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The effect of process parameters on physical and mechanical properties of commercial low density polyethylene/ORG-MMT nanocomposites

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Abstract Polyethylene/organo-montmorillonite clay (org-MMT) nanocomposites were prepared utilizing PP-g-MA as a compatibilizer by melt intercalation method. In order to increase the miscibility of polyethylene (PE) with nanoparticle surface at firs, a primary masterbatch consist of compatibilizer and org-MMT was prepared then, this compound was melt intercalated with PE to synthesis the PE/org-MMT nanocomposites. In this study, the presence of commercial low density polyethylene in Nanocomposites structure and also the effect of process parameters such as: amount of nanoparticles, mixing rate and mixing time on nanocomposite structure and properties have been investigated. The X-ray diffraction (XRD) and transmission electron microscopy (TEM) results showed that the interlayer distance of nanoparticle layers increased and a partially intercalated structure was prepared by melt intercalation method. Interaction between polyethylene chains and nanoparticle layers could be improved if the control of above parameters causes to penetrate the chains into nanoclay layers; by an optimization, this effect could improve the physical and mechanical properties. The DSC data revealed that melting temperature has slowly increased and crystalinity has lightly decreased. Consequently we can claim the thermal properties of LDPE/clay nanocomposite did not considerably change with clay content. A rise in the mechanical properties such as yield stress and modulus was observed by tension test; by addition of 5% clay content the tensile strength increased about 7%, the tensile modulus enhanced about 60% and the yield stress increased about 16% in comparison with the pure LDPE.

Introduction

Nanocomposites have attracted attention in recent years because their mechanical, physical, optical, and rheological properties can often be modified with a minimal increase in density as a result of low inorganic loading [1–4]. Interest in polyolefin nanocomposites has emerged due to their improved performance in packaging and engineering applications. Because of the light weight, good process ability, low cost, etc. polyethylene is the most common polymers which, used as a matrix [3–6]. Recently, three ways are used to prepare PE/clay nanocomposites: the solution method, in situ polymerization and melt intercalation method. Of these methods, melt intercalation method is the easiest and most various method to prepare nanocomposites [5–9]. Zhang et al. [5] studied the preparation of high density polyethylene/clay nanocomposite by melt intercalation using PP-g-MA as a compatibilizer. Their results indicated that clay particles in the composite were intercalated and the mechanical properties improved. Zaho et al. [7] also synthesized polyethylene/clay nanocomposites using melt blending. They used two intercalating agent to the modification of clay particles: Dioctadecydimethylammonium chloride and octadecyldimethylammonium chloride. They succeeded in getting intercalated nanocomposites. In the research of Morawiec and Galeski, by adding about 3–6% of nanoparticles to the polyethylene, tensile modulus and yield stress increased; meanwhile, in their study the ratio of compatibilizer to nanoclay remained

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constant at about 2 [8]. Low density polyethylene (LDPE), a widely used packaging material, seems to be especially attractive for nanocomposite preparation, mostly due to the expected improvement of barrier properties [10–17]. In our study the dependence of several industrial process parameters on the physical and mechanical properties was found to better understand the structure of nanocomposites and to develop practical means for explanation the role of commercial low density polyethylene in the end-use properties.

Experiments

Material

The organo-montmorillonite clay (org-MMT) was used as supplied closite 15A; southern clay product, Ganzales, texas; ion exchange with Dimetylalkylammoniumhalide (65% C_{18}, 30% C_{16}, 5% C_{14} and CEC = 125 meq/100 gr clay). Maleic anhydride-modified polypropylene (PP-g-MA, 1 wt% malice anhydride, ADMERN Q) from Mitsui co. was selected as a compatibilizer. Low density polyethylene (LDPE 0200, MFI = 2 gr/10 min at 190 °C and 2.16 kg) from Bandare Imam Petrochemical Company (BIPC) as a matrix was utilized.

