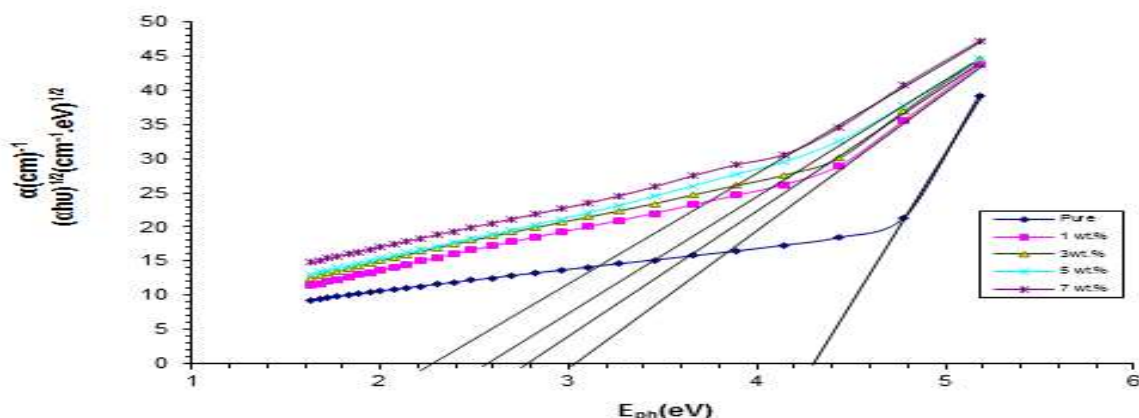


Fig. 7: Optical energy gap for the allowed indirect transition $(\alpha h\nu)^{1/2}$ versus photon energy of PMMA and (PMMA/kaolin) nanocomposite films

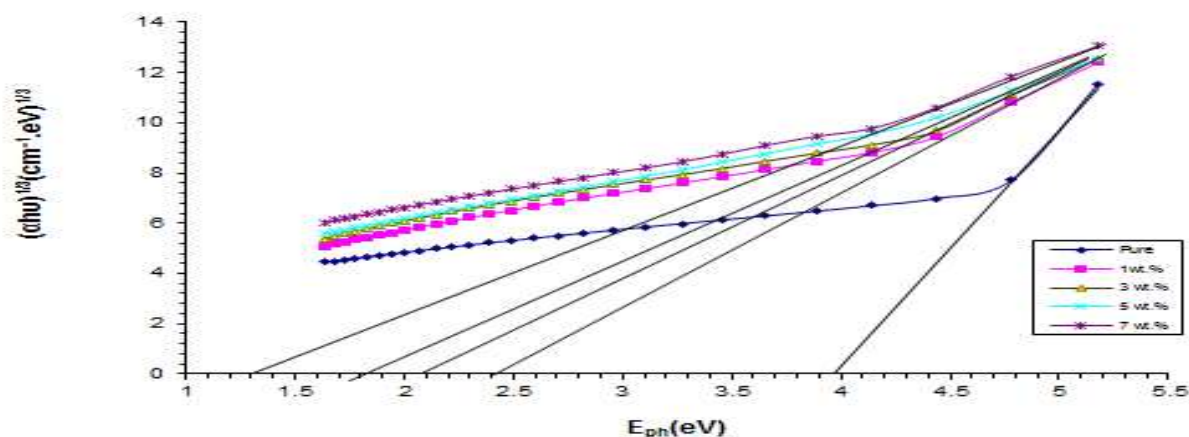


Fig. 8: Optical energy gap for the forbidden indirect transition $(\alpha h\nu)^{1/3}$ versus photon energy of PMMA and (PMMA/kaolin) nanocomposite films

Table 1: Optical energy gap values for the allowed and forbidden indirect transition of PMMA and (PMMA/kaolin) nanocomposite films

Samples (PMMA/kaolin) nanocomposite films.	Allowed Indirect Transition (eV)	.Forbidden Indirect Transition (eV)
PMMA	4.27	3.99
PMMA- 1wt. %	3	2.4
PMMA- 3wt. %	2.8	2.1
PMMA- 5wt. %	2.49	1.8
PMMA- 7wt. %	2.23	1.3

Figure (9) shows the change of refractive index for PMMA and (PMMA/kaolin) nanocomposite films versus wavelength. In visible region, the refractive index increase with increasing reinforced nano-kaolin

content. This attributed to the high transmittance of pure PMMA in compare with that value of composite (PMMA/kaolin) nanocomposite. but in the UV region it gets the opposite.

