

Properties of Paraffin Wax/Montmorillonite Nanocomposite Coatings

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ABSTRACT

Results are reviewed from a study aimed at enhancing the performance of paraffin wax based materials for barrier coating applications. Nanocomposites prepared by ultrasonic processing from paraffin wax matrices and reinforced with organically modified montmorillonite clay have been shown to demonstrate significantly improved mechanical properties. This includes substantially increased stiffness, strength and ductility relative to pure paraffin wax. Subsequent to processing, the clays were found to be well-dispersed as exfoliated and intercalated platelets of about 50-150 nm in length and a few nanometers in thickness. Dilatometry results presented here show that the relative volume expansivity of the organo-clay reinforced nanocomposites are significantly decreased compared with that of the pure wax. The corresponding topology study shows that the formation of micron-size cracks on the wax surface during cooling is inhibited by the clay. It is also shown that the presence of organo-clay appears to stabilize the properties of melt processed samples. For example, the contact angle for water on solid paraffin wax surfaces decreases with increased periods of heating time for molten samples. The extent of the observed changes is significantly less in the nanocomposites. Our study demonstrates that there are a number of benefits associated with the addition of organo-clay to paraffin wax barrier coatings. In addition to enhanced strength, durability and aesthetics, the presence of the nano-disperse particles also appears to maintain or improve properties that decay with processing.

Key Words: Paraffin wax, Nanocomposite, Mechanical properties.

INTRODUCTION

Paraffin or macrocrystalline wax is an inexpensive thermoplastic composed primarily of normal alkanes with carbon numbers that range from about 18 to 45. In their solid form, paraffin waxes are semicrystalline with low melting points (i.e., ~40 to 60 °C) and heats of fusion on the order of 150 J/g. In the melt, paraffin wax has a low viscosity and a surface tension of approximately 25 mJ/m². Paraffin wax is used in a variety of products and applications. Here the interest is in its use as a moisture barrier [1,2].

The modest cost, ease of processing, low surface tension and viscosity all combine to make paraffin wax a seemingly excellent sealant against liquid and vaporous water. For example, wax will readily flow into porous structures such as paper or fabric to fill its network of pores providing it with a low energy surface and enhanced structural stability. However, wax is quite brittle with a low stiffness and strength and cracks readily form due to thermal stresses as it cools severely diminishing its barrier properties. In addition, paraffin wax possesses a series of pre-melting or rotator phases at temperatures just prior to its melting transition [3]. In these mesophases, alkane molecules acquire increased rotational freedom while retaining positional order, which is why they are often referred to as rotator phases. These modifications in crystal structure are accompanied by significant changes in strength and wetting behavior.

In this paper, preliminary results of a study on the influence of exfoliated organo-clay on the processing and wetting of paraffin wax are reviewed. In previous publications it was shown that Cloisite[®] 20A, a natural montmorillonite organically modified with a quaternary ammonium salt, could be readily dispersed and exfoliated/intercalated in a paraffin wax matrix up to about 5%. The presence of the clay platelets simultaneously and substantially enhanced the stiffness, strength and ductility of wax at room temperature. Here, results on the performance properties of the wax are reviewed. It would be expected that the presence of the exfoliated organo-clay would influence the performance of the wax as a moisture barrier treatment and impact its dimensional stability. These effects are reported on here. Furthermore, it was found that heating molten wax over a long time period, consistent with its industrial application as a moisture barrier treatment, results in a change in its wetting behavior. As will be discussed, this change could be characterized as a decay, which is arrested by the introduction of organo-clay platelets.

MECHANICAL ENHANCEMENTS OF PARAFFIN WAX WITH ORGANO-CLAY

Figure 1 shows thermomechanical data for a commercial paraffin wax. Two transitions are evident in the differential scanning calorimetry (DSC) thermoscans shown in Fig. 1a. The higher temperature transition is due to the melting of the wax while the lower temperature event is a phase transition between a crystalline state and the

lowest temperature rotator phase for the wax. Although they are often difficult to locate via conventional thermomechanical techniques, a wax can possess multiple rotator phases in the region prior to the melting transition. As would be expected, in the rotator phase region the strength and stiffness of the wax decreased considerably. This can be seen from Fig. 1b, which shows the young's moduli, tensile/yield strength and the elongation at break for several temperatures. The data was extracted from stress-strain data collected using an Instron Inc. (Norwood, MA) model 5543 tensile tester equipped with an environmental chamber according to ASTM standard D638-95.

At low temperatures, the wax demonstrates brittle fracture, and the maximum stress occurs at breakage. As the temperature nears the low temperature crystalline-rotator phase transition, the modulus and strength of the wax decreases significantly, it begins to yield prior to breaking and demonstrates greater elongations at breaks.