Melt processing

The org-MMT was melt-blended with compatibilizer by a Banbury internal mixer (made by BRABENDER company in Germany) at 180 °C and rotor speed of 70 rpm for 12 min, in order to prepare a pre-intercalated master batch or Pre-Intercalated Compound(PIC). For all samples Filled-Factor = 0.75 was applied. The ratio of compatibilizer to org-MMT was maintained at 3:1. The pre-intercalated masterbatch was mixed with LDPE at twin screw extruder (made by BRABENDER company in Germany) to obtain LDPE/clay nanocomposite (LDCN). Temperature profile in extruder heat zones was adjusted at 170, 180, 190, 200, and 210 °C; meanwhile, the screw speed of extruder was set at 150 rpm. For further studies 1 mm thick cast film of all samples were prepared by opt a slit die with 8 cm in width. To investigate the effects of clay content on LDCN, LDPE/clay nanocomposites with various clay contents were prepared. The compositions of the LDPE/clay nanocomposites are listed in Table 1.

Table 1 Compositions of LDCN

Composition (wt%)	Type of LDCN		
	LDCN0	LDCN2.5	LDCN5
Clay	0	2.5	5
Compatibilizer (PP-g-Ma)	0	7.5	15
LDPE content	100	90	80

Characterization

X-Ray diffraction (WAXS) analysis was carried out with an x'pert model by Philips with CuKα radiation in reflection mode to investigate the clay distribution and interlayer distance. The diffractograms were scanned in 2θ ranges from 1 to 10° at 2°/min. The morphologies of the PE/clay nanocomposites were observed using transmission electron microscopy (TEM: JEM 2010 F) with an acceleration voltage of 200 kV. A 70 nm ultra-thin film of the composite was prepared using a microtome under a liquid nitrogen atmosphere. Differential Scanning Calorimetry (DSC) was performed on DSC-METTLER at temperature range from 20 to 180 °C at a heating rate of 10°/min. Thermal properties such as melting point and crystallinity of the LDPE/clay nanocomposites were indicated by DSC analysis. In order to analysis the tensile properties of the LDPE/clay nanocomposites, tension tests were carried out on a tension test machine (Instron-4465) at a crosshead speed of 50 mm/min according to the ASTM638. Dambel shape specimens were prepared by a punch machine (CEAST) with 5 cm length and 1 cm width. Five tests were performed for each condition.

Results and discussion

Structure of LDPE/clay nanocomposites

Effect of clay (proportionally compatibilizer) content

The polarity of clay mainly consists in its interlayer surface. Through the ion exchange with common alkyl ammonium, the surface of the clay would change from hydrophilic to hydrophobic, and can be used to fabricate most of polymer/clay nanocomposites. But for non-polar polyethylene, the hydroxyl groups at the edge of clay layers impair the formation of nanocomposites. Only conventional microcomposites can be obtained by directly melt compounding PE and common alkyl ammonium modified clay, and therefore, we chose a reactive intercalating agent for the modification of clay surface. The molecule of the reactive intercalating agent PP-g-MA contains both exchangeable cations that act as ammonium cations to replace the interlayer Na+ and reactive methoxylsilane groups that could react with hydroxyl groups at the edges of clay layers. The latter reaction could further reduce the interlayer attraction and improve the wettability between PE and organoclay, and ultimately enhance the intercalation of PE into interlayers of clay. X-Ray

Table 2 XRD data

Material	2θ (Peak value)	d (Å)
Clay	3.4	29
PIC	3.2	32
LDCN (2.5% clay)	2.7	36
LDCN (5% clay)	3	34

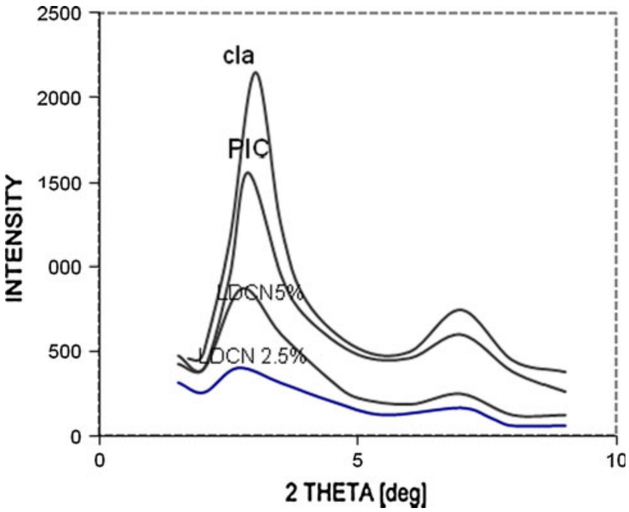

Fig. 1 XRD patterns of the clay, Pre-Intercalated Compound and LDPE/clay nanocomposites

diffraction was used to observe the changes in the interlayer distance and intensity of prominent picks for various clay contents. Table 2 shows the XRD data of the clay, PIC, and LDCN.