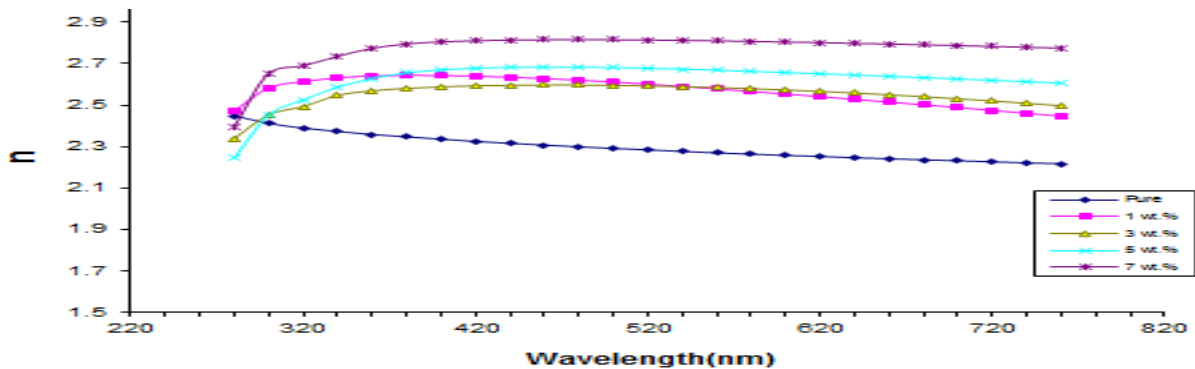
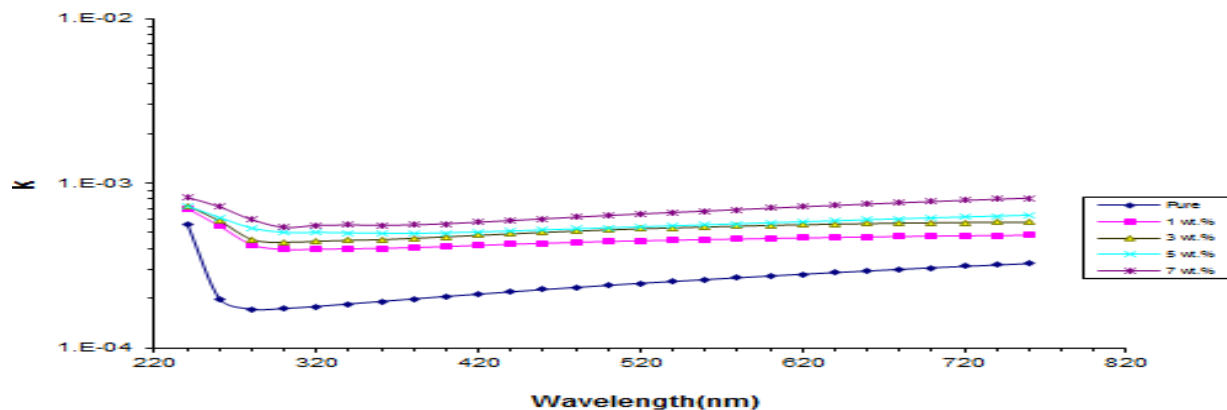
**Fig. 9: The refractive index versus wave length for PMMA and (PMMA/kaolin) nanocomposite films**

Figure (10) shows the change of extinction coefficient (k) for pure PMMA and (PMMA/kaolin) nanocomposite films versus wavelength. It can be noted that k increase with increasing reinforced nano-kaolin

content in all regions. This is because of the close relationship between absorption coefficients with extinction coefficient as in the equation (4).

**Fig. 10: The extinction coefficient versus wave length for pure PMMA and (PMMA/kaolin) nanocomposite films**

Conclusions

- Improve the absorbance of UV radiation for (PMMA/kaolin) nanocomposite films at 7 wt% allows use for protection purposes, such as solar radiation shield, in the manufacture of sunglasses to protect the human eye from UV radiation damaged to the tissues of the body and as packaging for storage drugs.

- The energy gap for indirect transition (allowed and forbidden) decreases with increasing reinforced nano-kaolin content. According to this result it is possible to apply in transistor, capacitors, and solar cells.
- The refractive index and extinction coefficient of pure PMMA and (PMMA/kaolin) nanocomposite films are increasing with increasing reinforced nano-kaolin content.

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