Also shown in Fig. 1 (part b) are tensile test results for paraffin wax in which 2% organo-clay has been dispersed and exfoliated/intercalated. The Cloisite® 20A was added to melted wax and mixed with a high intensity sonicator probe. The clay was shown to be a mixture of exfoliated and intercalated morphology throughout the matrix with transmission electron microscopy (TEM). Images indicated that the organo-clay was present as thin tactoids containing a single or only a few clay layers. These particles were about 50-150 nm long and a few nanometers thick with an approximate aspect ratio of 15-40.

As was discussed in previous publications [4,5], the introduction of nanodispersed organo-clay significantly enhances not only the stiffness and strength of the paraffin wax, but also its ductility. Nanocomposite samples began yielding prior to failure at much lower temperatures and their elongations at break were substantially increased relative to the pure paraffin wax. The observed enhancements were diminished as the temperature of the nanocomposites were increased and it entered the onset of the crystalline-rotator phase transition.

DILATOMETRY AND THERMAL STRESS

An issue with using wax as a barrier coating is its high thermal expansivity. This combined with its low stiffness and strength result in extensive cracking when wax coatings are solidified on rigid surfaces. The presence of cracks significantly increases its permeability to liquids and gases. The thermal stability of wax/clay nanocomposites were investigated using dilatometry. Figure 2 shows the relative volume expansion of pure paraffin wax and its nanocomposite produced with 2 wt.% organoclay as a function of temperature. When the temperature is below 24 °C, the relative expansivity values for pure wax and the nanocomposite sample are almost same. When

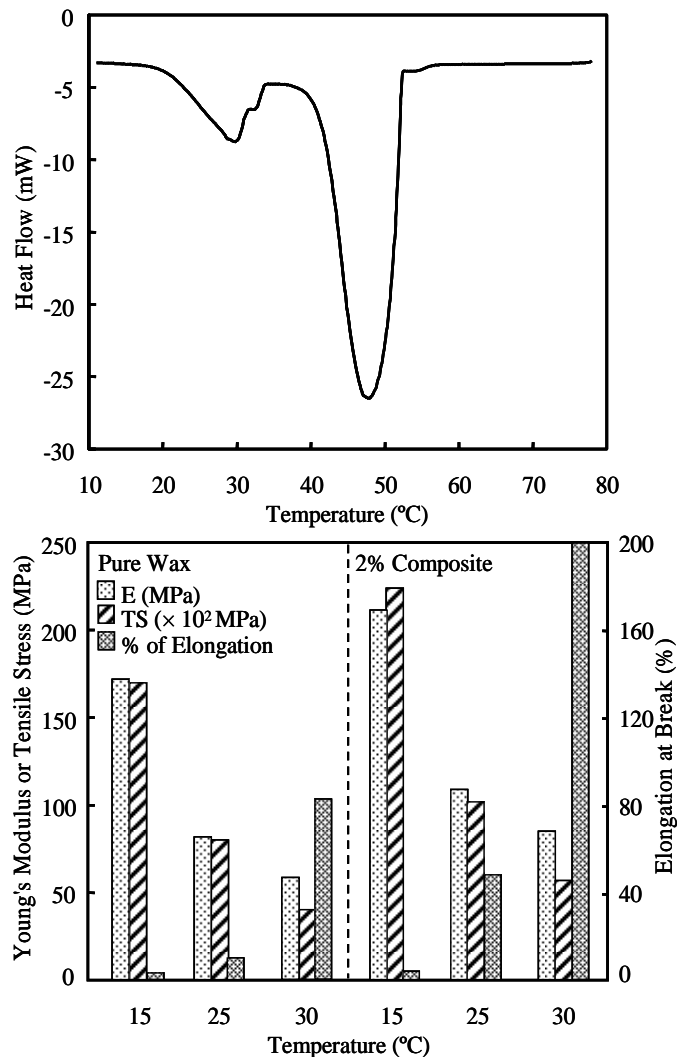


Figure 1: a.) Differential scanning calorimetry thermoscan of the commercial paraffin wax. b.) Mechanical properties including the Young's modulus, tensile/yield strength and elongation at break for the pure paraffin wax and its nanocomposites at various temperatures.

temperature increases to above 24 °C, the pure paraffin wax shows a higher increase rate than that of nanocomposite. The maximum expansion temperature for pure paraffin wax and its nanocomposite are 43.7 and 38.2 °C, respectively. The maximum relative expansivity value for pure paraffin wax is about twice that of the nanocomposite.