The peak value of 2θ for PIC was 3.2, which was smaller than that of the clay (3.4). This indicated that treatment with the compatibilizer (PP-g-MA) has increased the interlayer distance from 29 to 32 Å. MA Group in compatibilizer interacts with Alkyl-ammonium groups in org-MMT and helps polyethylene chains to penetrate into clay interlayer more easily. Figure 1 shows XRD patterns of the clay, Pre-Intercalated Compound (PIC) and LDCNs prepared with PP-g-MA for various clay contents; where, the exemplary X-ray diffractograms are plotted against the respective range of 2θ angles. As figure shows a small peak appears between 2θ value of 6 and 8 which is related to unimproved clay layers while by addition the compatibilizer intensity of the peak decreased. XRD main peak appears between 2θ values of 2 and 4. In both nanocomposites the peak significantly was reduced, indicating good intercalation of the clay in the LDPE matrix, although the intercalation was less in LDCN 5% than in LDCN 2.5%. The intensity difference between the structure of the clay and LDCNs demonstrates clearly the influence of grafted groups of the compatibilizer on the interactions between the filler and the polymer, allowing PP-g-MA chains to access between platelets of the clay. The same phenomenon is clearly seen in Fig. 2, which shows TEM images of 2.5 and 5% clay content nanocomposites. In 2.5% clay content material, clays were better intercalated and dispersed than those in 5% clay content material even though some of intercalated layers are still observed.

Effect of mixing rate and mixing time

In order to research on the effect of process parameters on the structure of LDPE/clay nanocomposites, different specimens of LDCN 5% were prepared at various mixing rates and characterized by X-Ray diffraction and transmission electron microscopy (Figs. 3, 4).

By increasing the mixing rate from 90 to 120 rpm and then to 150 rpm, 2θ of main peak, respectively, transmitted

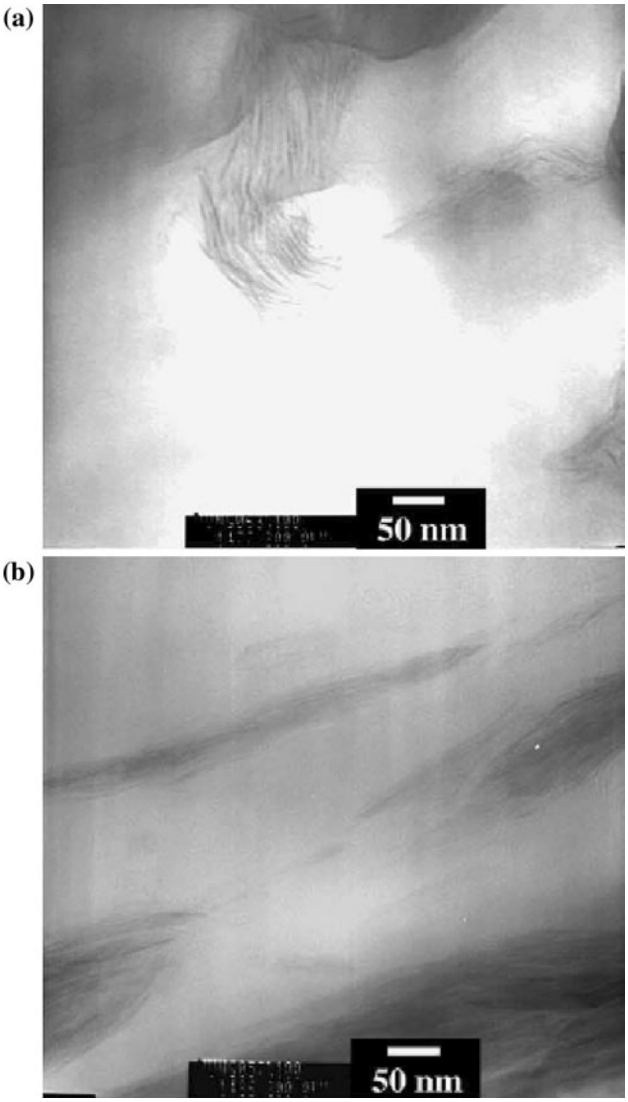

Fig. 2 TEM micrographs of nanocomposites with 2.5 and 5% clay Contents: **a** 100 k (2.5%), **b** 100 k (5%)

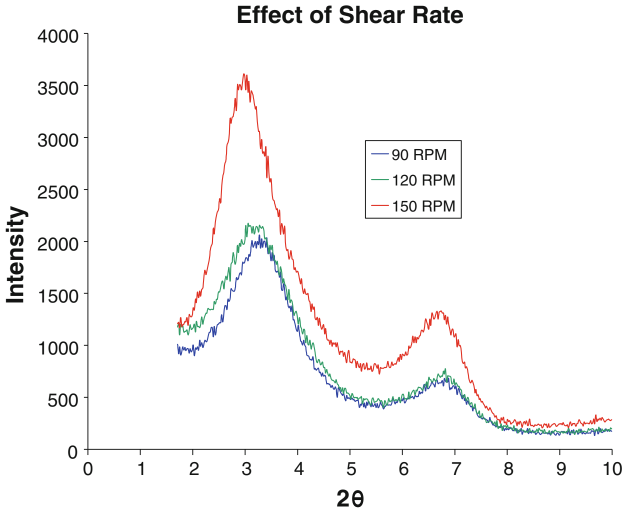

Fig. 3 XRD patterns of LDCN 5% prepared at three different mixing rates: 90, 120, and 150 rpm

down to 3.4, 3.2, and 3. This reveals that because of higher shear rate and hydrodynamic forces, interlayer distances of the clays have been mostly extended. On the other world when the mixing rate was decreased to 90 rpm, hydrodynamic forces were not sufficient to overcome on intermolecular forces between clay layers whereas the intensity changed dramatically, hitting a peak of $2\theta = 3.4$ in this rate. Besides this viscosity reduction of the matrix during mixing procedure, is another argument and it leads to the penetration of matrix chains in clay layers. Indeed, an increase of the shear thinning is observed with the increase of the degree of exfoliation. TEM micrographs show partial exfoliation in the both nanocomposites with 5% clay (Fig. 4). The exfoliation seems to be more pronounced in the nanocomposite prepared at 150 rpm than that manufactured at 90 rpm therefore, the cohesive forces between clay layers can be overcome during melt compounding and delamination is observed. This subject conforms to the X-ray diffraction results (Fig. 3). The effect of mixing time on structure of LDPE/clay nanocomposites, as other parameters, has been investigated in this section too.

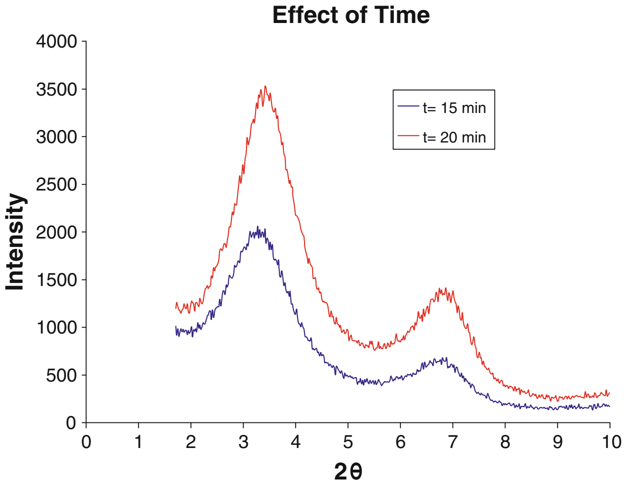

Fig. 5 XRD patterns of LDCN 5% prepared at 90 rpm and two different mixing times: 15 and 20 min

Figure 5 shows XRD patterns of LDCN 5% prepared at two different mixing times (15 and 20 min).

Figure 5 depicted that 2θ values at the both mixing time (and at the constant mixing rate of 90 rpm) were the same. This indicates at such restricted area of mixing time, there is no significant change on interlayer distances. On account of this observation, the effect of mixing time has been ignored in the next sections.