Figure 3 shows scanning electronic microscopy (SEM) images of the pure paraffin wax and nanocomposites containing 2 and 5 wt.% organo-clay. Changes in topology due to the clay addition are evident from the images. Small ridges in the size range of about 50 microns cover the composites surface in random patterns while the pure wax surface has a plain flat surface. It was also found that the development of micron-size cracks appeared to be inhibited with increasing organo-clay

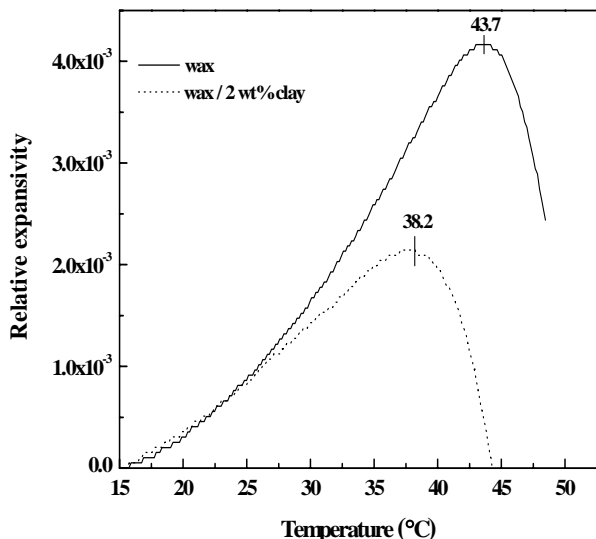


Figure 2: Relative thermal expansivity of paraffin wax and its nanocomposite with 2 wt.% organoclay.

content. In pure wax, extensive cracking is apparent. The cracks grow up to several hundred microns in length. There are significantly fewer cracks and they are shorter in the 2 wt.% organo-clay sample. While the 5 wt.% organo-clay content sample appears to possess a crack-free morphology.

The inhibition of crack formation upon cooling is likely governed in large part by the modification of the thermal expansivity of the wax, but the increased strength and ductility imparted by the organo-clay also plays a role. Although no permeability data are reported here, preliminary measurements showed that films of the nanocomposite containing 5 wt.% organo-clay demonstrated significantly lower permeability to moisture than those from the pure wax.

SURFACE ENERGY AND WETTING

The wetting of paraffin wax films by water is of interest when its barrier properties are sought after. The introduction of organo-clay does not appear to significantly influence contact angle values. However, an interesting observation is that contact angles are influenced by the length of time molten wax is heated. Figure 4 shows dynamic contact angle results for pure paraffin wax and its 2 wt.% organo-clay nanocomposite measured at 16 °C. The x-axis is the time period the molten wax was heated prior to being solidified to form 2 mm thick films covering a 20x20x0.2 mm steel plate. The dynamic contact angle measurements were performed following the Wilhelm plate method with a Kruss (Hamburg, Germany) Model K100 tensiometer. For the advancing angles, both the pure wax and organo-clay composite have relatively constant contact angle values. However, the receding angle decreases with increased heating time periods, and it can be seen that the

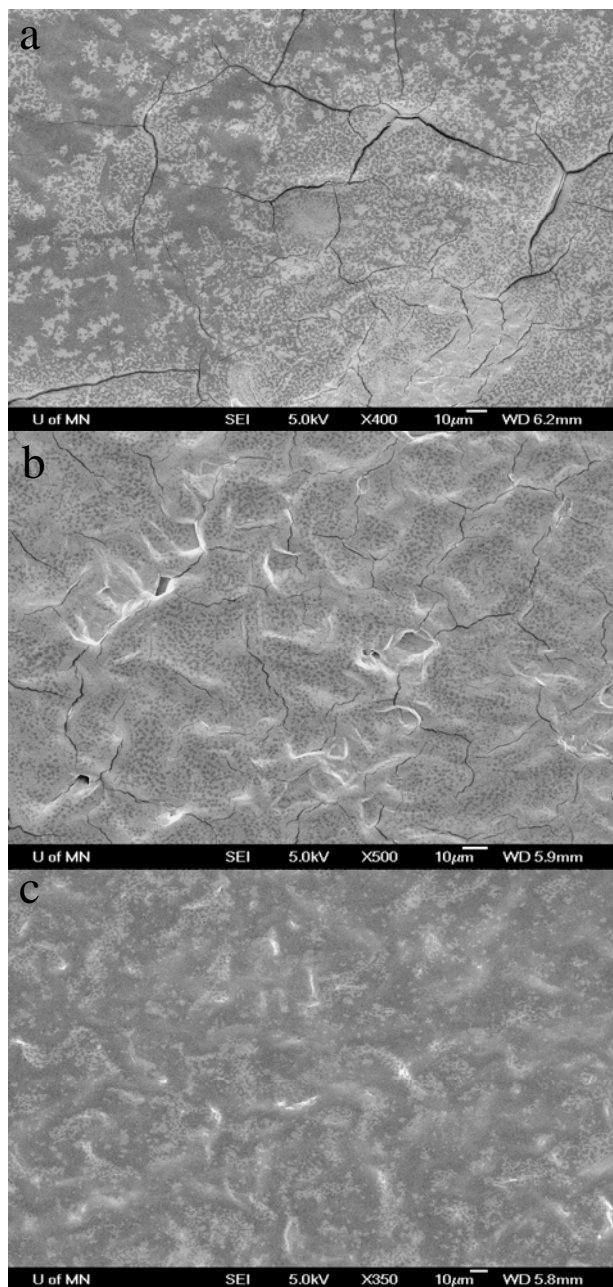


Figure 3: SEM image on clay/wax morphology. (a) pure wax; (b) 2 wt.% organo-clay; (c) 5 wt.% organo-clay.

decay is significantly tempered by the presence of the clay. For samples being heated for ten hours before solidification, the receding angle for pure wax dropped about 35 degrees, while the receding angle for its organo-clay nanocomposite only decreased slightly.