Thermal properties

According to the previous study, by the clay loading the melting temperature in PE/clay nanocomposites was increased and the degree of crystallinity was decreased, but these mutations depend on the crystallization mechanisms: amount of nucleation agents and crystal propagation rate [18, 19]. Figure 6 shows the DSC curves of the nanocomposites with various clay contents.

There was no significant difference in melting temperatures and amount of crystallinity between LDCN 2.5%, LDCN 5%, and neat LDPE. This behavior indicates no expressive nucleation activity of org-MMT in LDPE based

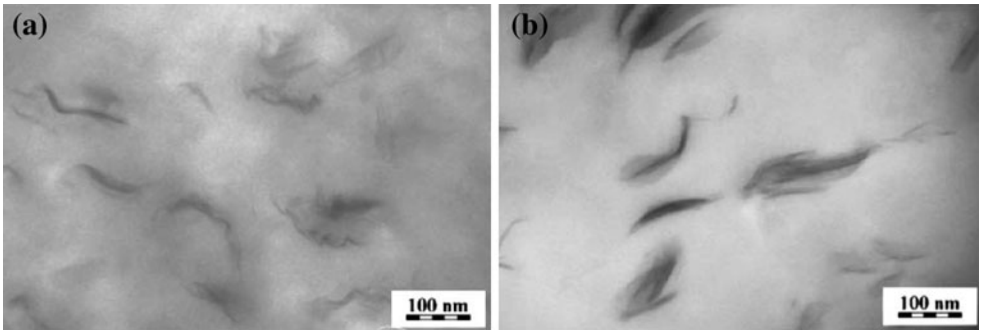

Fig. 4 TEM micrographs of nanocomposites with 5% clay prepared at two different mixing Rates: **a** 50 k (150 rpm), **b** 50 k (90 rpm)

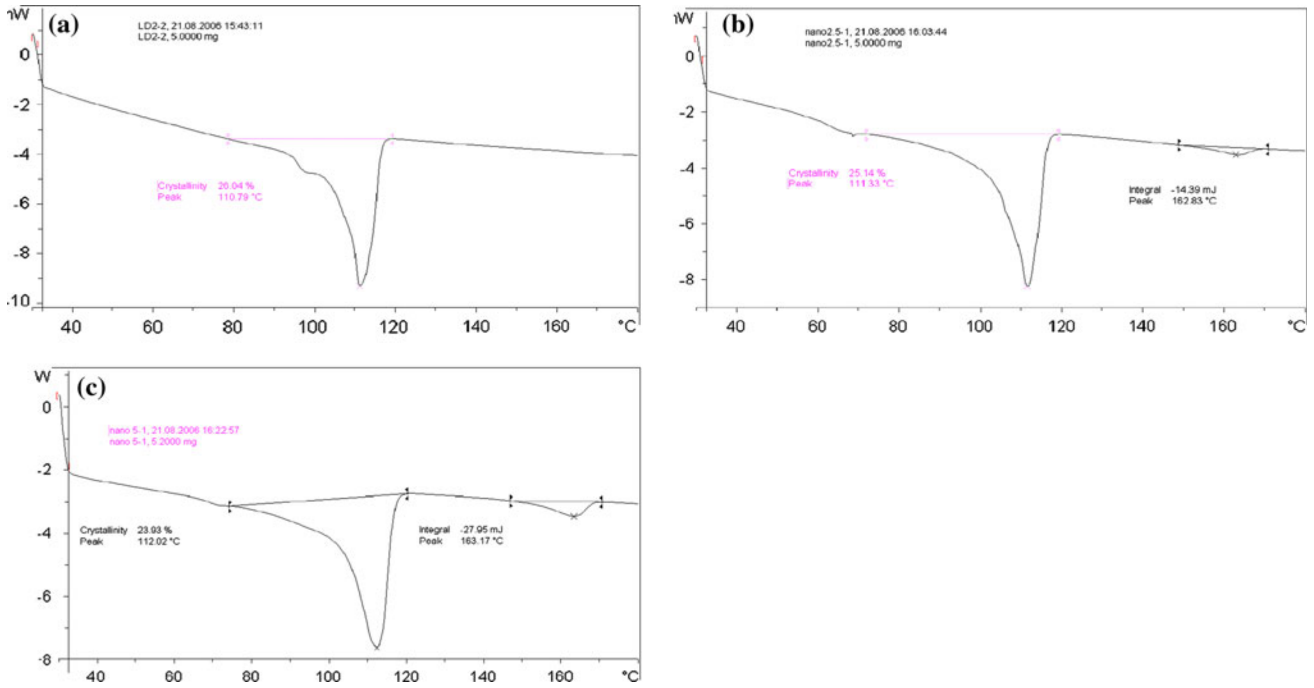

Fig. 6 DSC curves of LDPE/clay nanocomposites for various clay contents: **a** 0%, **b** 2.5%, **c** 5%