DSC and x-ray diffraction (XRD) results show that the crystallinity of pure paraffin wax decreases by more than 50% with 10 hours of heating of the melted wax prior to solidification, while little change was observed for the nanocomposite for the same heating time. The melt point also decreased slightly with the drop in crystallinity and the wax was noticeably softer and weaker. Paraffin wax crystals have a well-defined lamella layer structure with a

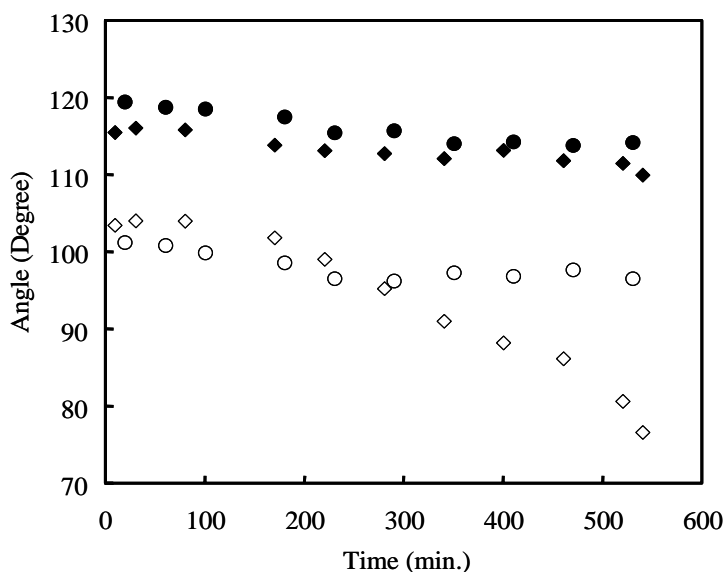


Figure 4: Molten heating time dependence of the advancing (solid) and receding (open) contact angle for pure wax (circles) and wax/clay nanocomposite at 2 wt.% clay concentration (diamonds) at 16 °C.

REFERENCES

1. H. Oscar, B. Howard. *Industrial & Engineering Chemistry Research*, 27, 1296-1300, 1988.
2. M. Martin-Polo, C. Mauguin, and A. Voilley, *Journal of Agricultural and Food Chemistry*, 40,407-412, 1992.
3. M. Nowak, S. Severtson, *Journal of Materials Science*, 36(17), 4161-4168, 2001.
4. J. Wang,, S. Severtson, and A. Stein, *Advanced Materials*. 18(12), 1585-1588, 2006.
5. J. Wang, S. Severtson, and P. Geil, *Materials Science and Engineering A*. (In Press).
6. D. Dorset, *Acta Crystallographica Section B*, 51, 1021-1028, 1995.
7. C. Extrand, *Langmuir*, 19, 3793-3796, 2003.
8. L. Gao, T. McCarthy, *Langmuir*, 22, 6234-6237, 2006.

distinctive stepped platelet of monomolecular or bilayer thickness [6]. The hydrocarbon molecular chains are positioned almost perpendicular to the lamella layers in the crystallites. With the decrease in crystallinity, a more disordered structure is exposed to the surface. The greater disorder would be expected to increase surface energy, which would produce relatively more hydrophilic regions. It has been suggested that the contact line may interact preferentially with the heterogeneities; the increasing relative hydrophilic area has more impact on the receding process [7]. A defect of lower contact angle within the contact line perimeter will impede receding, causing a lower receding contact angle [8]. This may be the reason for the nearly constant advancing angle and the decrease in receding angle observed here.

Other probe liquids, such as formamide and ethylene glycol, also showed the same tendency of the dynamic contact angle change for pure and the organo-clay/wax composites.

CONCLUSIONS

The dispersion and exfoliation of the Cloisite® 20A in paraffin wax matrices enhances stiffness, strength and ductility of the formed Nanocomposite. The addition of the clay platelet reinforcements also appears to provide the composites with greater dimensional stability with heating and cooling, which likely accounts for the lack of crack formation in the films. The clay also appears to produce greater stability in the surface properties of the composites, which manifests itself in more stable wetting behavior for films generated from the melt.