Table 3 Thermal properties of LDCN for various clay contents

Clay content	T_m (°C)	Crystallinity
0	110.79	26.04
2.5	111.33	25.14
5	112.02	24.2

Table 4 Mechanical properties of LDCN for various clay contents

Clay content	Tensile strength (Mpa)	Tensile modulus (Mpa)	Yield stress (Mpa)
0	16.7 ± 1.1	120 ± 18	9.7 ± 0.9
2.5	17.4 ± 1.4	215 ± 24	10.9 ± 0.6
5	17.8 ± 1.2	235 ± 28	11.2 ± 0.8

systems which are so different from those found in HDPE and iPP based. This phenomenon might be related to the high branching chains of LDPE in nanocomposites structure. The thermal properties of nanocomposites are summarized in Table 3.

Mechanical properties

Tension test was performed, to investigate the mechanical properties such as tensile strength, tensile modulus and yield stress.

Effect of clay content

The mechanical properties of nanocomposites depends on many factors such as the aspect ratio of the filler, the degree of dispersion of filler in the matrix, the adhesion at filler-matrix interface, etc. Table 4 shows the average tensile of the nanocomposites for various clay contents. The tensile strength, modulus, and yield stress enhanced significantly with increasing clay content.

With 5% clay loading, the tensile strength increased about 7%, the tensile modulus enhanced about 60% and the yield stress increased about 16% as compared with the pure LDPE. The increase in the tensile properties was higher for low clay content region. This is adapted with X-Ray diffraction and TEM results and implied that the clay layers were better intercalated at a lower clay content and provide a good reinforcing, while with further increase of the clay content, some of the clay remained partially stacked, which weakened the reinforcing effect.

Effect of mixing rate

Figure 7 demonstrates the changes in mixing rate, generating prominent mutations in tensile properties.

According to the observed witnesses in X-Ray diffraction and TEM results, when the mixing rate raised the distinguished quota of polyethylene chains could penetrate into clay layers; this effect would improve the adhesion at filler-matrix interface. Consequently, by increasing the

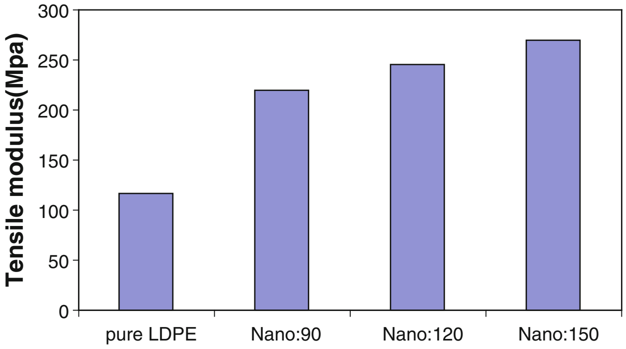

Fig. 7 Tensile modulus of LDCN 5% prepared at three different mixing rates: 90, 120, and 150 rpm

mixing rate from 90 to 120 rpm and then to 150 rpm, tensile modulus of LDCN 5%, respectively, increased to 215, 240, and 260 Mpa.

Conclusions

A partially intercalated LDPE/clay nanocomposite was synthesized using the melt-intercalation method with PP-g-MA compatibilizer. The intercalation of clay layer and the adhesion at filler-matrix interface leads to an improved mechanical properties of the composite. However, the mechanical performance of the system is not governed only by the clay content but also by the presence of sufficient amount of the compatibilizer and the selection of suitable mixing conditions. Consequently by an optimization on mentioned process parameters, with 5% clay added to commercial low density polyethylene matrix the tensile strength increased about 7%, the tensile modulus enhanced around 60% and the yield stress increased just over 16% as compared with pure matrix.

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